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IN SITU NON-HYDROLYTIC SOL-GEL SYNTHESIS:
AN INNOVATIVE APPROACH TOWARDS POLYMERIC MATRIX/TITANIUM
DIOXIDE HYBRID NANOCOMPOSITE MATERIALS

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy in Materials Science

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ACKNOWLEDGMENTS

Some years ago somebody told me: “PhD is the typical thing that if you know what is it about, you will never start”. Yes, it was all true. Actually, at that time, I did not agree, but now I definitely do. In the last four years I had very stressful and tiring days, but if I look back and I think about the future this experience satisfied me and made me stronger.

Before beginning the long common thanks list I would like to explain the reason why these acknowledgments are so important to me. Let's start from the beginning.

After my master degree, I did not want to keep on studying, as a PhD student, I was tired and I probably just needed something different maybe only a bit of rest. After a sabbatical I figured out how much I missed the scientific research and how much it could be captivating and stimulating. These reasons drove me to apply for the PhD. Since then, I dedicated a lot of my energy to what I would not define a real job, but an engaging passion.

Indeed this route was hard, but it allowed me to learn and do many things that, just few years ago, I would not imagine to be able to do.

For all these motivations, I would like to start saying a huge thanks to my girlfriend, Giulia, who dedicated a lot of her time helping me and psychologically supporting me. My families are greatly acknowledge, especially my Mother and Sergio for always encouraging me during the difficult moments.

I am definitely so grateful to who convinced me and permitted me to experience the outstanding and fascinating world of science, so I must acknowledge my supervisors Professor Federica Bondioli and Professor Massimo Messori.

Finally, I think that I must thank all my office mates and lab mates for incredible friendship and the interesting long scientific discussions that gave me the chance to improve my scientific knowledge and myself.

ABSTRACT

Nowadays, polymeric composite materials are widely employed for many different technological applications especially in the automotive field, but also in electronics, polymeric solar cells, household products, packaging industry, aircraft interiors and device components.

The incorporation of inorganic nanoparticles, as metal or non-metal oxides, in polymeric matrices leads to organic/inorganic hybrid materials characterized by enhanced properties as compared to both unfilled polymers and polymers filled with micrometric particles.

This project is mainly dedicated to the preparation of organic/inorganic nanocomposites based on polymers as matrix and titanium dioxide (TiO_2) as filler. Subsequently, the obtained composites were characterised from a chemical, physical and mechanical point of view.

Exploiting the well-known non-hydrolytic sol-gel (NHSG) chemistry, TiO_2 nanoparticles were *in situ* generated within polymers in order to obtain nanostructured hybrid composites. This approach allowed overcoming the typical rheological problems related to the conventional mixing methods.

First of all, a study was carried out on the NHSG synthesis of TiO_2 nanoparticles, using different organic solvents, in order to make these types of reactions suitable for the *in situ* filler generation in presence of polymers. The organic solvent plays a double role in this process; it dissolves the polymer and acts as oxygen source in the TiO_2 nanoparticles formation. For this reason the NHSG reactions have to be previously and carefully studied and the solvent has to be carefully chosen.

Four types of polymeric matrices were filled with TiO_2 nanoparticles: poly methyl methacrylate (PMMA), two widely used epoxy resins (DGEBA and CE), ethylene-propylene diene monomer rubber (industrially known as EPDM) and polyurethanes (described in the “appendix A”).

The *in situ* filler generation led to homogeneous particles dispersion and remarkable adhesion at the organic/inorganic interphase as confirmed by the scanning electron microscopy investigations. In addition, the reported method led to the expected filler contents proving the effectiveness of this approach.

The dynamic mechanical thermal analyses showed a significant increase of the storage modulus (E') in the rubbery region (temperature range over the glass transition temperature) by increasing the nanoparticles content and independently on the matrix used. This behaviour indicates that the incorporation of nanoparticles is able to increase the stiffness of the pristine polymeric matrices.

The PMMA/TiO₂ based composites, unexpectedly, showed a very fast photodegradation rate when exposed at ultraviolet light. On one hand the incorporation of TiO₂ nanoparticles improves the mechanical properties of neat PMMA, on the other hand it makes these hybrids excellent as disposable materials thank to their fast photodegradation.

EPDM/TiO₂ based hybrid-composites exhibited an improved mechanical behaviour, even though the filler particles partially limited the vulcanization process.

The epoxy resins showed to be the matrix most affected by the presence of titania nanoparticles. For thermoset matrices, in the rubbery region, the E' is governed by the cross-linking density of the polymeric matrix. The observed remarkable increase of this parameter suggests that the particles do not only act as rigid reinforcing filler, constraining the chains mobility, but also as real cross-linking “densifier”. A further evidence of this result was obtained by comparing the E' of composite (having equal filler content) obtained by *in situ* filler generation and *ex situ* filler synthesis followed by a mechanical dispersion. The composite prepared by *in situ* synthesis is characterized by higher E' with respect to the sample prepared by *ex situ* synthesized particles. This behaviour proves, once again, a stronger stiffening effect due to the *in situ* TiO₂ nanoparticles synthesis that act as a real cross-linking point between chains.

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(Appendix A)

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(Appendix A)

NOMENCLATURE

–OBz	Benzyl group
–OH	Hydroxyl group
–R	Generic alkyl group
A	Constant related to the shape particles
A_0	Normalized area of the epoxy signal before the curing step
A_t	Normalized area of the epoxy signal after the curing step
ATR	Attenuated total reflectance
B	Constant related to the ratio between filler and matrix moduli
BET	Brunauer–Emmett–Teller theory
BzOH	Benzyl alcohol
C_0	Starting MB concentration
CE	3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexanecarboxylate epoxy resin
C_t	MB concentration at the generic time t
CuK α	Source and wavelength of the X-ray radiation
D	Average crystallite size
DCP	Dicumyl peroxide

DGEBA	Bisphenol A diglycidyl ether
DLS	Dynamic light scattering
DMF	Dimethylformamide
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
E'	Storage modulus
E'_1	Storage modulus of the pristine matrix
EDX	Energy dispersive X-ray spectrometry
E_{in}	Initial modulus
E_{IT}	Indentation modulus
EPDM	Ethylene-Propylene Diene Monomer
$E_{sec,\epsilon=100\%}$	Secant modulus for deformation of 100%
$E_{sec,\epsilon=200\%}$	Secant modulus for deformation of 200%
$E_{sec,\epsilon=300\%}$	Secant modulus for deformation of 300%
ESI	Electro spray ionization
ETH	Polytechnic of Zurich
EXO	Exothermic
f	Extractable fraction

FESEM	Field emission scanning electron microscope
f_{ORG}	Normalized f to the actual organic phase content
FT-IR	Fourier transform infrared spectroscopy
G	Gel content
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
HPLC/MS	High performance liquid chromatography equipped with mass spectrometry
HSG	Hydrolytic sol-gel
HV	Vickers harness
JCPDS	Joint Committee on Powder Diffraction Standards
L_{C1}	First critical load
L_{C2}	Second critical load
M	Molar ($\text{mol}\cdot\text{L}^{-1}$)
m_0	Starting mass of the sample
MB	Methylene Blue
Mc	Polymer molecular weight between two cross-linking points
m_d	Dried mass of the sample after 24 h extraction

MDI	4,4'-diphenylmethane diisocyanate
m_s	Swollen mass of the sample
n	Apparent cross-linking density
NHSG	Non-hydrolytic sol-gel
P	Correction parameter related to the effective thickness of the particle-matrix interfacial
PC	Propylene carbonate
pd	Photodegradation
PEG_200	Polyethylene glycol, average molecular weight 200 g·mol ⁻¹
PEG_400	Polyethylene glycol, average molecular weight 400 g·mol ⁻¹
phr	Per hundred of resin
PMMA	Poly(methyl methacrylate)
PU	Polyurethane
q	Front factor
q	Swelling ratio
q_{EPDM}	Normalized q to the actual EPDM weight
R	The gas constant
R	Radius of the dispersed particles

R.E.	Reinforcing efficiency
Rietveld-RIR	Reference Intensity Ratio method
rpm	Revolution per minute
SEM	Scanning electron microscope
S _N 1	Uni-molecular nucleophilic substitution
S _N 2	Bi-molecular nucleophilic substitution mechanism
SSA	Specific surface area
T	Absolute temperature in K
tanδ	Loss factor
tanδ ₁	Loss factors referred to the pristine matrix
tanδ _{max}	Maximum value of loss factor
tBuOH	tert-Butyl alcohol
TEM	Transmission electron microscopy
T _g	Glass transition temperature
TiCl ₄	Titanium tetrachloride
TGA	Thermogravimetric analysis
TiO ₂	Titanium dioxide
TONSET	Onset temperature of thermal degradation

UV	Ultraviolet light
UV-Vis	Ultraviolet–visible spectroscopy
UVA	Ultraviolet light A (400 – 315 nm)
UVB	Ultraviolet light B (315 – 280 nm)
UVR 6990	Triphenylsulfonium hexafluoroantimonate
w_{EPDM}	Weight fraction of EPDM
w_{org}	Weight of organic fraction
wt%	Weight percent to mass fraction
Yb(OTf)_3	Ytterbium(III) trifluoromethanesulfonate hydrate
α	Epoxy conversion
β	Full width at half maximum
ΔR	Effective thickness of the particle-matrix interfacial region
ε_b	Deformation at break
θ	Diffraction angle
λ	Wavelength of the X-ray
ν	Poisson's ratio
ρ	Density

σ_b	Stress at break
ϕ_2	Filler volume fraction
ϕ_m	Maximum packing fraction of the particles
ϕ	Average particles diameter by Eq. 2
Ψ	Reduced concentration term

Chapter 1

INTRODUCTION

1. Introduction

1.1 – Polymeric Composites

Polymeric composites became very common and widespread used materials since the second half of 1900s. The incorporation of filler in polymeric matrices has always been a very simple method in order to gain higher strength, stiffness and later to improve solvent or fire resistance. Moreover, the lightweight of the structure and cost effectiveness made, soon, these materials very interesting especially from an industrial point of view.

In the second half of 1800s canoe builders experimented with gluing together layers of kraft-paper and shellac (resin secreted by the female of lac-bug) to form paper laminates. While the concept was successful, the materials did not perform well. Because the available materials were not up to the job, for this reason in few years the idea faded. At the same time, the tyres industry started blending carbon black, zinc oxide, and/or magnesium sulphate particles with vulcanized rubber in order to reduce the wear tyres [1].

In the years between 1870 and 1890, a revolution was occurring in chemistry. The first synthetic resins were developed which could be converted from a liquid state to a solid state by a curing process (crosslinking of molecules). The early synthetic resins included also celluloid and melamine.

The chemist Leo Baekeland first produced a soluble phenol-formaldehyde resin called “Novolak” that never became a market success, then turned to developing a binder for asbestos which, at that time, was commonly moulded with rubber. By controlling the pressure and temperature applied to phenol and formaldehyde, Baekeland produced a hard mouldable material. That material, known as “Bakelite”, was patented in 1907 [2, 3] and can be considered a sort of primitive composite.

The history of modern widespread composites probably began in 1937 when Salesmen from the Owens Corning Fiberglass Company started selling fiberglass around the United States [4]. Fiberglass soon became the first filler industrially employed for reinforcing phenolic resins (the most common at that time) for producing watercraft and airplane's components.

During the years of war world two, the composite field had a great development thanks to the just discovered epoxy and unsaturated polyester resins that became the preferred matrices due to the simpler procedure and milder conditions of the curing process if compared to the phenolic resins. These materials were wide used for building military vehicles such as airplanes, helicopters and rockets.

During the 1960s some new fillers such as graphite, boron and aramid fibres were investigated and employed for preparing new composites. In that period, the aerospace industry was probably the most important market for composites, which drove to a great development. The most famous material, of this second generation of composites, was probably Kevlar that was commercially introduced by DuPont in the 1971. Kevlar is fibre based on an aramid compound, which belong to the nylon polymers family, developed by Stephanie Kwolek back in 1964 [5].

Between the 1970s and the 1980s, the military and aerospace demand suddenly declined, for this reason the composite industry had to identify new appealing markets, such as civil applications, sport products and automotive. These fields needed of new lightweight materials that were also characterized by enhanced mechanical properties. This special need led to the scientific community to turn their studies toward the boundary between the two phases [6-8] for improving the interaction between phases. This new approach to design composites was significantly helped by the use of computers that allowed a faster and deeper understanding of the phenomena involved in the mechanical properties improvements.

Despite this early interest, the broad scientific community was not galvanized by composites world until the early 1990s, when reports by Toyota researchers revealed that addition of clay to nylon could produce a five-fold increase in the yield and tensile strength of the material [9-11].

Subsequent developments have further contributed to the growing interest in polymer/nanoparticle composites. In particular, the large availability of nanoparticles with precise size and shape and the development of instrumentations to probe nanometric scale, such as scanning force, laser scanning fluorescence and electron microscopes, stimulated research aimed at probing the influence of particle size, shape and nature on the properties of polymer/nanoparticle composites.

Nowadays, the interest of researchers is focusing more and more on using nanofillers with specific properties such as fullerenes, carbon nanotubes, metal nanoparticles, metal or non-metal oxide nanoparticles, dendrimers and bionanoparticles [12, 13]. Hybrids are the last generation of composites in which some peculiar mechanical and functional properties of both organic polymers and inorganic materials are combined in a synergistic way by joining the different phases at the nanoscale. The extremely high surface area of embedded filler allowed using very low amount of it for obtaining remarkable enhancements as compared to both unfilled polymers and polymers filled with micrometric fillers.

Hybrid composite materials represent not only a new and exciting scientific branch of basic research, but also offer perspectives for several new technological applications. The very large set of accessible materials span a wide spectrum of properties, which yield innovative industrial applications in various fields such as optics, micro-electronics, transportation, health, energy, housing, smart materials[14] and the environment among others [15].

For hybrids preparation two approaches are typically followed, the first invented is the “top-down approach”, whereas the most innovative and academically studied is the “bottom-up approach” [16].

1.1.1 – Top Down Approach vs. Bottom Up Approach

The keys challenge in the preparation of nanocomposites is the establishment of homogeneous filler dispersion and the good phases interaction in order to obtain homogeneous properties. The optical, physical and mechanical properties are strongly dependent not only on the individual features of each component, but also on important aspects of the involved chemistry such as phase continuity, filler morphology, filler orientation and the molecular mixing at the phase boundaries [17].

For a long time, thermoset or thermoplastic polymers reinforced/filled with nanoparticles had been prepared only through the dispersion of filler into polymers (melted or in solution) or monomers by using conventional mechanical mixing methods according to the so called “top-down approach”. Although this approach is still interesting from an industrial point of view it has two main drawbacks especially

in the case of fillers with hydrophilic character such as oxides nanoparticles. The first disadvantage is the strong tendency of particles to agglomerate that leads to a non-homogeneous final product and the second one is the complex rheology that makes these systems difficult to process and scale up.

In order to achieve the desired properties, a method for producing polymeric nanocomposites, capable of controlling the interface and filler dispersion, becomes fundamental. For overcoming the limitations of top-down approach, previously described, organic/inorganic hybrids can be produced by *in situ* generation of nanoparticles according to the so called “bottom-up approach”. By this approach, the polymeric matrix and the molecular filler precursor are dissolved in a suitable organic solvent. The use of a filler precursor, instead of pre-formed filler, leads to a lower viscosity and deeper phase mixing. The consecutive *in situ* nanoparticles synthesis is able to induce the desired formation of hybrid structures, in which filler and organic phase are intimately mixed each other at the nanometric scale [18]. This innovative approach represents an efficient alternative to design new composites for both academic research and industrial applications [18, 19].

It is now clear that for preparing composites, by bottom-up approach, a suitable chemical reaction for the *in situ* filler synthesis is needed.

1.2 – Sol–Gel Chemistry

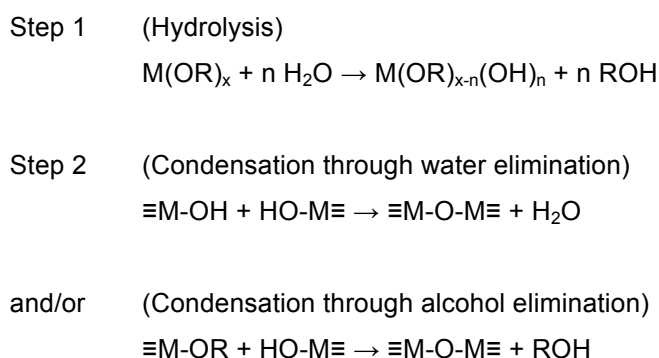
Among the many different synthetic procedures reported in literature [20], the sol-gel chemistry represents one of the preferred methods for the preparation of polymer/oxide hybrid composites according to the bottom-up approach.

The sol-gel process is a chemical method to prepare inorganic materials, initially employed to synthesize high purity inorganic networks as glasses and ceramic materials. Mild conditions characterize this method that become strategic parameters to carefully consider when organic materials are involved into the process permitting to avoid their thermal degradation. Typical precursors are metal or non-metal alkoxides (or halides) that reacting with an oxygen source leads to oxide nanoparticles characterized by narrow grain size distribution with dimensions that range from few nanometres up to 100 nm.

Two categories of sol-gel reactions can be distinguished based on the nature of oxygen source. The hydrolytic (or aqueous) sol-gel (HSG) route, which employs water, and non-hydrolytic (or non-aqueous) sol-gel (NHSG) route, which employs oxygen-containing organic solvents.

1.2.1 – Hydrolytic Sol-Gel Synthesis

The first extensively studied and used sol-gel method was the HSG route. It can be described by a series of consecutive reactions consisting of: hydrolysis, which produces hydroxyl groups, and condensation involving the polycondensation of hydroxyl groups and residual alkoxy groups forming a three-dimensional network [21]. The series of reactions can be schematized as follows:



Scheme 1.2.1.1 – Series of reactions involved in a hydrolytic sol-gel reaction. ‘M’ can be a metal or metalloid

The HSG had been intensively investigated through all the 1980s [22, 23] by several researchers worldwide, but surely Wilkes *et al.* and Schmidt *et al.* [24-27] had a pioneering role in applying this technic to the *in situ* synthesis of oxide nanoparticles for obtaining polymeric composite materials.

However, the HSG reactions have some intrinsic disadvantages. On the one hand due to generally low crystallinity of the as-synthesized products [28] and on the other hand, due to the high reactivity of the metal oxide precursors towards water (difficult control on hydrolysis and condensation rate). Moreover, a large number of reaction parameters have to be strictly controlled (pH, temperature, method of mixing, rate of oxidation, the nature and concentration of anions, catalysts) in order to provide good reproducibility of the synthesis protocol [22, 29].

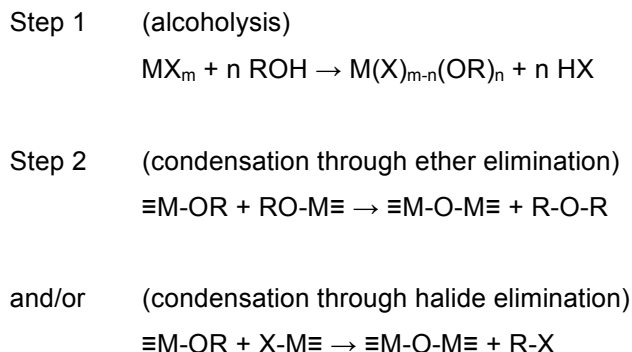
When a HSG reaction is employed for *in situ* generating nanoparticles in polymeric matrices an additional significant drawback has to be considered. The immiscibility between the organic phase and the aqueous sol-gel system typically leads to the formation of nanoparticles agglomerates if no surfactant or coupling agent is added to the reactive system [30], increasing the number of parameters to control.

1.2.2 – Non Hydrolytic Sol-Gel Synthesis

In order to overcome the typical problems related to HSG, the non-hydrolytic sol-gel (NHSG) route can be used for synthesizing oxides nanoparticles characterized by high purity and crystallinity.

As in the case of the aqueous route, the NHSG process can be described by two consecutive reactions. The first step (alcoholysis) involves the reaction of a metal (or non-metal) halide or alkoxide with an organic solvent as oxygen source (such as alcohol, ether, etc.). The second step (condensation) can follow different pathways depending on nature of the precursor and/or the employed oxygen donor [31].

Concerning the reaction between metal halide and alcohols the most common condensation reactions occur through alkyl halide elimination and/or ether elimination as schematically indicated [32, 33]:



Scheme 1.2.1.2 – Series of reactions involved in a non-hydrolytic sol-gel reaction. ‘M’ can be a metal or metalloid

The early studies on similar reactions started at the end of the 19th century when the reaction between various metal alkoxides and alcohols were investigated. Ebelmen, for example, found that silicon tetrachloride forms silica when reacts with ethanol [34]. About 80 years later, Dearing and Reid presented their work entitled “Alkyl Orthosilicates” [35] proposing an aqueous and non-aqueous route to obtain silica. Gerrard *et al.* [36-38] and other European researchers continued to work on this topic also exploring the use of others oxide precursors and organic solvents [39-44]. Nevertheless, these publications were more or less isolated efforts that did not received a lot of attention by the scientific community.

However, in the middle of 1980s, and more intensively at the beginning of the 1990s NHSG had a great development. Many organic solvents and oxide precursors were tested for synthesizing several nanometric metal oxides by NHSG [45, 46]. A pioneering role in the field of NHSG has also been played by Vioux and co-workers, who synthesised a variety of metal and non-metal oxides by using many different organic solvents [47-49].

Niederberger *et al.* have worked on many transition metals by the well-known “benzyl alcohol route” as reported in [50-53]. This NHSG pathway was also widely used by Pinna *et al.* who investigated new oxides preparation methods [54-56], especially for mixed metal oxides [57, 58]. Recently, Nair *et al.* proposed an

innovative NHSG route, which employs cellulose as oxygen source [59], showing that polymeric reagents can be used instead of common organic solvents.

From the second half of the 1990s these reactions have been also employed in the *in situ* filler generation for preparing polymer nanocomposites [18]. The presence in the reactive medium of an organic solvent, instead of water, permitted to achieve better miscibility of the polymeric phase and the sol-gel system, limiting the formation of particles aggregates. Moreover, the wide variety of suitable organic oxygen sources and the few reaction parameters to control make the NHSGs the most appropriate chemical reactions for *in situ* synthesizing oxide nanoparticles in polymers [12].

Eventually, by using NHSG, size and shape of reaction products can be controlled by the organic solvent (according to “solvent-controlled approach”), avoiding the use of expensive surfactant (according to “surfactant-directed approach”) that are usually needed for controlling HSG reactions. The pros and cons of these approaches are well documented by Pinna *et al.* in [60].

1.3 – Oxides

Oxides represent the most diverse class of materials with wide range of applications in several fields of science, thanks to their properties that cover, basically, all studied characteristics in materials science [61].

Without any doubts, oxides play an outstanding role in many applications that are regarded as particularly promising within the broad area of nanotechnology, such as nanophotonics, spintronics, energy storage and conversion, catalysis and biomedical applications.

The great variety of structures and properties of oxides made this class of materials not only the primary target in solid state chemistry, but also represent a major inspiration for designing new materials.

All these properties, on the nanoscale, are strongly affected by the particles size and shape [62, 63]. In the last decades much research has been aimed at the development of “soft chemistry” pathway to the synthesis of inorganic oxides that allowed controlling the particles size and shape, but also polymorphism, crystallinity, purity and particles surface functionalization.

Transition metal oxides and oxides deriving from the so-called “metalloids” elements have been intensively studied both from a chemical and physical point of view. Especially, Al_2O_3 , SiO_2 , ZrO_2 , Fe_3O_4 , TiO_2 , ZnO , Cu_2O , Ga_2O_3 , In_2O_3 , Ta_2O_5 and SnO_2 have been attracting considerable attention because of their intrinsic properties [64]. Furthermore, a wide range of mixed oxides can be also synthesized when one element, composing the pristine oxide, is exchanged with another suitable metal or non-metal. This can lead to either an enhancement of the exiting properties or new features.

1.3.1 – Titanium Dioxide

Nowadays, titanium dioxide (TiO_2) is still playing an important role in many fields of the scientific research and industrial world. Three polymorph phases of TiO_2 are known, the most thermodynamically stable one is the rutile, whereas the metastable ones are anatase and brookite that convert to rutile upon heating at 550°C and 750°C respectively [65].

In the early twentieth century, TiO_2 was widely employed for several products such as pigments, sunscreens, paints, ointments and toothpaste. In 1972 Fujishima and Honda [66, 67] discovered the phenomenon of photocatalytic splitting of water on anatase electrode under ultraviolet (UV) irradiation. Since then, the interest on crystalline anatase based materials increased quickly up to reaching nearly all fields of materials science, physic and chemistry [68].

TiO_2 has also found application in optics [69, 70], catalysis [71, 72], photocatalysis [73, 74], dye-sensitized solar cells [75, 76], plastic solar cells [77, 78], gas sensors [79, 80] and precursor materials for mesoporous materials [81, 82]. Moreover, TiO_2 is widely used for innovative ceramic materials and coatings [83-86], but also as common filler for organic/inorganic hybrid nanocomposites [12, 13]. Among fillers for nanocomposite, TiO_2 nanopowder has increasingly been investigated because it is non-toxic, chemically inert, low cost, has a high refractive index, is a broadband UV filter, kills bacteria by photo irradiation, is corrosion resistant and has a high hardness [87].

Among the various available methods [68], the NHSG process represents one of the most innovative and widely studied technic for synthesizing crystalline TiO_2 nanoparticles.

1.4 – State of the Art

1.4.1 – Composite Based on Polymeric Matrix / TiO₂

Oxide particles/polymer nanocomposites have been having a great development since the second half of the 1990s. It is well known that rigid fillers, embedded in a polymer, are able to improve the mechanical proprieties, due to the constrained chains mobility, and the thermal properties of the neat matrix. Al₂O₃, SiO₂, TiO₂, ZrO₂ and ZnO particles are the most commonly used oxides, inducing a significant reinforcing and stiffening effect to the polymeric matrix.

The incorporation of TiO₂ nanoparticles can also lead to other interesting properties, for this reason, polymer/TiO₂ hybrids have found application in many different fields such as antibacterial materials [88], UV filters [89], high reflective index materials [27] and in the field of organic solar cells [77]. Furthermore, as explained by Zhao *et al.* in their review [13], nanocomposites play an important key role also in environmental applications field.

The preparation of polymer/TiO₂ hybrids was proposed in literature by using either the conventional mechanical dispersion or ultrasonic irradiation, as described in the follows.

Polyurethane/titania [90] and ethylene-vinyl alcohol copolymer/titania [88] were suggested as antibacterial materials, exhibiting excellent antimicrobial activity under UV irradiation. In the case of ethylene-vinyl alcohol copolymer, the presence of TiO₂ nanoparticles led also to an enhanced photodegradation rate of the polymer, through the sunlight irradiation, providing an effective alternative to the biodegradation.

Antonello and co-workers described a method for tuning the reflective index of a polymeric coating by means of the incorporation of titania nanoparticles [91]. Whereas, Smith *et al.* [89] prepared transparent polymeric UV filters by a simple mechanical dispersion of titania nanoparticles in a solution of poly(vinyl alcohol) or poly(vinyl pyrrolidone), providing interesting examples of possible applications.

Poly(L-lactide-co-ε-caprolactone)/TiO₂ [14], poly(L-lactide)/TiO₂ [92], poly(methyl methacrylate) (PMMA)/titania [93] are other examples of thermoplastic matrices in which the nanoparticles were mechanically dispersed in solution mixing.

Concerning thermoset organic matrices, Zhou *et al.* [94] and Al-Turaif [95] yielded studies on the effect of particle size and weight fraction on mechanical properties and failure mode of epoxy resins filled with titania. TiO₂ nanoparticles were also used for reinforcing EPDM rubber, leading to an enhancement not only of mechanical properties but also of thermal stability and crosslinking density thanks to an effective filler capping [96].

Taking advantage of employing sol-gel chemistry for *in situ* generating oxide nanoparticles, the preparation of polymer/titania nanocomposites was already proposed in the literature as described in the follows.

The preparation of poly(amide-imide)/titania composites was suggested by Tsai *et al.*, exploiting sol-gel reactions between tetraethyl orthotitanate (titania precursor) and acetylacetone (reaction solvent and oxygen donor) in the presence of pre-polymerized poly(amide-imide) [97]. Polyimide/TiO₂ nanocomposites were also prepared by using very similar procedure and polymeric matrices, through the reaction between a titanium alkoxide and a suited oxygen source [98-101].

Polyacrylate/TiO₂ and polycaprolactone/TiO₂ are other significant examples of organic/inorganic hybrids synthesized by means of *in situ* sol-gel synthesis [102, 103].

Transparent PMMA ternary nanocomposites containing silica and titania that present enhanced thermal stability were prepared starting from methyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate as monomers, tetraethoxysilane and titanium ethoxide as inorganic oxides precursors [104]. A similar synthetic approach was also proposed by Du and co-workers for the preparation of PMMA/silica/titania and PMMA/silica/zirconia nanocomposites with improved thermal and thermo-oxidative stabilities for potential applications in optical devices [105-107]. Polyimide/silica/titania [108] is an additional example of thermoplastic/matrix ternary nanocomposites in which the filler nanoparticles were obtained through NHSG process.

Concerning uncommon investigated organic matrices, poly(amidoamine) dendrimers/titania hybrids were successfully prepared through the hydrolysis and condensation of titanium(IV) ethoxide, previously embedded in the dendrimeric hosting template. The obtained hybrids showed high transparency, good thermal

stability and brittleness due to the enhanced interaction of the inorganic material with dendrimers through hydrogen bonds [109].

Di Gianni and co-workers showed a typical example of thermal and mechanical properties improvements of phenolic hyperbranched polyester by *in situ* generation of titania nanoparticles. The authors reported a procedure based on the synthesis of TiO_2 nanoparticles, from titanium isopropoxide, in polymer solution subsequently thermally cured by 1,6-diisocyanatohexane. The curing step produced a three-dimensional network in which the titania nanoparticles resulted in a typical reinforcing and stiffening effect due to the presence of the homogeneous dispersed rigid nanofiller. In order to further improve these properties, the matrix was also partially modified with alkoxy silane groups that reacting with $-\text{OH}$ s on titania nanoparticles surface led to the formation of real covalent bonds between organic and inorganic phase [110].

In comparison with the samples prepared by conventional mechanical mixing methods, these hybrids exhibit higher optical transparency and equal mechanical properties but using a lower content of filler. Moreover, the *in situ* particles synthesis usually leads better phases mixing and distribution of the filler avoiding the rheological problems related to the conventional approach. Despite of these advantages, the literature still lacks of numerous examples, probably because of the complexity of these systems. Indeed, for employing this approach an initial study for adapting the NHSGs to the *in situ* nanoparticle synthesis in polymers is needed. Furthermore, a systematic study on the effect of nanoparticles on different polymeric matrices would allow a deeper insight into the mechanisms that control these systems in order to make the proposed approach interesting from an industrial point of view.

1.5 – The Aim of this Study

Polymer nanocomposites are already a part of many important of worldwide businesses, driving the scientific research to develop innovative, simple to scale up and cost effective methodologies for producing these materials.

The main objective of this dissertation is the preparation of organic/inorganic hybrid nanocomposites based on polymers as matrix and titanium dioxide (TiO_2) nanoparticles as filler.

Exploiting the non-hydrolytic sol-gel chemistry, TiO_2 nanoparticles were *in situ* generated within polymers in order to obtain homogeneous nanostructured organic/inorganic hybrid composites. In addition, the proposed approach allowed overcoming the typical rheological problems related to the conventional mixing methods, nowadays still industrially used, proposing an effective alternative.

First of all, a study was carried out on the NHSG synthesis, using different organic solvents, in order to make these types of reactions suitable for the *in situ* filler generation in presence of polymers or monomers. The organic solvent plays a double role in this process; it dissolves the organic matrix and acts as oxygen source in the titania nanoparticles formation. For this reason the NHSG reactions have to be previously studied and the solvent has to be carefully chosen.

Four types of polymeric matrices were filled with TiO_2 nanoparticles: poly methyl methacrylate (PMMA), two widely used epoxy resins (DGEBA and CE), ethylene-propylene diene monomer rubber (industrially known as EPDM) and polyurethanes.

Finally, the obtained composites were characterised from a chemical, physical and mechanical point of view in order to contribute to the understanding of the effects of the TiO_2 particles incorporation on the polymer's proprieties.

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Chapter 2

MATERIALS AND METHODS

2. Materials and Methods

2.1 – Materials

All chemicals following reported were high purity reactants and were used as received without any further purification. All reagents were purchased by Sigma Aldrich (Milan, Italy).

Common solvents: toluene, chloroform, dichloromethane, dimethylformamide, acetone, ethanol, methanol, acetonitrile and diethyl ether.

Other solvents: benzyl alcohol (BzOH), tert-butyl alcohol (tBuOH) and propylene carbonate (PC).

Reagents: titanium(IV) chloride (TiCl_4), triphenylsulfonium hexafluoroantimonate (UVR 6990), ytterbium(III) trifluoromethanesulfonate hydrate ($\text{Yb}(\text{OTf})_3$), dicumyl peroxide (DCP), formic acid and methylene blue (MB).

Polymeric matrices: bisphenol A diglycidyl ether (DGEBA, Dow D.E.R.TM 332 with an epoxide equivalent weight of 172-176), 3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexanecarboxylate epoxy resin (CE), poly(methyl methacrylate) (PMMA, Optix[®] CA-1000 I Clear) commercial grade was obtained by Plaskolite West Inc. California (melt flow rate 2.3 g/10 min at 230°C/3.8 kg), Ethylene-Propylene Diene Monomer (EPDM rubber, Polimeri Europa Dutral[®] TER 4038, density $\rho_{\text{EPDM}} = 0.91 \text{ g}\cdot\text{cm}^{-3}$) was kindly provided by ATG Italy (Castel d'Argile, BO, Italy).

2.2 – Powder Synthesis

NHSG were studied in order to implement these reactions for *in situ* synthesising nanoparticles in polymeric matrices. Three different suitable organic oxygen donors were employed, depending on the polymer used as matrix.

2.2.1 – Synthesis in Benzyl Alcohol

According to “benzyl alcohol route” (designed and optimized by professor Niederberger and co-workers, Department of multifunctional materials, ETH, Zurich, Switzerland) [1], a given quantity of TiCl_4 was added drop-wise to BzOH at room temperature under vigorous stirring (reagents amounts in Table 2.2.1.1). The reaction was left stirring at room temperature for 15 min and consequently heated for 24 h. The reaction was studied as a function of the $\text{TiCl}_4/\text{BzOH}$ ratio and the reaction temperature (70°C and 100°C, respectively), in order to understand how these parameters affect the morphology, phase and particles size of the synthesized powders.

Sample Code	BzOH (mL)	TiCl_4 (mL)	Reaction temperature (°C)	Molar Ratio $\text{TiCl}_4/\text{BzOH}$
T_Bz_1	20	9.50	70	0.491
T_Bz_2		4.70	70	0.222
T_Bz_3		2.90	70	0.137
T_Bz70_4		0.42	70	0.020
T_Bz100_4		0.42	100	0.020

Table 2.2.1.1 – Used reagents amounts, reaction temperature and related reagents molar ratio

2.2.2 – Synthesis in tert-Butyl Alcohol

Benzyl alcohol has a very high boiling point (206°C) that makes it difficult to completely eliminate, especially when it is used for an *in situ* generation of metal oxide in polymeric matrices. For this reason, an alternative route that employs a solvent characterized by a lower boiling point (easier to remove) was also studied. tBuOH presents a boiling point at around 82°C and it can act as oxygen donor for the NHSG [2] as good as BzOH. A typical preparation was as follows: a correct

amount of TiCl_4 (Table 2.2.2.1) was added drop wise at room temperature under vigorous stirring to the tBuOH. The reaction was kept stirring at room temperature for 15 min and then warmed up to 70°C for 24 hours. In this case, the reaction was only studied as a function of the ratio $\text{TiCl}_4/\text{tBuOH}$.

Sample Code	tBuOH (mL)	TiCl_4 (mL)	Molar Ratio $\text{TiCl}_4/\text{tBuOH}$
T_tBu_1	20	2.00	0.087
T_tBu_2		1.03	0.040
T_tBu_3		0.30	0.013
T_tBu_4		0.09	0.004

Table 2.2.2.1 – Used reagents amounts and related molar ratio

2.2.3 – TiO_2 Nanoparticles Purification

The whitish obtained suspensions were firstly centrifuged at 4000 rpm for 30 min in order to remove as much as possible reaction solution. After this first purification step, the synthesized powders were carefully washed and centrifuged (for 15 min at 4000 rpm each time) as follows: twice with 15 mL of dichloromethane, twice with 15 mL of acetone and once with 15 mL of diethyl ether (each addition of fresh solvent was followed by 15 min of sonication in order to remove all traces of unreacted reagents that were not chemically bonded). Finally, samples were dried overnight under an aspiration hood at room temperature and for 6 hours in an oven at 80°C under vacuum.

2.3 – Composite Preparation

Nanocomposites based on polymeric matrices were prepared by *in situ* filler generation employing the NHSG reactions above described.

2.3.1 – Preparation of Composites Based on Poly(methyl methacrylate)

PMMA/TiO₂ nanocomposites were prepared by using both BzOH and tBuOH. These solvents have a double role; in fact they are not only the oxygen donor for the sol-gel process but also the reaction solvent where the polymeric matrix is dissolved.

PMMA/TiO₂ composites, obtained by using BzOH, having nominal TiO₂ contents of 5 and 10 wt% were prepared varying the amount of titania precursor (TiCl₄). A typical preparation was as follow: 10 g of PMMA were dissolved in 100 mL of BzOH at around 50 °C over night. After the dissolution, the TiCl₄ (0.8 and 1.5 mL, for obtaining 5 and 10 wt% of titania, respectively) were added drop wise at room temperature under vigorous stirring. The reaction solutions were left stirring at room temperature for 15 min in order to remove the yielded hydrochloric acid and consequently heated to the chosen temperature (70 and 100°C) for 24 h. The obtained suspensions (titania suspended in PMMA/BzOH solution) were precipitated drop by drop in 500 mL of methanol cooled down by ice bath. The precipitated composite flakes were filtered and carefully washed twice with methanol and dried at room temperature for 12 h and at 85 °C in an electric oven for further 5 h. Finally, the composites were dried under vacuum at 170 °C for 3 h to eliminate the residual BzOH.

PMMA/TiO₂ composites, obtained by using tBuOH, having nominal TiO₂ contents of 5, 15, and 20 phr (parts per hundred resin) were prepared varying the amount of titania precursor (TiCl₄). A typical preparation was as follow: about 2 g of PMMA was dissolved in 100 mL of tBuOH at 50 °C. After the dissolution step, the TiCl₄ (0.15, 0.43, and 0.58 mL, for obtaining 5, 15 and 20 phr of titania, respectively) was added drop wise at room temperature under vigorous stirring. The reaction was kept under stirring at room temperature for 15 min and then heated at 70 °C for 24 h. The obtained whitish suspensions were partially dried (about 50 % of the initial

volume) by rotary evaporator at 40°C under vacuum. In order to completely eliminate the residual tBuOH and other volatiles, the remaining suspensions were cast in a mould and maintained under an aspiration hood overnight. Finally, the specimens were placed in an electric oven at 75 °C for 5 h and under vacuum for other 5 h. All samples, prepared by using both solvents, are listed in Table 2.3.1.1.

Sample Code	TiO ₂ content	Solvent	Reaction temperature (°C)
PMMA_0	-	Benzyl Alcohol	-
PMMA_5T70	5%	Benzyl Alcohol	70
PMMA_10T70	10%	Benzyl Alcohol	70
PMMA_5T100	5%	Benzyl Alcohol	100
PMMA_10T100	10%	Benzyl Alcohol	100
PMMA_0T_t	-	t-Butyl Alcohol	-
PMMA_5T_t	5 phr	t-Butyl Alcohol	70
PMMA_15T_t	15 phr	t-Butyl Alcohol	70
PMMA_20T_t	20 phr	t-Butyl Alcohol	70

Table 2.3.1.1 – Sample codes and concerning descriptions

2.3.2 – Preparation of Composites Based on Epoxy Resins

These composites were prepared using BzOH as oxygen donor and two different epoxy resins (CE and DGEBA) that were cured using both a thermal and UV initiator. The procedure used for preparing the composites was rather the same for both resins. TiO₂ nanoparticles were synthesized by the reaction between TiCl₄ and benzyl alcohol, which is also reactive towards the photo and thermal polymerisation of epoxy resins induced by cationic initiators. In particular, it is well known that the propagation step in the cationic ring-opening polymerisation of epoxy groups involves nucleophilic attack of oxygen atoms from the monomer molecules on the cationic growing species (oxonium ions) according to the mechanism known as the ‘active chain end’ mechanism [3]. If hydroxyl groups containing compounds (such as benzyl alcohol) are present in the system, oxygen atoms coming from HO-groups may compete with the epoxy rings in reaction with oxonium ions. Such a mechanism is known as the ‘activated monomer’ mechanism [4, 5]. Titania suspensions in benzyl alcohol were thus polymerised with epoxy resin in the

presence of cationic either photo or thermal initiators in order to obtain a highly cross-linked epoxy-based materials reinforced with *in situ* generated titania nanoparticles. Moreover, this method allowed avoiding the solvent evaporation step that is particularly difficult when a high boiling point solvent is involved in the process (as in this case, BzOH boiling point is 206°C).

Concerning the thermally cured samples, a given quantity of TiCl_4 (see composition details in Table 2.3.2.1) was added drop wise to 1.50 g of BzOH at room temperature under vigorous stirring. The reaction was left stirring at room temperature for 15 min and then heated to 70°C for 24 h. After reaction was completed a stable suspension was obtained.

A typical thermally-curable formulation was prepared by mixing the previously obtained titania suspensions, epoxy resin and a solution of $\text{Yb}(\text{OTf})_3$ in PC (1:3 wt/wt ratio) as thermal cationic initiator (see composition details in Table 2.3.2.1) by using a T18 Ultra-Turrax® Ika disperser (5 min mixing time) followed by 15 min treatment in an ultrasonic bath. The formulations were casted into silicone molds having cavities with dimension $4 \times 1 \times 0.2 \text{ cm}^3$. All formulations were cured at 120°C for 25 min and a post-curing 20 min long at 160°C was subsequently applied.

A similar procedure was followed for preparing UV-cured samples. Two sorts of specimens were prepared, in this case, by the addition of UVR 6990 as UV cationic initiator (2 phr). For dynamic-mechanical thermal analysis, the formulations were placed between two microscope glasses (covered by a polypropylene film in order to ensure an easy detachment of the free-standing photo-cured films), spaced each other of about 200 μm by using a suitable mask in order to obtain a cured film having dimension $5 \times 25 \text{ mm}^2$. The specimens were irradiated for 4.5 min each side employing a UV lamp (Italquartz), with radiation intensity on the sample surface of about $48.5 \text{ W} \cdot \text{m}^{-2}$ (UVA) and $35.2 \text{ W} \cdot \text{m}^{-2}$ (UVB). Whereas, for nano-indentation and scratch tests, the formulations were coated onto microscope glasses by using a wire-wound applicator (film thickness of about 100 μm). The specimens were irradiated three times employing a medium vapour pressure mercury dynamic UV lamp (Fusion, H bulb), with radiation intensity on the sample surface of $280 \text{ mW} \cdot \text{cm}^{-2}$ and a belt speed of $2.5 \text{ m} \cdot \text{min}^{-1}$ was used to induce the photo-polymerisation.

Sample Code	Resin Type	BzOH (g)	TiCl ₄ (mL)	Initiator (g)	TiO ₂ content (phr)
Ep	CE	1.50	-	(UV)	-
Ep-T3	CE		0.21	(UV)	3
Ep-T6	CE		0.34	(UV)	6
Ep-T10	CE		0.69	(UV)	10
CE_T0	CE		-	(thermal)	-
CE_T3	CE		0.21	(thermal)	3
CE_T5	CE		0.34	(thermal)	5
CE_T10	CE		0.69	(thermal)	10
DGEBA-T0	DGEBA		-	(thermal)	-
DGEBA-T3	DGEBA		0.21	(thermal)	3
DGEBA-T5	DGEBA		0.34	(thermal)	5
DGEBA-T10	DGEBA		0.69	(thermal)	10

Table 2.3.2.1 – Sample codes and concerning descriptions

2.3.3 – Preparation of Composites Based on EPDM rubber

In a preliminary study a conventional SG reaction was employed to *in situ* generate SiO₂ in EPDM rubber [6]; after this early experience a NHSG synthesis was used in order to improve the filler dispersion and decrease the agglomeration rate due to the low miscibility of the aqueous sol-gel system with the organic matrix.

Once again, tBuOH was used as oxygen source but considering the low miscibility of EPDM in this solvent, toluene was used as reaction media. The tBuOH / TiCl₄ molar ratio was maintained at 25 whereas the amount of TiCl₄ was varied in order to obtain composites having a nominal content of TiO₂ (i.e. considering the complete conversion of TiCl₄ to TiO₂) of 0, 10, 20 and 30 wt% with respect to EPDM rubber.

EPDM rubber was dissolved in toluene (about 3 g in 100 mL) at room temperature. After complete dissolution, the sol-gel system was prepared as follows: a given amount of TiCl₄ was added drop-wise to tBuOH under vigorous stirring at room temperature. After stirring for 15 minutes, the resulting sol was mixed with a previously prepared EPDM solution in a round-bottom flask and heated in an oil bath at 70 °C for 24 hours in order to complete the NHSG reaction

in the presence of the organic matrix. The obtained suspensions were concentrated by rotary evaporation at 50 °C in order to eliminate about 70% of the volatile substances (toluene, unreacted tBuOH and by-products of the NHSG reaction). The high viscous suspensions were then cast in a Petri dish and the volatiles were completely eliminated by leaving the systems under an aspiration hood overnight. For all the samples, DCP (dissolved in 1 mL of toluene) was also added at a concentration of 4 phr (with respect to EPDM) as vulcanizing agent and mechanically mixed before the end of the solvent elimination step, when the viscosity of the suspension was not too high to inhibit the mixing. Some of the films (about 0.5 mm thick) were vulcanized by hot-pressing at 160 °C for 20 min. The unvulcanized and vulcanized materials were coded as EPDM_x and EPDM_x_V, respectively, in which x represents the nominal final weight percent of titania (Table 2.3.3.1).

Sample Code	TiO ₂ content (wt%)	Vulcanization	Toluene/tBuOH (mL/mL ratio)
EPDM_0	-	No	-
EPDM_10	10	No	10.1
EPDM_20	20	No	4.5
EPDM_30	30	No	2.6
EPDM_0_V	-	Yes	-
EPDM_10_V	10	Yes	10.1
EPDM_20_V	20	Yes	4.5
EPDM_30_V	30	Yes	2.6

Table 2.3.3.1 – Sample codes and concerning descriptions

2.4 – Characterization Technics

2.4.1 – Technics for Powders Characterization

The synthesized titania powders were analyzed with a computer-assisted conventional Bragg-Brentano diffractometer using the Ni-filtered CuK α monochromatic radiation ($\lambda = 1.5418 \text{ \AA}$) (X'Pert PRO, Panalytical) to identify the crystalline phase. The X-ray diffraction (XRD) patterns were collected at room temperature in a 2θ range of $10\text{--}90^\circ$, with a scanning rate of $0.005^\circ\cdot\text{s}^{-1}$ and a step size of 0.02° . Average crystallites size was estimated from X-ray line broadening measurements; it was calculated using the TiO₂ (101) diffraction line according to the Scherrer formula (Eq. 1): [7]

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta}$$

Equation 1

Where D is the average crystallite size, λ is the wavelength of the X-ray, θ is the diffraction angle, and β is the full width at half maximum.

Particles morphology was examined by transmission electron microscopy, (JEM 2010 TEM, Jeol). A drop of the so obtained suspensions was diluted in 5 mL of ethanol, sonicated and finally placed on a copper grid (Carbon Film 200 Mesh Cu, Agar Scientific) followed by drying at 40°C . TEM images were analyzed and processed by ImageJ open-source software in order to also evaluate the average particles size.

Titanium dioxide particles size distribution was analysed by dynamic light scattering (DLS, Malvern - Zetasizer nano series) on suspension as obtained from the reaction.

The amount of organic volatile fraction was evaluated by gravimetric analysis, measuring the percentages of weight loss (starting weight about 0.5 g) after a treatment at high temperature. The treatment was carried out at 500°C for 4 hours in an electric furnace (Optolab – FS5), up to constant mass was reached. Moreover, the thermal behaviour of the synthesised powders was monitored by a Perkin-Elmer TGA7 thermogravimetric analyzer (TGA) under air flow, from 30 up to 750°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

The qualitative investigation of the residual organic groups and/or free –OH chemically bonded on the particles surfaces was performed by Fourier transform infrared (FT-IR) analysis on the prepared powders. The analysis was carried out using an FT-IR VERTEX 70 spectrometer (Bruker) in attenuated total reflectance (ATR) mode from 4000 to 500 cm⁻¹, equipped with ZnSe crystal [8, 9].

The specific surface area (SSA) and density (ρ) of the powders were determined by the BET method [10] (Gemini 2360 apparatus, Micromeritics) and by a picnometer (Accupic 1330 apparatus, Micromeritics), respectively.

Assuming the particles are closed spheres, average particle size was also calculated from the data of specific surface area, using the Eq. 2 [11]:

$$\phi = \frac{6}{\text{SSA} \cdot \rho} \quad \text{Equation 2}$$

Where ϕ is the average diameter of the spherical particle, SSA is the specific surface area of the powder, and ρ is the experimental density of powders.

The photocatalytic activity of the powders, synthesized by BzOH and tBuOH, was evaluated by the decomposition of methylene blue (MB) dye. About 0.01g of TiO₂ was added to MB aqueous solution (volume = 75 mL, concentration = 3 E⁻⁵ M). The suspension was irradiated by means of ultraviolet (UV) light in a dark chamber for 24 h under vigorous stirring. A medium pressure mercury lamp (Hamamatsu LC-8) equipped with an optical waveguide was used as light source with wavelength that ranges between 325 and 390 nm and light intensity of 5.5 mW·cm⁻².

The MB solution color disappearing was repeatedly monitored every hour by an ultraviolet-visible (UV-Vis) spectrophotometer (Perkin-Elmer, Lambda 19) measuring the maximum of absorbance at 660 nm. Calibration based on Lambert-Bee law was used to quantify the dye concentration. The photodecomposition (*pd*) of MB was calculated by the following equation:

$$pd = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad \text{Equation 3}$$

Where C_0 is the starting MB concentration and C_t is the MB concentration at the generic time t .

2.4.2 – Technics for Composites Characterization

The actual titania contents were evaluated by gravimetric analysis (starting sample mass about 0.5 g), calculating the amount of residual titania after a treatment at high temperature in an electric furnace (Optolab – FS5). The treatment was carried out at 500°C for 4 hours, up to constant mass was reached.

The filler volume fractions of the final nanocomposites were calculated taking into account the experimentally determined density values of pristine matrix and titania powders under the assumption of density additivity.

In order to evaluate the thermal stability of the EPDM/TiO₂ composites, a thermogravimetric analysis (TGA) was performed by a Perkin-Elmer TGA7 thermogravimetric analyzer under nitrogen flow, from 30 up to 700 °C at a heating rate of 10 °C·min⁻¹.

Differential scanning calorimetry (DSC) analysis was carried out by a Thermal Analysis TA2010 Instruments at a scanning rate of 5 °C·min⁻¹, under nitrogen flow. The glass transition temperature ($T_{g, DSC}$) was assumed as the mean value of the energy jump of the thermogram (average value between the onset and the endpoint of the glass transition range). For EPDM/TiO₂ composites was carried out from -70 to 200°C, whereas for the samples based on epoxy resins the measure ran from 0 to 200°C.

The polymer molecular weight and their distribution were measured by gel permeation chromatography (GPC) using chloroform as eluent (elution rate of 0.3 mL/min) on a HPLC Pump Waters 1515 equipped with a refractive index detector Waters 2410 and a PLgel Mixed-D column.

The prepared specimens were broken in liquid nitrogen in order to have a brittle fracture and the cross-sections were analysed by field emission scanning electron microscopy (FESEM, FEI STRATA DB235M Dual beam FIB-SEM instrument) by the application of an accelerating voltage of 15 kV. The cross sections were previously coated with gold (thickness 10 - 15 nm) by an electro-deposition method to impart electrical conduction. The obtained images were analyzed and processed by ImageJ open-source software. The qualitative chemical analysis of the prepared materials was carried out by energy dispersive X-ray spectrometry (EDX).

Fourier transform infrared (FT-IR) spectroscopy was performed using an Avatar 330 FT-IR Thermo Nicolet spectrometer, equipped with a diamond crystal, operating in attenuated total reflectance (ATR) mode from 4000 to 500 cm^{-1} (32 scans and 4 cm^{-1} of resolution). For thermally-cured epoxy resins, the epoxy group conversion (α), was calculated by evaluating the area of the signal at 910 cm^{-1} [8], corresponding to symmetric stretching of the epoxy group, normalized with respect to the constant signal (typical carbonyl signal at 1730 cm^{-1} for CE and the C=C aromatic ring stretching at 1510 cm^{-1} for DGEBA) [8]. The conversion of epoxy group (α) was calculated by the following equation:

$$\alpha = 100 - \left(\frac{A_t}{A_0} \cdot 100 \right) \quad \text{Equation 4}$$

in which A_0 is the normalized area of the signal at 910 cm^{-1} of the mixture before the curing process and A_t is the normalized area of the signal at 910 cm^{-1} after the curing process.

Concerning the UV-cured epoxy resin the polymerization kinetic was monitored by means of real-time Fourier transform infrared (FT-IR) spectroscopy, employing a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer by using a wire-wound applicator (about 25 μm thick) and exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which *in situ* analyses the extent of the reaction. A medium pressure mercury lamp (Hamamatsu LC-8) equipped with an optical waveguide was used to induce the photo-polymerisation (the applied light intensity on the sample surface of about 33.5 $\text{W}\cdot\text{m}^{-2}$ UVA and 24.4 $\text{W}\cdot\text{m}^{-2}$ UVB). The IR absorbance can be considered proportional to the monomer concentration; thus conversion versus irradiation time profiles may be obtained. To this aim, the epoxy ring opening mechanism was followed by monitoring the decrease in the absorbance of the peak centred at 910 cm^{-1} [8].

Extractable fraction (f) was determined on the cured/vulcanized specimens by measuring the weight loss after 24 h of extraction in chloroform at room temperature for samples based on epoxy resins. Whereas, in the case of EPDM rubber based composites, toluene was used as extracting solvent, according to an adaptation of the ASTM D2765-84 technical standard.

In both cases, extractable fraction was calculated by the following equation:

$$f = \frac{m_0 - m_d}{m_0} \cdot 100 \quad \text{Equation 5}$$

Where m_0 is the mass of the sample before its immersion in the solvent and m_d is the dried mass of the sample after 24 h extraction. (Gel content (G) is described as: $G = 100 - f$).

The values of f were also normalized to the actual organic phase content (i.e. the extractable phase in the case of incomplete cross-linking), and these values were called f_{ORG} , respectively. Their values were calculated as follows:

$$f_{ORG} = \frac{f}{w_{ORG}} \quad \text{Equation 6}$$

where w_{org} is the weight of organic fraction present in the composite.

Swelling experiments were carried out only on EPDM/TiO₂ composites by the immersion of punch-cut specimens (size 10×10×0.5 mm³) in 15 mL of toluene at room temperature for 24 hours in order to eliminate all uncross-linked fractions, such as unvulcanized EPDM chains, which would lead to wrong values of the swelling ratio. When the swollen mass (m_s) reached a constant value, the sample was dried to a constant mass (i.e., the dried mass m_d), and the absolute swelling ratio (q) was evaluated according to the following equation:

$$q = \frac{m_s}{m_d} \quad \text{Equation 7}$$

The value of q was normalized to the actual EPDM weight (the swellable phase and in the case of incomplete vulcanization the extractable phase). The obtained data was called q_{EPDM} and calculated as follows:

$$q_{EPDM} = \frac{q}{w_{EPDM}} \quad \text{Equation 8}$$

where w_{EPDM} is the weight fraction of EPDM present in the composite.

Dynamic-mechanical thermal analyses (DMTA) were carried out on an MK III Rheometrics Scientific Instrument at 1 Hz frequency in the tensile configuration (single cantilever for Polyurethane), 0.1% of strain and employing a heating rate of 5°C · min⁻¹. The storage modulus (E') and the loss factor ($\tan\delta$) were measured from

0°C up to the temperature at which the rubbery state was attained for epoxy resins and PMMA based composites, whereas from -100 to 100°C for composites based on EPDM. The glass transition temperature ($T_{g, DMTA}$) was assumed as the maximum of the loss factor curve.

Uniaxial tensile tests were performed on EPDM/TiO₂ composites by a Hounsfield dynamometer (model H5KS). The experiments were run at room temperature, on strips 32×13×0.5 mm³ in size, using a gauge length of 10 mm and a crosshead speed of 100 mm·min⁻¹.

The nano-hardness was measured by depth-sensing Vickers nano-indentation (Nano-Indentation Tester, CSM Instruments) on the carefully polished surface of the samples (using a 2500 mesh SiC paper). The maximum load was fixed at 20 mN (5 indentations per sample, loading/ unloading rate of 16 mN·min⁻¹).

Scratch test was carried out on a CSM Micro-Combi tester. A controlled scratch on the coating surface is made with a diamond tip (Rockwell C diamond scratch indenter with tip radius of 800 μm) on the sample (five samples each). The tip is drawn across the coated surface under progressive load (from 20 mN to 20 N) over a scratch length of 3 mm.

The photocatalytic activity of the composites, prepared by tBuOH, was evaluated by the decomposition of methylene blue (MB) dye. A specimen of PMMA/TiO₂ was immersed into MB aqueous solution (volume = 75 mL, concentration = 3 E⁻⁵ M). The solution was irradiated by means of ultraviolet (UV) light in a dark chamber for 24 h under vigorous stirring. A medium pressure mercury lamp (Hamamatsu LC-8) equipped with an optical waveguide was used as light source with wavelength that ranges between 325 and 390 nm and light intensity of 5.5 mW·cm⁻². The MB solution color disappearing was repeatedly monitored every hour by an ultraviolet-visible (UV-Vis) spectrophotometer (Perkin-Elmer, Lambda 19) measuring the maximum of absorbance at 660 nm. Calibration based on Lambert-Bee law was used to quantify the dye concentration. The photodecomposition (*pd*) of MB was calculated by Eq. 3.

The photodegradation of the samples based on PMMA/TiO₂ (prepared by BzOH) was tested under ultraviolet (UV) radiation exposure test. The specimens (dimensions 22×8×2 mm³) were placed in a black box and exposed to UV radiation for 1200 h, by using an Osram Ultravitalux UV 300W lamp as UV source (315-400

nm 13.6W, 280-315 nm 3.0W). The specimens and lamp were spaced 18 cm apart, in order to have irradiation intensity on the samples surface in the range of 5.3–5.5 mW·cm⁻². The effect of the photodegradation was evaluated by FT-IR analysis and by measuring both gloss and weight loss as a function of the irradiation time. FT-IR analysis was carried out on the exposed surface of the irradiated specimens employing an Avatar 330 FT-IR Thermo Nicolet spectrometer equipped with a ZnSe crystal operating in attenuated total reflectance (ATR) mode from 4000 to 500 cm⁻¹ (32 scans and 2 cm⁻¹ of resolution). Gloss measurements were performed on the UV exposed surface of the irradiated specimens by a Novo Gloss Trio apparatus; measuring the value at 60° as standard geometry.

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Chapter 3

RESULTS AND DISCUSSION

3. Results and Discussion

3.1 – Powders Characterizations

3.1.1 – TiO₂ Synthesized by Using Benzyl Alcohol

XRD patterns of the powders synthesized in BzOH are reported in Figure 3.1.1.1, in which is shown that all samples are composed by anatase as crystalline phase (JCPDS reference code: 00-021-1272). In Figure 3.1.1.1 is also clearly shown that the all investigated powders have nanometric crystallites dimensions as underlined by the typical broad reflections. The average crystallites size, determined by Scherrer equation (Eq.1), ranges from 6 to 10 nm dependent on the reaction temperature and the TiCl₄/BzOH molar ratio; as both ratio and reaction temperature are increased, the sizes increase as well (Table 3.1.1.1).

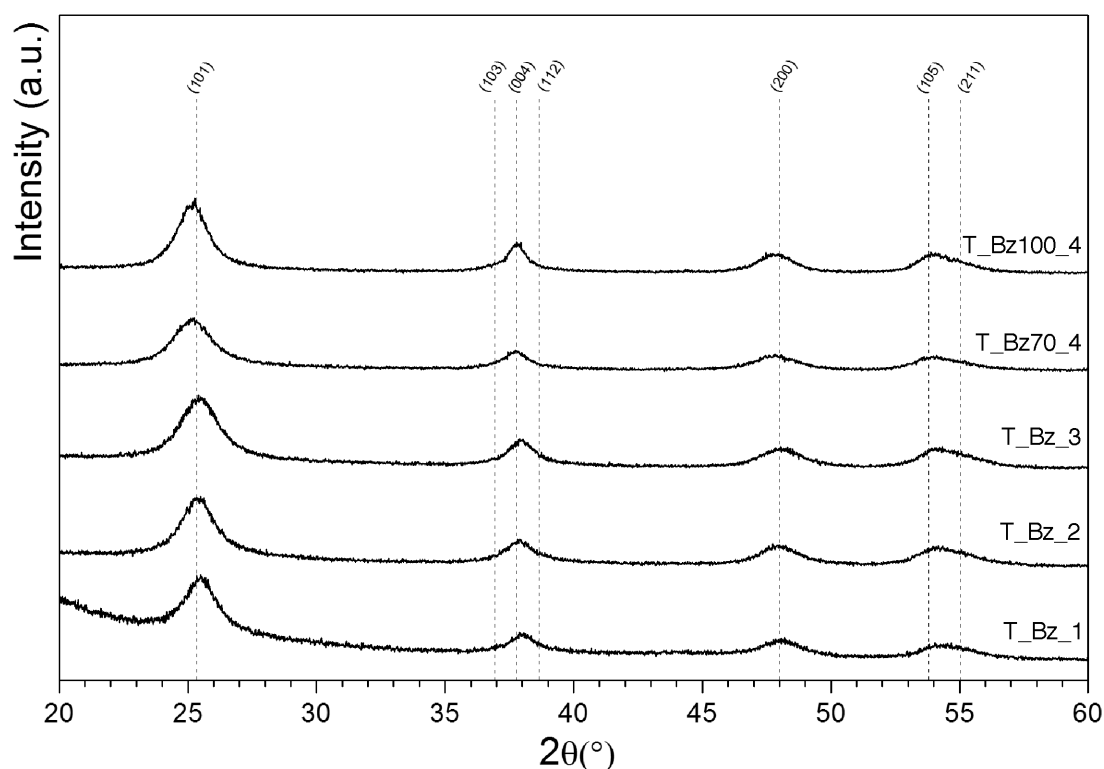


Figure 3.1.1.1 – XRD patterns of the synthesized powders. The (101) reflection at 25° (2θ) was used for determining the average crystallites size by Eq. 1

For quantifying the amorphous phase, Rietveld-RIR analysis was carried out. As expected, the NHSG route led to powders with a higher degree of crystallization in

comparison to aqueous sol-gel synthesized oxides, which usually leads to complete amorphous oxides as reported elsewhere [1]. In particular, as the temperature is increased, a slight increase of the anatase phase with respect to the amorphous phase was found (Table 3.1.1.1). Moreover, the amount of anatase is also inversely dependent on the $\text{TiCl}_4/\text{BzOH}$ molar ratio, as shown in Table 3.1.1.1.

Sample Code	Molar Ratio $\text{TiCl}_4/\text{BzOH}$	Crystallites size by Eq.1 (nm)	Particles size by TEM (nm)	Anatase phase quantity (%)	Density ($\text{g}\cdot\text{cm}^{-3}$)	SSA ($\text{m}^2\cdot\text{g}^{-1}$)	Residual at 500°C (%)
T_Bz_1	0.491	10 ± 1	9 ± 3	11.2 ± 0.2	1.393 ± 0.001	25.85 ± 1.71	24.1
T_Bz_2	0.222	9 ± 1	6 ± 2	36.2 ± 0.2	2.014 ± 0.001	48.34 ± 0.09	69.4
T_Bz_3	0.137	8 ± 1	7 ± 2	42.8 ± 0.1	2.598 ± 0.002	118.23 ± 0.04	70.4
T_Bz70_4	0.020	6 ± 1	4 ± 1	38.8 ± 0.1	2.830 ± 0.001	86.75 ± 1.74	70.5
T_Bz100_4	0.020	9 ± 1	6 ± 1	42.7 ± 0.2	-	-	69.7

Table 3.1.1.1 – Summary of the data obtained by the characterization of washed and dried powders

The shape and dimensions of the primary particles were evaluated by TEM. The nanostructured primary particles have quite uniform shape and the average size is in the range 4 - 9 nm, increasing with the precursor concentration in good agreement with results obtained by Scherrer's equation and as previously observed by Stucky *et al.* [2] in a similar system. In particular, the micrographs (Figure 3.1.1.2) demonstrate that $\text{TiCl}_4/\text{BzOH}$ molar ratio did not affect the morphology of the nanoparticles showing, for all samples, a value of roundness factor that ranges from 0.82 to 0.89.

The obtained images (Figure 3.1.1.2) also show that the agglomeration rate becomes more and more evident by increasing the $\text{TiCl}_4/\text{BzOH}$ molar ratio. The particles aggregation trend was also confirmed by DLS analysis (here not reported) that showed average particle size of 33 ± 4 nm and 55 ± 8 nm for T_Bz70_4 and T_Bz_2, respectively.

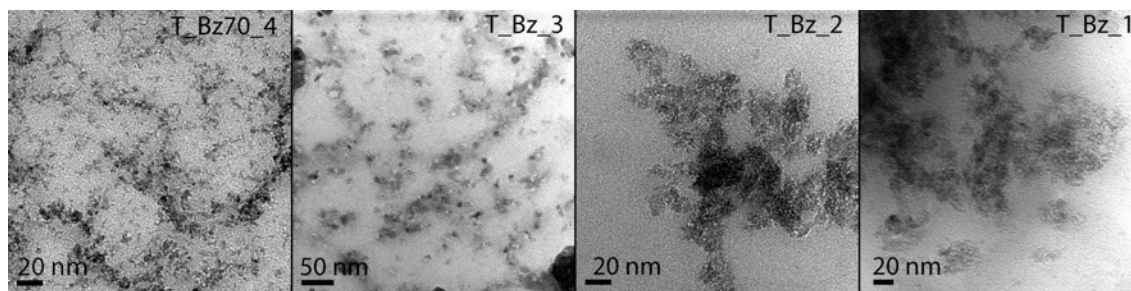


Figure 3.1.1.2 – TEM micrographs of the synthesized powders

Gravimetric analysis was carried out to evaluate the presence of volatile organics strongly adsorbed and/or covalently bonded to the TiO_2 particles surface. The obtained results showed the presence of a significant amount of organic species that increases with the added oxide precursor amount (Table 3.1.1.1).

The physical properties of powders are reported in Table 3.1.1.1. As expected for particle dimensions as small as shown by TEM micrographs, rather high SSAs were measured. The values range from a maximum of $118 \text{ m}^2\cdot\text{g}^{-1}$ for T_Bz_3 to a minimum of $25 \text{ m}^2\cdot\text{g}^{-1}$ T_Bz_1, showing a remarkable decrease by increasing the $\text{TiCl}_4/\text{BzOH}$ ratio. Analysing the data in Table 3.1.1.1 becomes evident that the particles dimension (by TEM) and SSA are inversely proportional showing a common size effect on the surface area.

In good agreement with the results of gravimetric analysis, the experimental density values (ρ_{exp}) are, for all powders, lower than the values in literature that is around $3.90 \text{ g}\cdot\text{cm}^{-3}$ for pure anatase and about $4 \text{ g}\cdot\text{cm}^{-3}$ for rutile and brookite [3]. This gap can be considered as deriving from a sort of hybrid materials composed of TiO_2 and a thin layer of organic substances covering the surface of the inorganic particles that decrease the value of density. This aspect was also confirmed by TGA, (Figure 3.1.1.3), in which all samples presented three main weight losses. In particular, the first is associated to an endothermic peak at 100°C , which was attributed to the desorption of water physical adsorbed. Whereas the second and the third weight losses are related to two exothermic overlapped peaks between and that were due to the hydroxyl group condensation (at 220°C) associated to anatase crystallization [4] and to the decomposition of organics (at 450°C), respectively.

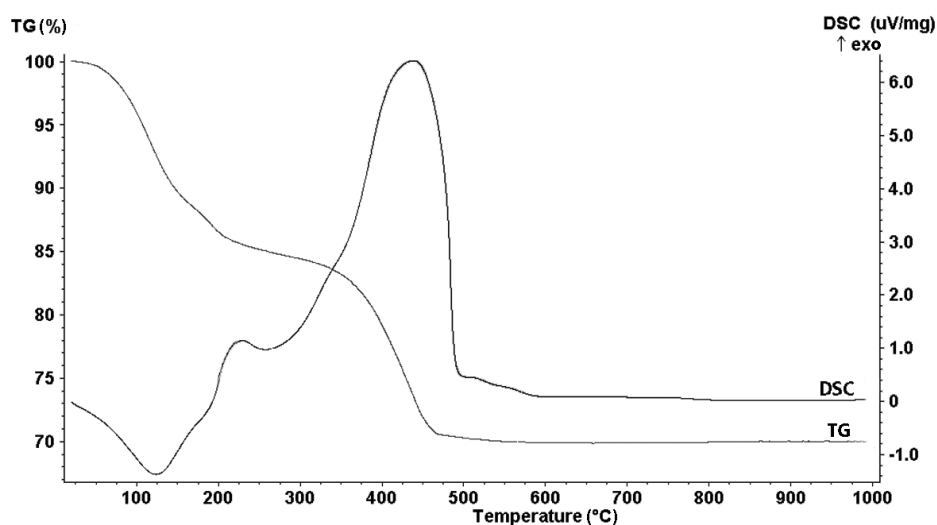


Figure 3.1.1.3 – TGA of T_Bz70_4 (representative for all samples)

In order to better investigate the nature of the organic phase on the particle surfaces, FT-IR analysis was performed. The presence of organic residual bonded on the particles surface, as determined by gravimetric analysis, was confirmed. In Figure 3.1.1.4 the spectra of powders and BzOH, are compared. Concerning the spectra of powders, centred at 3250 cm^{-1} , is clearly visible the common --OH stretching band and its related weak peak close to 1630 cm^{-1} , due to --OH bending vibration, was also observed [5, 6]. These results are in good agreement with TGA that showed the typical --OH condensation at 220°C .

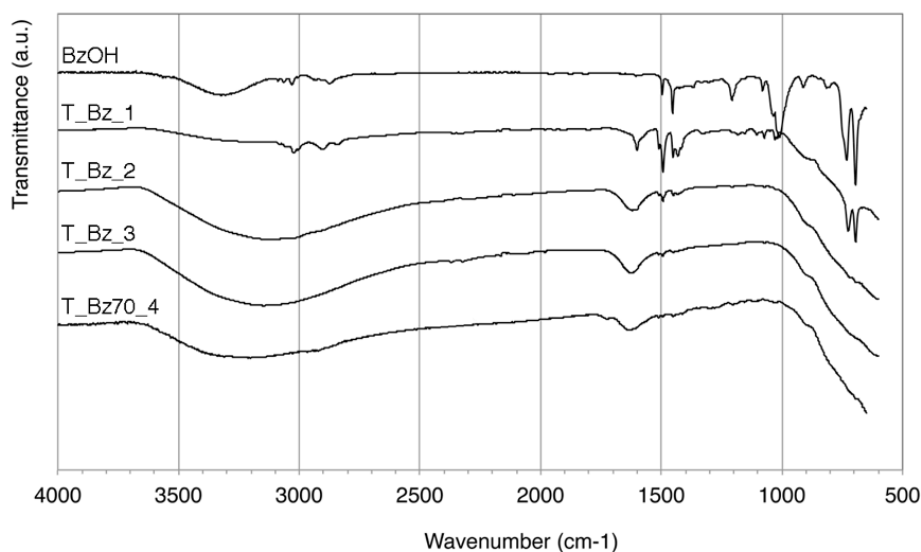


Figure 3.1.1.4 – FT-IR curves performed in ATR mode of synthesized powders and BzOH as reference

The shoulder at 2900 cm^{-1} (CH_2 stretching), the weak peaks located in the range $1500\text{--}1200\text{ cm}^{-1}$ (CH_2 bending), the peak at 1070 cm^{-1} (C--O stretching), the double peak at 745 (bending aromatic C--H) and 707 cm^{-1} (stretching aromatic C--C) match rather precisely to the spectrum of BzOH [5, 6]. All that signals are well visible in the sample T_Bz_1 and they become less and less strong when the $\text{TiCl}_4/\text{BzOH}$ ratio increases. Considering that each powder was carefully washed by using sonication and three sorts of solvents and eventually well dried, this suggests that some benzyl groups (BzO--) are chemically bonded to the particles surface.

The photo-catalytic activity of T_Bz70_4 was determined representative of all powders synthesized by BzOH . The catalytic activity, towards organic species, was determined by detecting the MB photodegradation (by Eq. 2) as a function of UV irradiation time. The obtained curves are reported in Figure 3.1.1.5 where a significant catalytic activity of titania is clearly shown. T_Bz70_4 was able to promote, when irradiated by UV light, an almost complete MB photodegradation (more than 90%) in about 6 h, whereas, in non-catalysed condition, the photodegradation of MB was about 65% after 20 h.

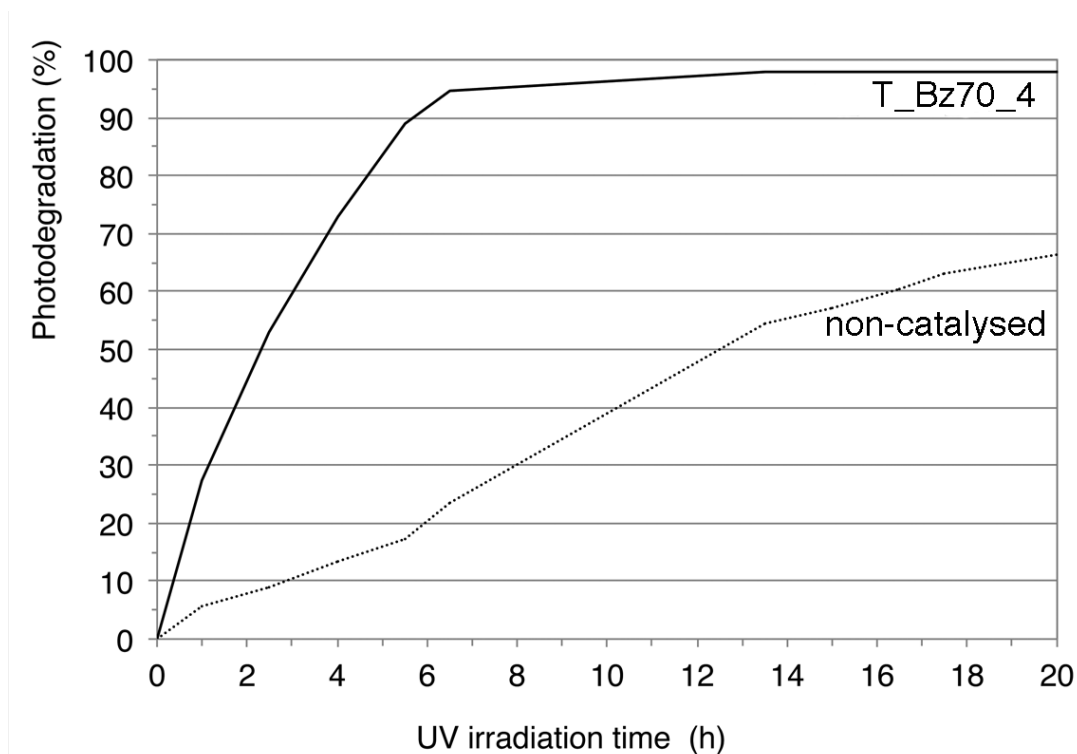


Figure 3.1.1.5 – Methylene blue (MB) photodegradation (%), catalysed and non-catalysed by T_Bz70_4 powder, as a function of UV irradiation time

3.1.2 – TiO₂ Synthesized by Using tert-Butyl Alcohol

XRD patterns of powders are reported in Figure 3.1.2.1, in which is clearly shown that all powders are composed by anatase as crystalline phase (JCPDS reference code: 00-021-1272). The broaden peaks indicate that samples are characterized by crystallites nanometric structure.

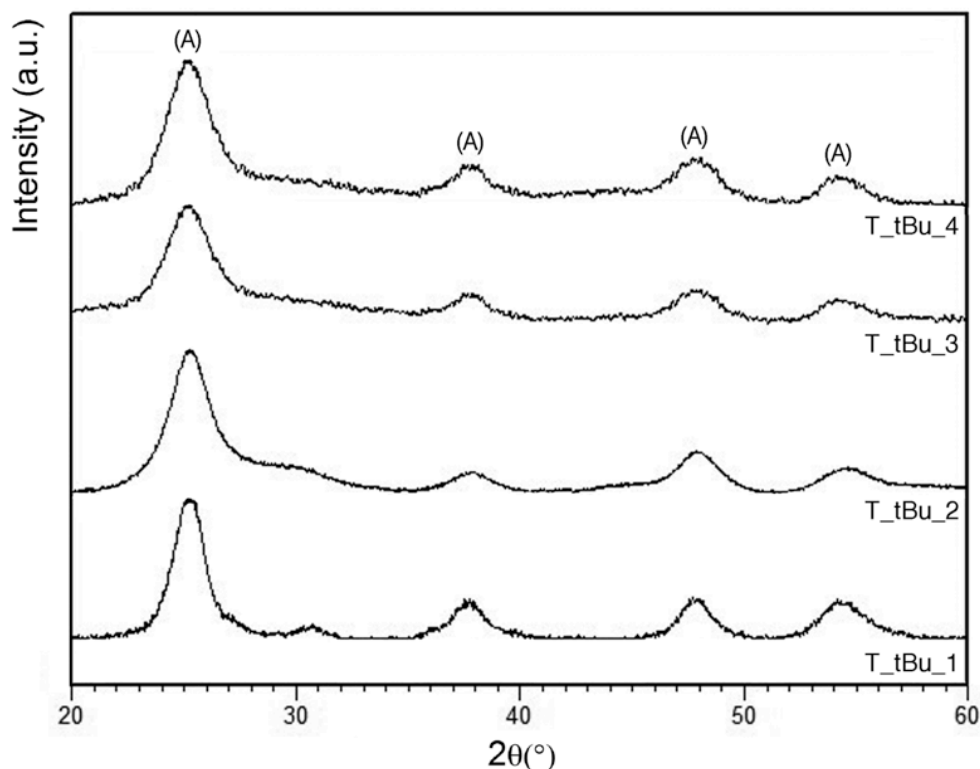


Figure 3.1.2.1 – XRD patterns of the synthesized powders (A: anatase)

For quantifying the amorphous phase of synthesized powder, the Rietveld-RIR analysis was applied. The sample T_tBu_3 was analysed in order to evaluate the effect, of the –R group of the used solvent/oxygen source, on the crystallinity. Even in this case, the crystallization degree (about 23 wt%) is higher in comparison to the only amorphous powders synthesized by the conventional aqueous sol-gel method as reported elsewhere [1]. Whereas, by comparing the values reported in the section 3.1.1, related to TiO₂ powders synthesized by NHSG in benzyl alcohol in comparable conditions (T_Bz70_4), it is possible to claim that the reaction in tBuOH leads to slightly lower crystallinity degree (23 instead of 39 wt%).

Sample Code	TiCl ₄ /tBuOH Molar Ratio	Particles size by Eq.2 (nm)	Particles size by TEM (nm)	Density (g·cm ⁻³)	SSA (m ² ·g ⁻¹)	Residual at 500°C (%)
T_tBu_1	0.087	24 ± 2	8 ± 2	2.61 ± 0.01	85 ± 1	70.4
T_tBu_2	0.040	32 ± 6	5 ± 2	2.60 ± 0.40	73 ± 2	71.4
T_tBu_3	0.013	27 ± 1	7 ± 2	2.83 ± 0.01	87 ± 2	87.0
T_tBu_4	0.004	22 ± 1	4 ± 1	2.81 ± 0.01	97 ± 2	84.0

Table 3.1.2.1 – Summary of the data obtained by the characterization of washed and dried powders

The measured physical properties of the synthesized powders are reported in Table 3.1.2.1. As expected, the SSA was between 73 and 97 m²·g⁻¹ that is a reasonable value whether considering the size of the primary particles. The real density, even in this case, is lower than 3 g·cm⁻³ (3.90 g·cm⁻³ for pure anatase and about 4 g·cm⁻³ for rutile and brookite) [3]. This difference may be due to the large amount of amorphous phase (more than 70%) that affected strongly the density value. This aspect was confirmed by TGA; in Figure 3.1.2.2 the sample T_tBu_3 (representative of all samples set) presented two main weight losses. In particular, the endothermic peak at 100°C, correlated to 6% of weight loss, was attributed to the desorption of water physically adsorbed. The second and third exothermic peaks, between 200°C and 450°C, are overlapped and related to a weight loss of 7%. As seen before, the peak at 200°C can be explained by the hydroxyl group condensation related to the anatase crystallization, behaviour already observed by Bondioli *et al.* [4]. Whereas, the peak at 450°C is very weak and due to a secondary not relevant exothermic event.

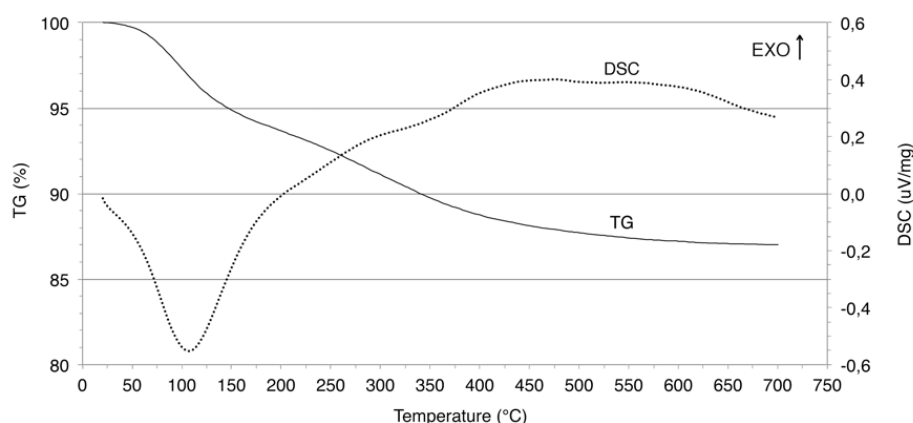


Figure 3.1.2.2 – TGA of T_tBu_3 as representative

All prepared powders presented very similar FT-IR spectrum: in Figure 3.1.2.3 is reported the T_tBu_3 spectrum as representative. The samples showed a broad band centred at 3100 cm^{-1} that is typically due to the stretching of O–H bonds (also known as titanols) [6]. The presence of titanols on the particles surface is in good agreement with both the second weight loss detected by TGA and the presence of amorphous phase evaluated by quantitative XRD analysis. It is well-known that the presence of –OH and amorphous phase are strictly related, as described by Jensen and co-worker [7]. Concerning the peak at 1630 cm^{-1} , it was attributed to the presence of adsorbed water [6] as confirmed by the weight loss at 100°C by TGA. It is now clear that by using tBuOH, no organic uncondensed molecules remain on the particles surface, contrary to that was observed for titania synthesized by BzOH, in which uncondensed benzyl groups were detected, by FT-IR analysis.

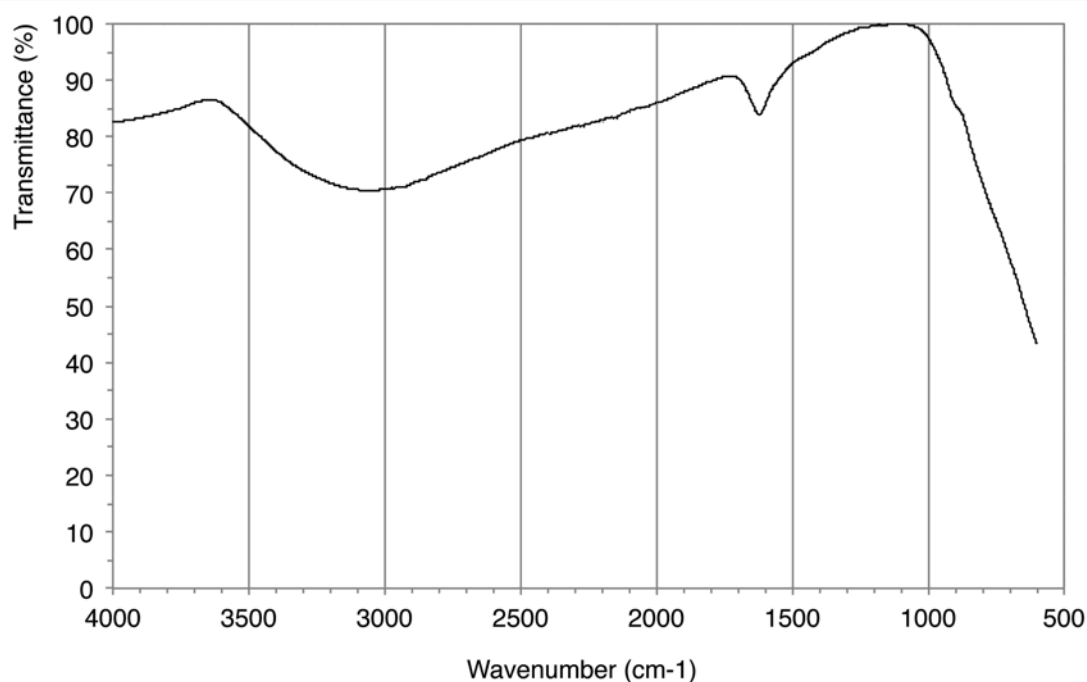


Figure 3.1.2.3 – FT-IR curve of T_tBu_3 as representative

In Figure 3.1.2.4 the TEM images of the obtained powders are reported. The Figure shows nanometric spherical particles that range from 4 to 8 nm tightly connected to create small agglomerates. Comparing the morphology and average grain size of primary particles obtained by both alcohols, it is possible to notice that they are not strongly affected by the –R group of solvent/oxygen source, as also already observed elsewhere [8].

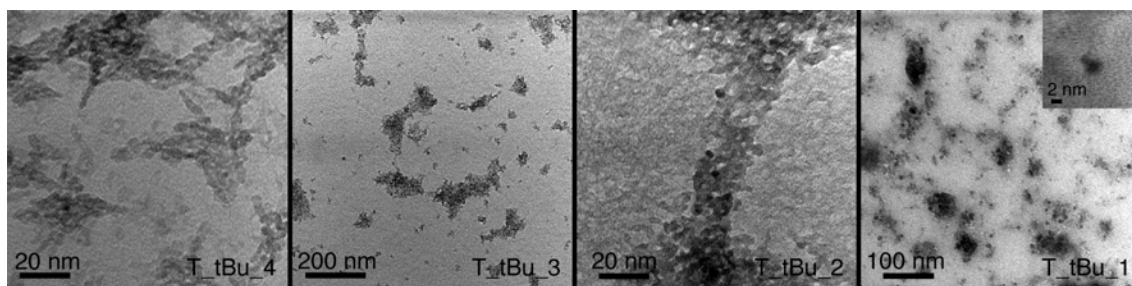


Figure 3.1.2.4 – TEM micrographs of the synthesized powders

Assuming that the particles are closed spheres with smooth surfaces (which is a reasonable hypothesis, supported by TEM), the average particles size was calculated employing SSA and density values (Table 3.1.2.1) following Eq. 2. The small gap, between the average particle size as measured by TEM and as calculated by Eq. 2, suggests the absence of massive agglomeration.

The photocatalytic activity of T_tBu_3 was determined, representative of all samples set. It was studied the UV photodegradation of MB taking into account the degradation due to the only UV light not catalysed by titania. The curves are reported in Figure 3.1.2.5 in which a significant catalytic activity of titania is clearly shown. T_tBu_3 was able to promote, when irradiated by UV light, an almost complete MB photodegradation (more than 90%) in about 15 h, whereas, in non-catalysed condition, the photodegradation of MB was about 65% after 20 h.

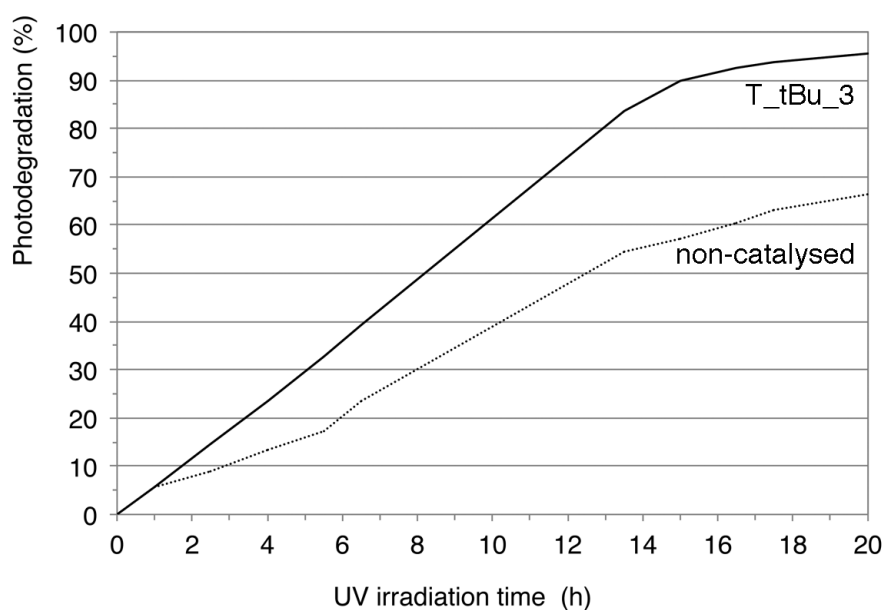


Figure 3.1.2.5 – Methylene blue (MB) photodegradation (%), catalysed and non-catalysed by T_tBu_3 powder, as a function of UV irradiation time

It is well known that anatase is the form that mostly induces the photoactivity [9]. Accordingly to this, the TiO_2 synthesised by BzOH showed a faster MB photodegradation if compared to the photodegradation rate obtained by using titania produced in tBuOH, because of its higher crystallinity degree.

3.2 – Composites Characterizations

3.2.1 – Composite Based on Poly(methyl methacrylate)

Prepared by Benzyl Alcohol

The actual filler content was evaluated for each sample by gravimetric analysis and the results are shown in Table 3.2.1.1. The actual amount of *in situ* generated titania is always significantly lower than the expected values with a maximum ostensible yield of about 45% for PMMA_10T100. The relatively low yield in titania could be either attributed to an incomplete conversion of TiCl_4 into TiO_2 nanoparticles and/or to a partial particles loss during the precipitation, filtration and washing procedure adopted to collect the composites. Some preliminary tests carried out using a longer reaction time, for both temperatures and with and without PMMA dissolved, showed that the final reaction yields is not kinetically affected, showing a reaction yield regularly between 84% and 90%. This result indicates that the low titania content, in the composites, is definitely due to the purification step (precipitation, filtration and washing). This idea was also strongly supported by the presence of a negligible amount of solid residue in the filtered fraction obtained after the filtration step.

Sample code	Nominal TiO_2 content (wt%)	Actual TiO_2 content (wt%) *	T_g (°C)
PMMA_0	-	-	122
PMMA_5T70	5	0.54 ± 0.03 (11%)	124
PMMA_10T70	10	1.68 ± 0.07 (17%)	127
PMMA_5T100	5	1.49 ± 0.16 (30%)	126
PMMA_10T100	10	4.49 ± 0.36 (45%)	126
PMMA_5T_C #	5	5.04 ± 0.29 (-)	126
* The percentage yield in titania with respect to the nominal concentration is reported in brackets			
# Sample prepared by mechanical dispersion of commercial titania in BzOH/PMMA solution			

Table 3.2.1.1 – Nominal and actual TiO_2 contents and glass transition temperature of the prepared materials

In order to evaluate possible degradation of the polymer chains, during the titania *in situ* generation due to the evolution of aggressive chemicals such as hydrochloric acid and other by-products, the polymeric chains molecular weight and molecular weight distribution were evaluated by GPC for all prepared composites and PMMA_0 as reference. For all samples the obtained chromatograms (here not reported) are completely overlapped. This result indicates that the *in situ* generation of titania, through sol-gel process, did not affect the molecular weight and molecular weight distribution of the polymer demonstrating the absence of significant degradation reactions during the filler generation.

Glass transition temperature (T_g) values are reported in Table 3.2.1.1. As expected, T_g increases from 122°C for unfilled PMMA to about 126-127°C for samples containing both *in situ* generated titania and mechanically dispersed titania (as a comparison) evidencing a slight stiffening effect due to the presence of rigid fillers within the polymeric matrix. It is worth noting the absence of a clear correlation between the amount of titania and the T_g values.

The FESEM micrographs of the fracture surface of PMMA-based composites are reported in Figure 3.2.1.1. A very rough fracture surface was present in all the investigated samples and the same matrix morphology was also observed for neat PMMA_0. The samples are characterized by the presence of very well distributed particles having spherical shape and maximum diameter less than 100 nm (see in particular Figure 3.2.1.1c, taken at higher magnification) was observed for all the composites. The chemical composition of the particles was consistent with the expected TiO_2 as indicated by energy dispersive X-ray spectrometry (EDX). FESEM analysis indicated that the NHSG method was an effective process to obtain nanocomposite materials with an effective dispersion and distribution of nanoparticles avoiding significant particles agglomeration and melt viscosity increase.

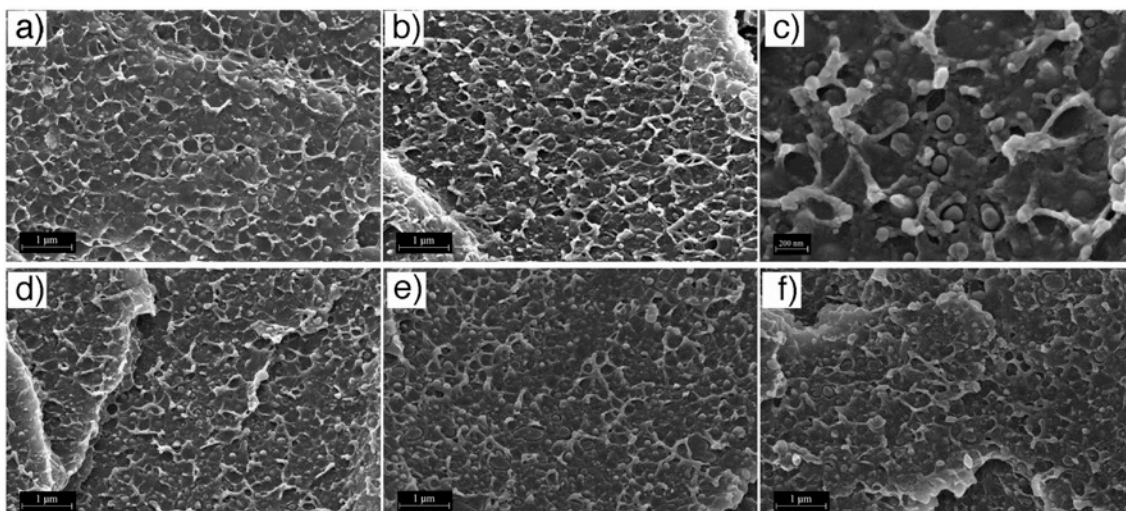


Figure 3.2.1.1 – FESEM micrographs of the fracture surface of: (a) PMMA_5T_C; (b) PMMA_5T70; (c) PMMA_5T100 (higher magnification); (d) PMMA_5T100; (e) PMMA_10T70; (f) PMMA_10T100

In order to evaluate the effect of the titania on the PMMA photodegradation, specimens were placed in a black chamber and aged by UV light irradiation for 1200 hours. FT-IR spectra recorded in ATR mode for the exposed surfaces of neat PMMA and filled with titania are shown in Figures 3.2.1.2 and 3.2.1.3. FT-IR/ATR spectra (Figure 3.2.1.2) of not aged PMMA_0 (a) and after 1200 h of UV irradiation (b) are substantially equivalent, indicating the absence of surface chemical modification and a significant degradation.

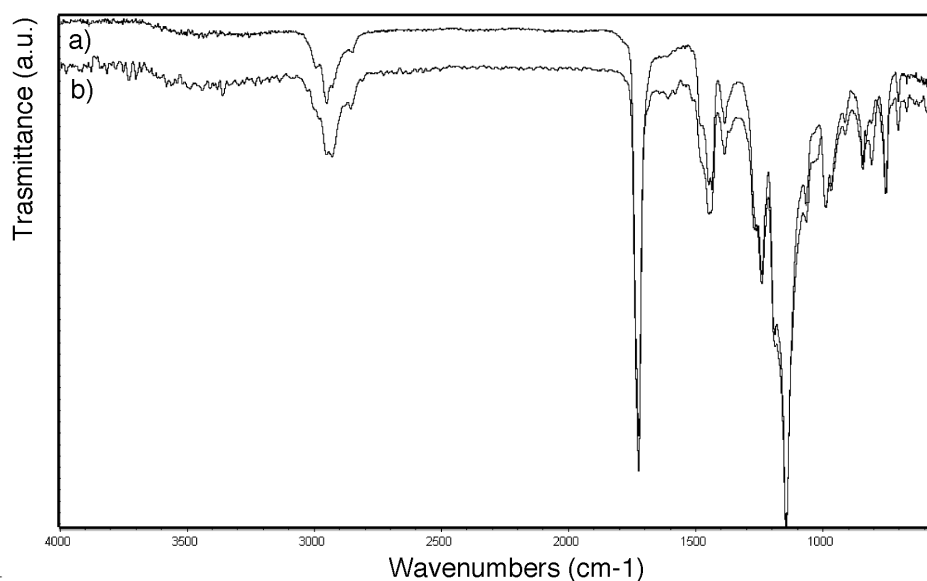


Figure 3.2.1.2 – FT-IR/ATR spectra of not aged PMMA_0 (a), PMMA_0 after 1200 h of UV irradiation (b)

On the contrary, the presence of titania led to a significant modification of the FT-IR/ATR spectra as a result of UV irradiation. In particular, the ratio between signals respectively attributable to PMMA and titania, decreases significantly with the UV irradiation time (comparison in Figure 3.2.1.3 (a) and (b) taking into account the spectrum (c) of pure titania). These results can be described through to the well-known degradation mechanism of PMMA that leads to the decomposition of the polymer by the formation of volatile by-products. In this way, the strong modification of FT-IR/ATR spectra can be explained as a sort of surface “erosion” of the PMMA induced by the UV irradiation and catalysed by titania nanoparticles that increases the surface concentration of titania with respect to the organic polymer.

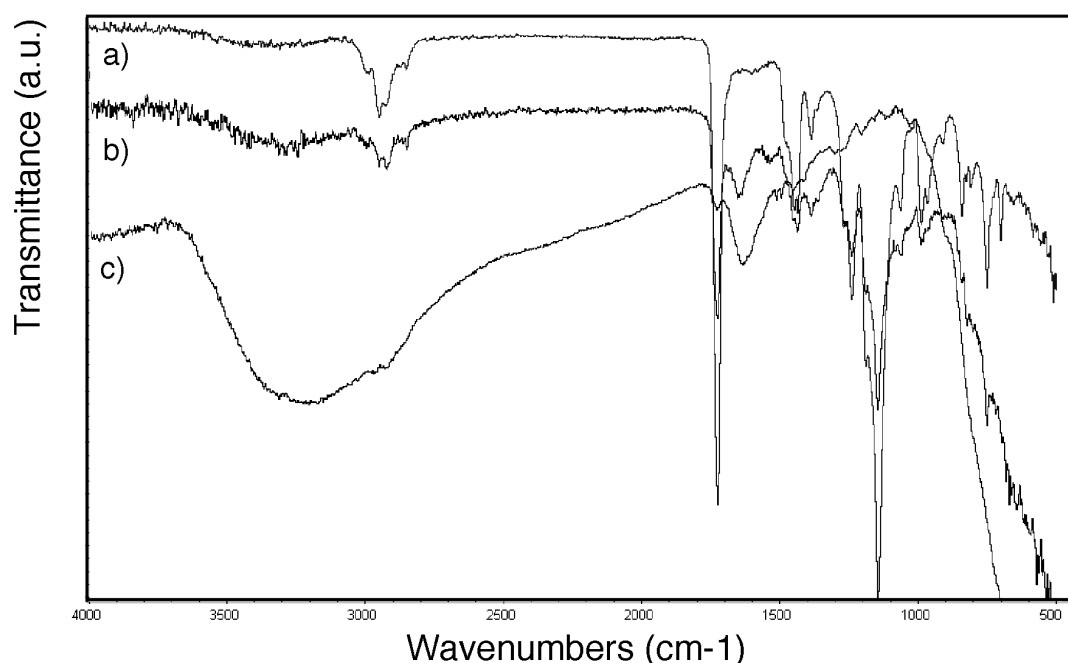


Figure 3.2.1.3 – FT-IR/ATR spectra of not aged PMMA_10T70 (a), PMMA_10T70 after 1200 h of UV irradiation (b) and of T_Bz70_020 (c)

Consistent effects were also observed by measuring the decrement of gloss and weight as a function of the UV irradiation time (Figures 3.2.1.4 and 3.2.1.5, respectively).

The gloss measurements can be considered as an evaluation of surface roughness that increases with the observed superficial erosion due to PMMA photodegradation. All samples showed (Figures 3.2.1.4) a decrease of gloss in the early stages of aging test (after 50 h for filled PMMA and after 200 h for unfilled

PMMA), followed then by substantially constant values for longer irradiation times. Only PMMA_5TC represented an exception with a progressive and almost linear decrease of gloss during all the investigated irradiation time range. In agreement with the above discussed FT-IR/ATR data, the presence of *in situ* generated titania enhanced the decrement of the gloss as evidenced by the plateau values: 83-84% for unfilled PMMA (PMMA_0), 67-73% for PMMA filled with titania (PMMA_5T70, PMMA_5T100, PMMA_10T70, PMMA_10T100).

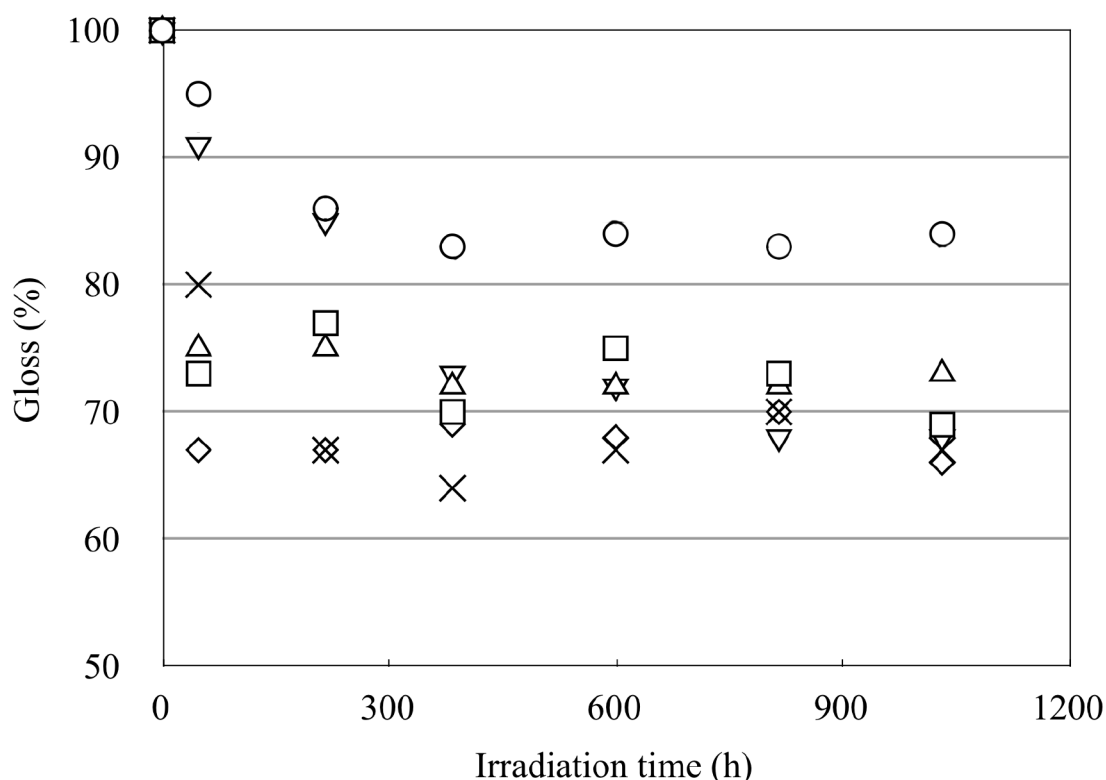


Figure 3.2.1.4 – Percentage of gloss (calculated with respect to the initial value) as a function of UV irradiation time. (○) PMMA_0; (□) PMMA_5T70; × PMMA_5T100; (△) PMMA_10T70; (▽) PMMA_10T100; (◇) PMMA_5T_C

Taking into account the degradation mechanism of PMMA (polymer decomposition with formation of low molecular weight by-products and their volatilization), a further possibility for the investigation of photodegradation effects could be represented by the specimen weight loss during UV irradiation. Figure 3.2.1.5 showed that the weight loss for unfilled PMMA was almost negligible (less than 0.5%). On the contrary, all the samples containing titania exhibited a significant and linear mass decrease over the entire irradiation time range. It is very interesting to observe that

the slopes of the curves increased by increasing the actual TiO_2 content (see Table 3.2.1.1) indicating the crucial role played by the amount of titania in the photodegradation reaction. It is also very fascinating that the curves corresponding to different samples prepared by *in situ* generation or mechanical mixing of titania, but with similar titania content (PMMA_10T100 and PMMA_5TC, with an actual titania concentration of 4.49 wt% and 5.04 wt%, respectively), are perfectly overlapped.

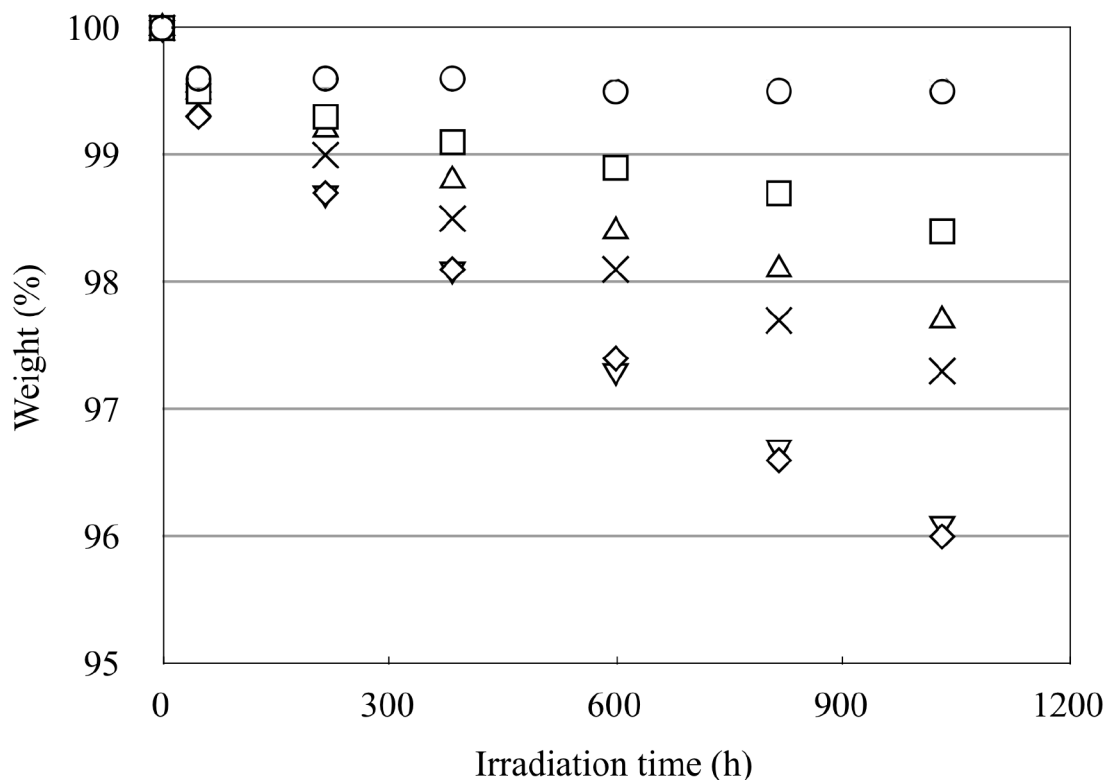


Figure 3.2.1.5 – Percentage of weight (calculated with respect to the initial value) as a function of UV irradiation time. (○) PMMA_0; (□) PMMA_5T70; (×) PMMA_5T100; (△) PMMA_10T70; (▽) PMMA_10T100; (◇) PMMA_5T_C

Prepared by *tert*-Butyl Alcohol

The composite actual filler contents were evaluated for each sample by gravimetric analysis and the final results are collected in Table 3.2.1.2. The actual titania contents, *in situ* generated, were significantly close to the expected values. This suggests that the sol-gel reaction yields were close to 100% for all samples and, therefore, that the conversion of TiCl_4 was not affected by the presence of PMMA in the reaction medium. This aspect represents a significant improvement with respect to the previously reported data on similar systems obtained by using BzOH (described in the section above) [10] instead of tBuOH. In that case, the necessity of precipitation, filtration and washing steps for the elimination of high boiling point BzOH led to a significant reduction of the actual titania content compared to the nominal one.

Sample Code	Nominal TiO_2 (phr)	Actual TiO_2 (phr)	T _g by DMTA (°C)	T _g by DSC (°C)	E' _{T_g+50°C} (MPa)	tanδ _{max} (-)	Photodegradation at 24 h (%)
PMMA_0T_t	-	-	121	102	1.46	1.30	49
PMMA_5T_t	5	5.0	127	113	1.78	1.12	59
PMMA_15T_t	15	14.9	132	115	2.45	0.93	71
PMMA_20T_t	20	20.6	134	119	4.23	0.79	72

Table 3.2.1.2 – Properties of the composites: nominal and actual TiO_2 content, glass transition temperature (T_g) by DMTA and DSC, storage modulus measured at T = T_g+50°C (E' _{T_g+50°C}), damping (expressed as maximum value of tanδ, tanδ_{max}) and photodegradation after 24 h of UV irradiation (calculated by Eq. 3)

In addition, as showed by the TGA curves reported in Figure 3.2.1.6, the TiO_2 nanoparticles did not change significantly the PMMA thermal stability. This represents a further positive results considering that the presence of *in situ* generated titania often cause a strong decrease in thermal stability as recently published for epoxy resin/titania composited prepared by aqueous sol-gel process [11].

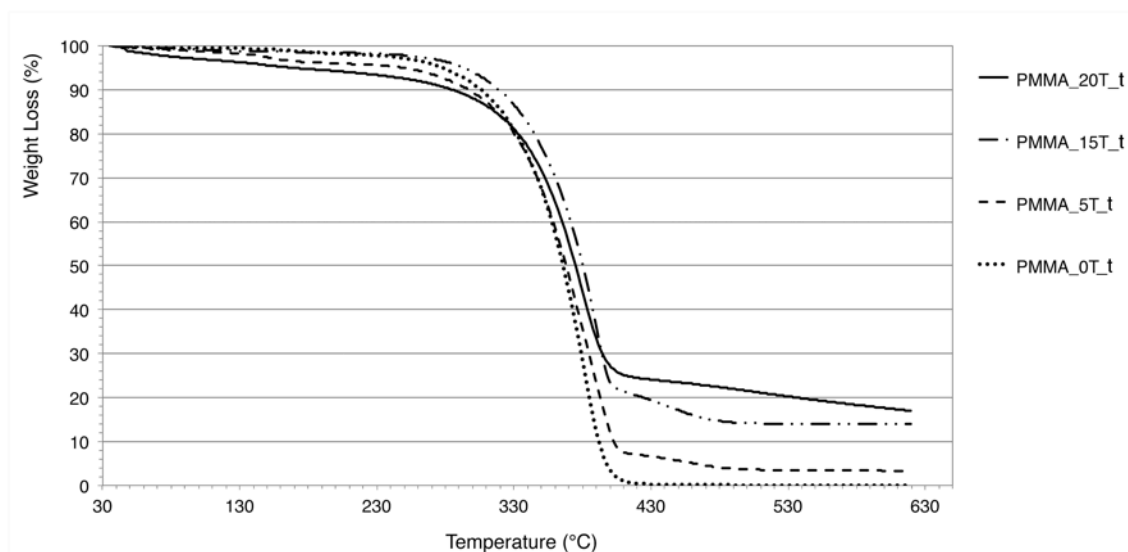


Figure 3.2.1.6 – TGA of PMMA/TiO₂ nanocomposites prepared by tBuOH

The FESEM micrographs of the fracture surface of PMMA_5T_t and PMMA_20T_t composites are reported in Figure 3.2.1.7b and 3.2.1.7c/d, respectively. A slightly rough fracture surface was present in both investigated samples and the same matrix morphology was also observed for neat PMMA_0T_t (Figure 3.2.1.7a). Morphology characterized by the presence of very well distributed particles having spherical shape and maximum diameter less than 100 nm was observed for all specimens (see in particular Figure 3.2.1.7d, taken at higher magnification). The chemical composition of the particles was consistent with the expected titania as indicated by energy dispersive X-ray spectrometry (EDX, here not reported). FESEM analysis indicated that the NHSG method was an effective process to obtain nanocomposite materials with good dispersion and homogeneous distribution of nanoparticles avoiding significant particles agglomeration.

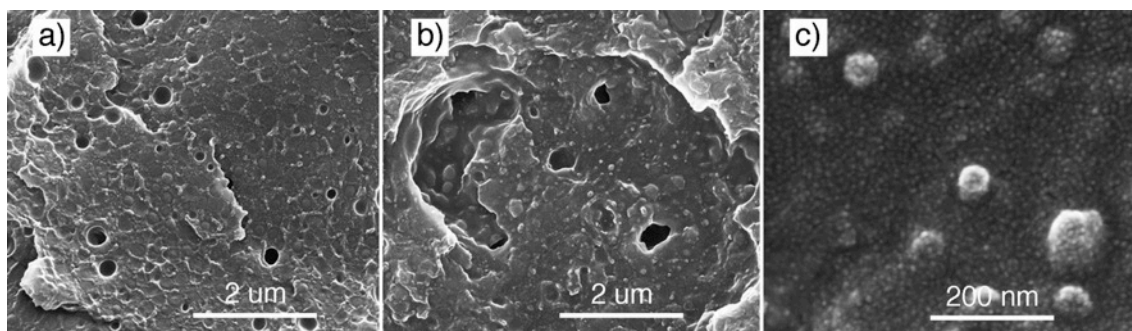


Figure 3.2.1.7 – FESEM micrographs of fracture surface of PMMA_0T_t (a), PMMA_5T_t (b) and PMMA_20T_t (c), higher magnification (d)

In order to evaluate possible degradation effects on the polymer during the sol-gel reaction, due to the evolution of aggressive chemicals such as hydrochloric acid and other by-products, the molecular weight and molecular weight distribution were evaluated by GPC. The chromatograms (here not reported) showed curves complete overlapped for all samples. This aspect indicates, once again, that the *in situ* generation of titania from TiCl_4 did not affect the polymer molecular weight and molecular weight distribution demonstrating the absence of significant degradation during the filler synthesis.

The values of E' measured in the rubbery region (about $T_g+50^\circ\text{C}$), damping (expressed as maximum value of loss factor, $\tan\delta_{\text{max}}$) and of glass transition temperature (determined as peak value of loss factor $\tan\delta$) are reported in Table 3.2.1.2. All described properties were changed by the presence of TiO_2 nanoparticles. As expected, a remarkable reduction of damping and an increment of T_g were found when the titania content is increased. T_g values increased from 121°C for unfilled PMMA (PMMA_0T_t) to about 127, 132 and 134°C for PMMA_5T_t, PMMA_15T_t and PMMA_20T_t respectively, evidencing a typical constrained chains mobility effect due to the presence of the incorporated rigid fillers in the polymeric matrix (Figure 3.2.1.8a). These results are in good agreement with data obtained by DSC analysis (values in Table 3.2.1.2) that confirmed an equal T_g trend.

Concerning the storage modulus (E') is not significantly affected in the glassy region, whereas an interesting increase was found in the rubbery region (values of E'_{T_g+50} reported in Table 3.2.1.2). E'_{T_g+50} of PMMA_0T_t (about 1.46 MPa) raised up to 1.78, 2.45 and 4.23 MPa for PMMA_5T_t, PMMA_15T_t and PMMA_20T_t, respectively. In Figure 3.2.1.8b is reported the curves of E' modulus as a function of temperature, in which is clearly shown the common stiffening effect due to the well-dispersed particles, in the rubbery region.

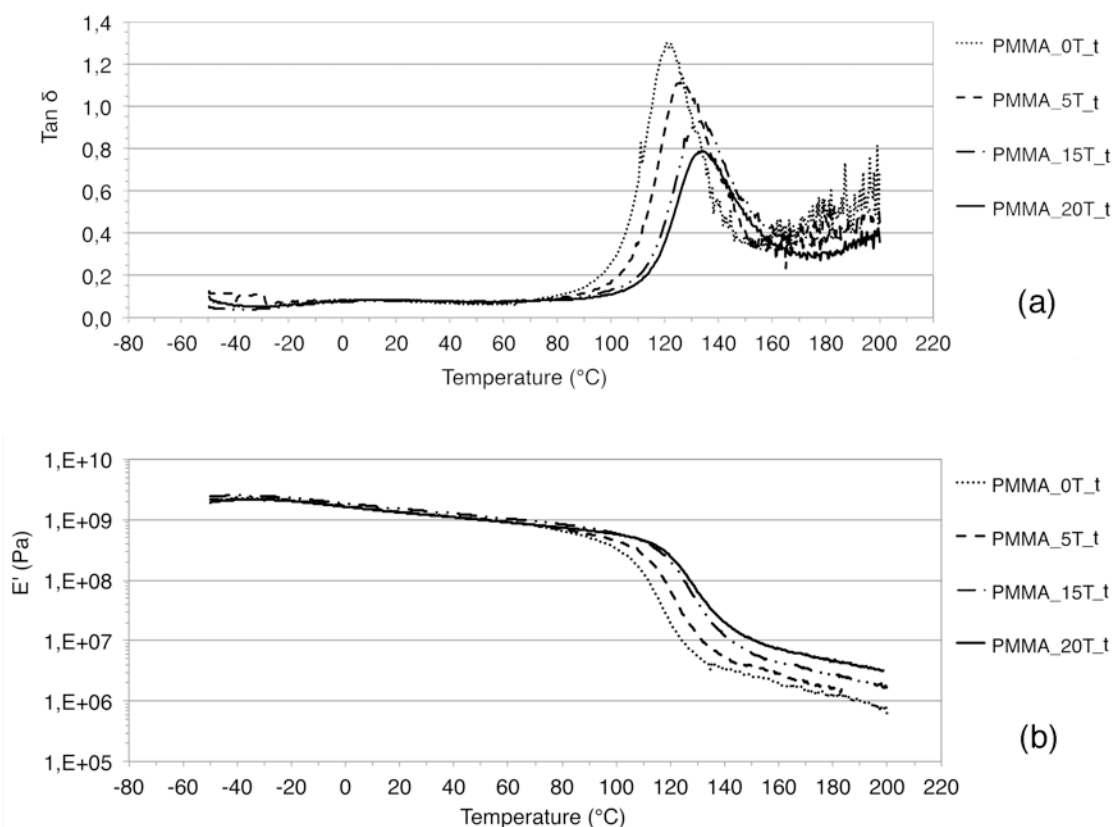


Figure 3.2.1.8 – Storage modulus (a) and loss factor (b) as a function of temperature

Finally, the specimens' photocatalytic activity was determined by following the photodegradation of MB taking into account the non-catalysed photodegradation of dye only due to the UV light. The degradation kinetic curves obtained are reported in Figure 3.2.1.9. The photodegradation rate in the early 8 h did not present substantial variations, whereas after 24 h (values in Table 3.2.1.2) remarkable differences were detected. PMMA_0T_t led to a photodegradation, after 24 h, slightly higher than MB non-catalysed photodegradation (0.48 and 0.39 respectively). Whereas, the values after 24 h for PMMA_5T_t, PMMA_15T_t and PMMA_20T_t increased to 0.59, 0.71 and 0.72 respectively. These results suggested that the titania, on the specimens surfaces, maintains its photocatalytic activity even when it is embedded in a polymer matrix. PMMA_15T_t and PMMA_20T presented the highest photodegradation rate. The values are, however, very similar, probably related to TiO₂ particles size which increases with the filler content, leading to a lower surface area that causes a decrease of expected trend.

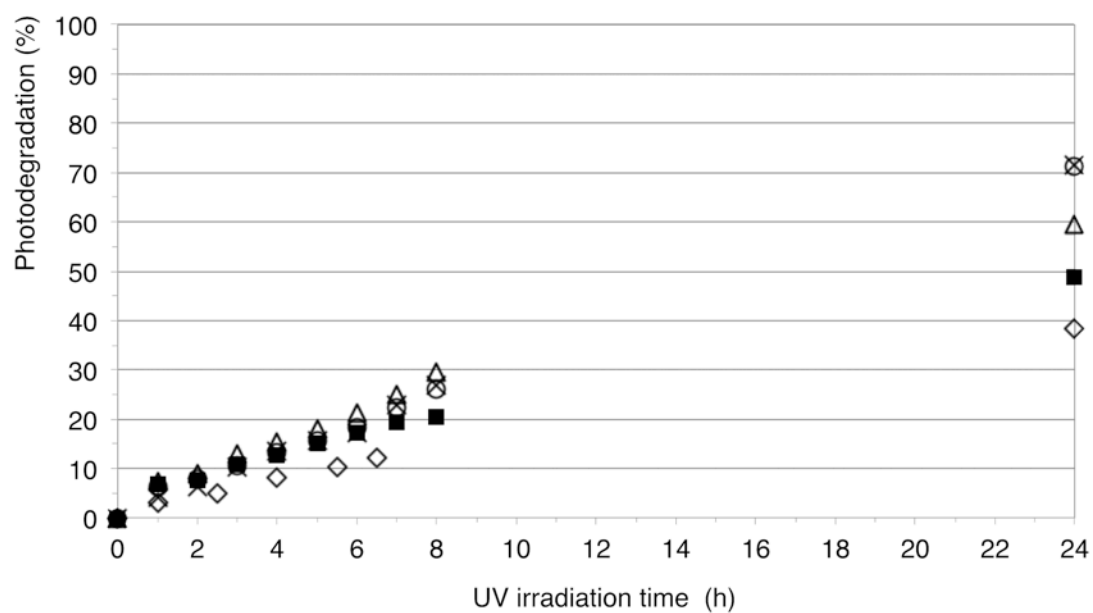


Figure 3.2.1.9 – Methylene blue photodegradation catalysed by nanocomposites (calculated by Eq. 3) as a function of UV irradiation time. ($\diamond$) non-catalysed photodegradation; ($\blacksquare$) PMMA_0T_t; ($\triangle$) PMMA_5T_t; ($\circ$) PMMA_15T_t; ($\times$) PMMA_20T_t

3.2.2 – Composite Based on Epoxy Resins

CE, UV cured

The kinetics of the photo-polymerisation was evaluated by Real-Time FT-IR spectroscopy. Epoxy conversion values as a function of irradiation time are reported in Figure 3.2.2.1. The photo-polymerisation rate was very high for unfilled epoxy 'Ep' which showed an epoxy conversion of 80% after about 8 s of irradiation and a maximum value of 97% after 180 s.

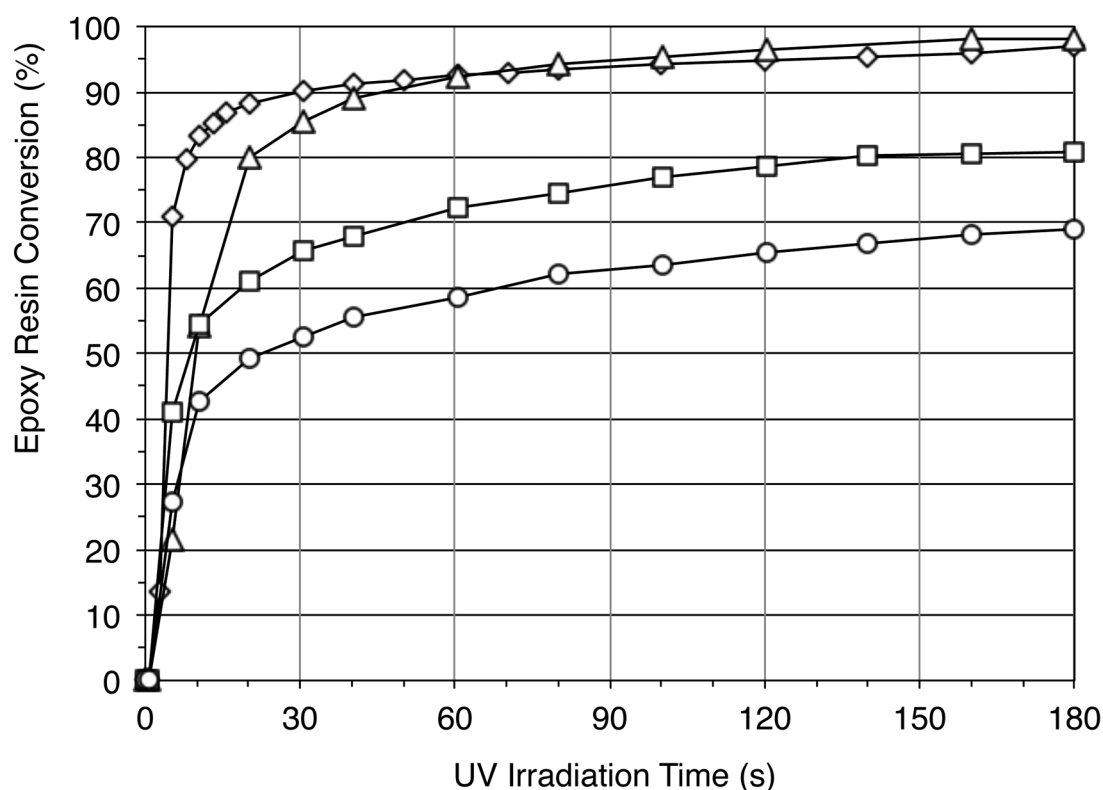


Figure 3.2.2.1 – Epoxy conversion values as a function of irradiation time for (◇) Ep, (△) Ep-T3, (□) Ep-T6 and (○) Ep-T10

The presence of titania in the photo-curable formulation led to a minimal decrement in the initial slope of the curves indicating a negligible effect on the initial photo-polymerisation rate. A maximum value of epoxy conversion, very similar to that one found for pristine epoxy was observed in the case of low titania content (97% after 180 s for 'Ep-T3' sample). On the contrary, the maximum epoxy conversion value significantly decreased by increasing the titania content for 'Ep-T6' and 'Ep-T10' samples (81% and 69%, respectively). These behaviours can be presumably

attributable to an earlier vitrification occurring in the case of highly filled nanocomposites (as deducible from the strong increase of glass transition temperature, see below) together with the UV absorption phenomena undertaken by titania in anatase form. This last effect competes with the photo-initiator UV absorption [12]. The efficiency of the cationic photo-initiator can be described by two quantum yields: the quantum yields of initiation, which represents the number of starting polymer chains per photons absorbed, and the quantum yields of polymerisation, which is the number of monomer units polymerised per photons absorbed. Therefore, it is clear that the competition in absorption with the inorganic filler implies a decrease of the photons absorbed by the photo-initiator. This can lead to a decrease of quantum yields and a lower epoxy group conversion.

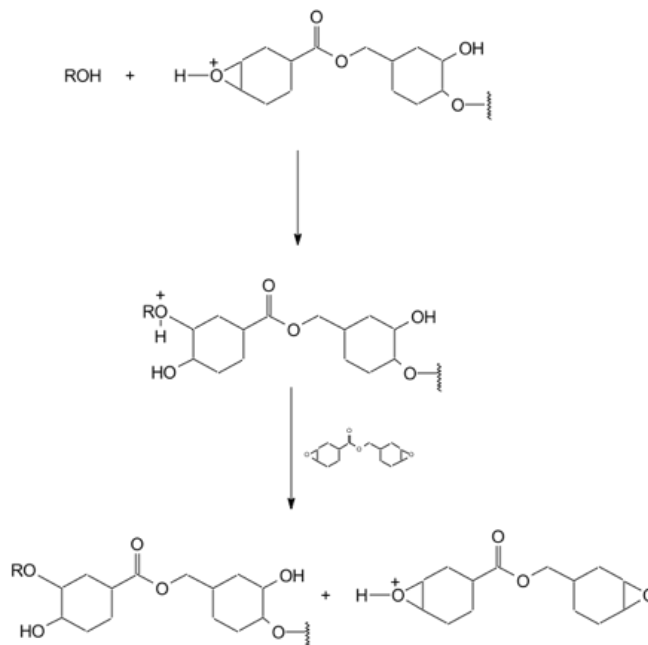
Gel content was determined in order to evaluate the effect of the maximum epoxy conversion on the cross-linked structure due to the presence of titania (data reported in Table 3.2.2.1).

Composite code	G (wt%)	T _g (°C)	tanδ _{max}	E' _{T=50°C} (GPa)	E' _{T=T_g+50°C} (MPa)	Mc (g/mol)	ΔR (nm)
Ep	99.7	113	1.525	1.12	1.26	8770	-
Ep-T3	99.9	137	0.993	1.26	5.01	2380	41
Ep-T6	99.9	168	0.660	1.20	12.59	1030	28
Ep-T10	99.8	178	0.538	1.12	19.95	680	22

Table 3.2.2.1 – Properties of the photo-cured composites: gel content (G), glass transition temperature (T_g), damping (expressed as maximum value of tanδ, tanδ_{max}), storage moduli measured at T=50°C and T=T_g+50°C (E'_{T=50°C} and E'_{T=T_g+50°C}), network density (average molecular weight between two adjacent cross-linking points, Mc) and effective thickness of the particle–matrix interfacial region (ΔR)

Gel content values (G) were extremely high (higher than 99.7%) for all investigated samples suggesting the formation of a fully gelled three-dimensional network (with a minimal amount of extractable sol fraction) even in the case of incomplete conversion of epoxy groups (which in turn remain as unreacted pendant groups but covalently linked to the cross-linked structure). This important result suggested that both ‘active chain end’ and ‘activated monomer’ mechanisms [13] (Scheme 3.2.2.1) occurred during the propagation step in the cationic ring-opening

polymerisation leading to a quantitative incorporation of BzOH (and corresponding by-products of NHSG reaction) within epoxy network, as indicated by the absence of species extractable in chloroform.



Scheme 3.2.2.1 – Schematic of the ‘Active chain end’ and ‘activated monomer’ mechanisms for the mixture CE/BzOH

Typical FE-SEM micrographs of fracture surface of photo-cured epoxy-titania composites are reported in Figure 3.2.2.2. The fracture surface of Ep-T3 (characteristic also for the other compositions) showed the presence of a dispersed phase attributable to a titanium rich phase as indicated by EDX analysis. The FE-SEM images suggested the presence of an organic layer surrounding the spherical particles, which can be taken as an indication of a diffused interphase between the inorganic titania and the bulk epoxy matrix. The distribution of the discrete second phase was very homogeneous within the polymer matrix even if the dispersion was not fully satisfactory due to the occurrence of aggregation phenomena as indicated by the higher average dimensions with respect to primary titania particles (see Figure 3.1.1.2 as a comparison).

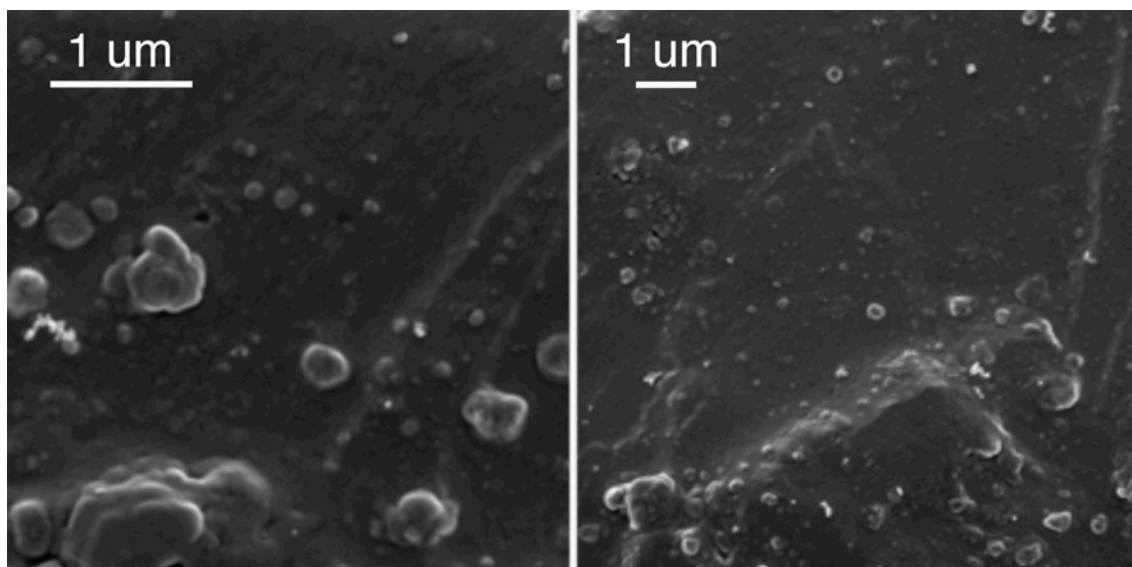


Figure 3.2.2.2 – FESEM micrographs of fracture surface of Ep-T3 (different magnifications)

Glass transition temperature (T_g), damping (expressed as maximum value of loss factor, $\tan\delta_{\max}$) and storage modulus (E') values of photo-cured nanocomposites obtained by DMTA are summarised in Table 3.2.2.1.

The DMTA results showed that the dynamic-mechanical properties of composites were greatly affected by the titania content. It is well-known that the addition of rigid fillers to polymer matrix made the polymer chains movement constrained, leading to a damping decrement and a shift of T_g values toward higher temperatures. Consistently, a significant reduction of damping (here evaluated as $\tan\delta_{\max}$) together with a strong increment of T_g values were observed in the nanocomposites, by increasing the titania content. The glass transition temperature of unfilled epoxy ($T_g = 113\text{ }^{\circ}\text{C}$) raised up to 137, 168 and 178 $^{\circ}\text{C}$ for ‘Ep-T3’, ‘Ep-T6’ and ‘Ep-T10’, respectively. Such increases in T_g are thought to result from the constrained chain mobility by well-dispersed fillers.

The observed increase in T_g and decrease in loss factor with filler content can be also considered as an indirect evidence of the presence of a strong filler-matrix interface. In this respect, Kim and co-workers [14] reported the preparation and the characterisation of epoxy composites filled with functionalised and unfunctionalised silica nanoparticles and showed that composites with weak interface exhibit essentially no change in T_g and damping with filler contents, opposite to composites

with strong interface which show a systematic increase of T_g and decrease of loss factor with filler content.

The storage moduli E' measured below glass transition temperature, that is at 50 °C, were not influenced by the presence and the amount of titania with values in the range 1.12 - 1.26 GPa for all filled and unfilled samples. On the contrary, a significant increment of storage modulus E' in the rubbery region was observed by increasing the titania content in the nanocomposites. E' values determined at $T_g+50^\circ\text{C}$ of unfilled epoxy (1.26 MPa) raised up to 5.01, 12.6 and 19.9 MPa for 'Ep-T3', 'Ep-T6' and 'Ep-T10', respectively.

The reduced storage modulus at $T_g+50^\circ\text{C}$ as a function of titania volume fraction is reported in Figure 3.2.2.3. In order to compare the experimental results with data predicted by the well-known models for composites materials, the generalized Kerner equation (Eq. 9) [15] for the reduced modulus of filled polymers was applied in order to evaluate its dependence on the volume nanoparticles content:

$$\frac{E'}{E'_1} = \frac{1 + AB\phi_2}{1 - B\Psi\phi_2} \quad (\text{Equation 9})$$

in which E' and E'_1 are the storage moduli of composite and unfilled epoxy, respectively.

The constant A , in the case of spherical filler particles and for any Poisson's ratio (ν) of the matrix, is defined as:

$$A = \frac{7 - 5\nu}{8 - 10\nu} \quad (\text{Equation 10})$$

The constant B depends on the ratio between filler and matrix moduli and it can be approximated to 1 for very large moduli ratios.

The parameter Ψ is a reduced concentration term, which depends on the maximum packing fraction of the particles (ϕ_m) according to the following definition:

$$\Psi = 1 + \frac{1 - \phi_m}{\phi_m^2} \cdot \phi_2 \quad (\text{Equation 11})$$

in which ϕ_2 is the filler volume fraction.

In the present study, the Poisson's ratio (ν) of the matrix and the maximum packing fraction of the particles ϕ_m were taken equal to 0.5 (epoxy in the rubbery

state) and to 0.601 (random loose packing, non agglomerated packing configuration), respectively [15].

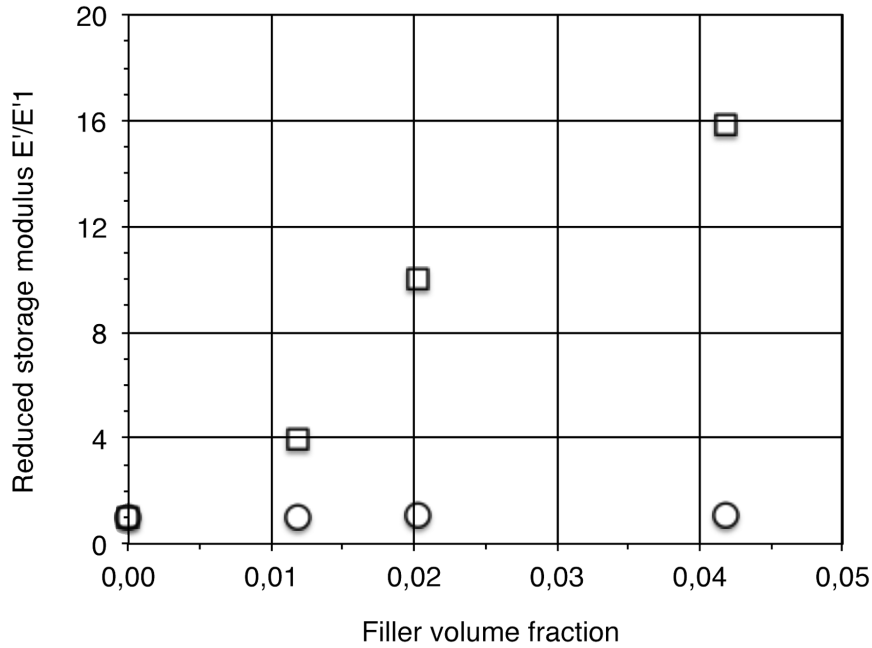


Figure 3.2.2.3 – Relative storage modulus dependence on the titania nanoparticles content: (□) experimental values and (○) prediction of generalised Kerner equation (Eq. 9)

Data indicated a dramatic increment of reduced storage modulus with respect to the values predicted by the generalised Kerner equation (Eq. 9). Taking into account that, in the rubbery region temperature range, the modulus value is mainly governed by the cross-linking density of the network. In other words, the *in situ* generated titania nanoparticles acted not only as rigid reinforcing filler but also as cross-linking points, increasing the cross-linking density of the composite material with respect to the pristine epoxy matrix.

In this respect, the network densities (that is the average molecular weight between two adjacent cross-linking points, M_c) have been determined in the rubbery region from the storage modulus values at $T_g+50^\circ\text{C}$ by using the following relationship:

$$E'_{T_g+50^\circ\text{C}} = 3qnRT = 3q\left(\frac{\rho}{M_c}\right)RT \quad (\text{Equation 12})$$

where, q is the front factor (usually equal to 1), n is the apparent cross-linking density, R is the gas constant ($R = 8.314 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$), ρ is the density of the material and T is

the absolute temperature in K [16]. Originally, Eq. 12 was used for single-phase materials, but it also gives very good results for biphasic systems [16, 17]. The values obtained by this formula are used only for comparing the network density of the samples investigated in the present work.

The calculated values of polymer molecular weight between two cross-linking points (M_c) are reported in Table 3.2.2.1. The network density increases with the titania content and consistently the M_c decreases. According to the dynamic-mechanic behaviour already discussed, the presence of the filler increases the local concentration of the cross-linking points and increases the network density in the composite compared to the neat matrix. As already mentioned, this behaviour could be tentatively explained taking into account that the *in situ* generation of titania and subsequent polymerisation of the suspending medium resulted in a very strong filler-matrix interaction with a significant improvement of the cross-linking density due to the titania contribution, which in turn incremented the glass transition temperature and the modulus values in the ‘rubbery’ region.

DSC curves of photo-cured nanocomposites are reported in Figure 3.2.2.4. Thermal properties of the photo-cured films resulted in good agreement with the data obtained by DMTA analysis with T_g values of unfilled epoxy (Ep, $T_g = 72\text{ }^{\circ}\text{C}$) increasing up to 94, 134 and $160\text{ }^{\circ}\text{C}$ for ‘Ep-T3’, ‘Ep-T6’ and ‘Ep-T10’, respectively.

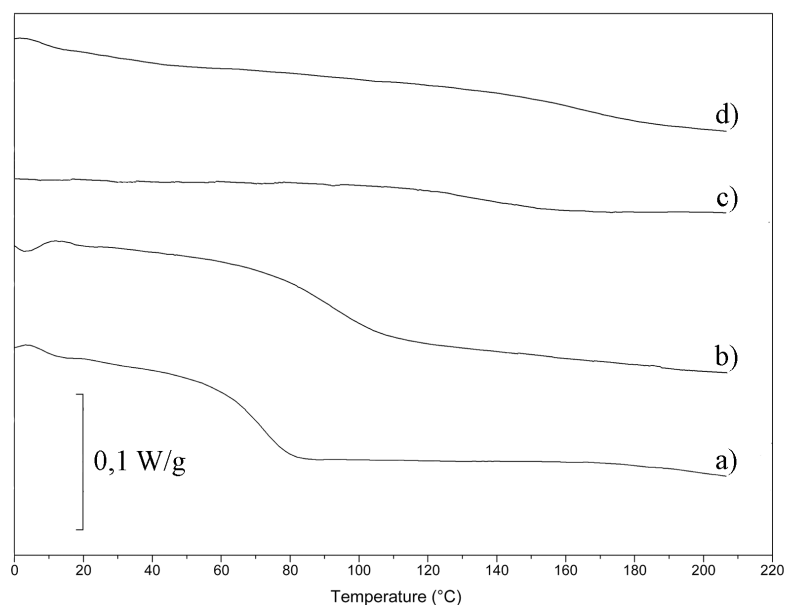


Figure 3.2.2.4 – DSC curves of the photo-cured composites: (a) Ep, (b) Ep-T3, (c) Ep-T6 and (d) Ep-T10

Effective thickness of the particle-matrix interfacial region. From the reduced damping values, the thickness of the polymer layer immobilised onto the titania nanoparticles surface was estimated at a temperature below glass transition temperature (50°C) by using the following equations:

$$\frac{\tan \delta}{\tan \delta_1} = 1 - P \cdot \phi_2 \quad (\text{Equation 13})$$

$$P = \left(1 + \frac{\Delta R}{R}\right)^3 \quad (\text{Equation 14})$$

in which $\tan \delta$ and $\tan \delta_1$ are the loss factors referred to the composite and to the pristine matrix, respectively, ϕ_2 is the filler volume fraction, R is the radius of the dispersed particles and P is a correction parameter related to the effective thickness of the particle-matrix interfacial region ΔR [18, 19].

The calculated values of the layer thickness ΔR for all the samples (considering an average diameter of titania particles of 33 nm) are shown in Table 3.2.2.1. A relative thick layer was observed for the composites (values of ΔR ranging from 22 to 41 nm) with decreasing values by increases as the titania content. This is explained by the decreasing of the polymer/filler ratio and, hence, the amount of the polymer which is able to wet the nanoparticles.

The values here calculated are of the same of magnitude of data reported by Friedrich *et al.* [16] for epoxy/alumina nanocomposites prepared by mechanical dispersion of preformed alumina nanoparticles treated with different silane coupling agents. Authors reported values of thickness of the particle-matrix interfacial region in the range 40 - 60 nm for alumina nanoparticles having diameter of 40 nm and SSA of 40 m²·g⁻¹. The observed discrepancy could be tentatively attributed to the absence of a coupling agent and to a higher SSA in the present case (about 85 m²·g⁻¹) of *in situ* generated titania nanoparticles.

The relatively high values of the effective thickness of the titania-epoxy interfacial region are in good agreement with the already discussed strong filler-matrix interaction responsible of the significant improvement of the cross-linking density.

Scratch tests were carried out on photo-cured films coated onto glass substrates. Several different methods are in use for evaluating scratches and for the determination of critical normal forces (L_C), but only microscope observation of the

scratch is recognised able to reliably differentiate between different failure modes. Major failure events have been classified in terms of plastic deformation, cracking (first critical load, L_{C1}) and spallation (where the coating flakes off, typically at the edges) (second critical load, L_{C2}).

Optical micrographs of the photo-cured coatings after scratch test are reported in Figure 3.2.2.5.



Figure 3.2.2.5 – Optical micrographs of the photo-cured coatings after scratch test (increasing load direction from left to right)

In the present case, only cracking events and L_{C1} values were detected due to the very strong adhesion between coating and glass substrate, which did not permit the identification of spallation events. During test, the load was increased from left to right and the appearance of a visible scratch on the surface was correlated to the first critical load L_{C1} (whose values are reported in Table 3.2.2.2). A significant scratch resistance enhancement was observed by increasing the titania content in the nanocomposites. L_{C1} value of unfilled epoxy (6.07 N) raised up to 7.85, 9.86 and 11.40 N for ‘Ep-T3’, ‘Ep-T6’ and ‘Ep-T10’, respectively.

Composite code	Lc1 (N)	HV
Ep	6.1 ± 0.7	21.5 ± 0.9
Ep-T3	7.9 ± 0.3	24.7 ± 0.2
Ep-T6	9.9 ± 0.3	28.4 ± 0.7
Ep-T10	11.4 ± 0.5	28.1 ± 0.5

Table 3.2.2.2 – Surface properties of the photo-cured composites: first critical load (LC1) measured by scratch test and nano-hardness (HV) measured by depth-sensing Vickers nano-indentation

For a more complete characterisation of surface mechanical properties, by using a depth-sensing Vickers nano-indenter, nano-indentation tests were carried out. The Vickers nano-hardness values are reported in Table 3.2.2.2. Once again, nano-hardness increment was noted by increasing the filler concentration in the epoxy/titania nanocomposites with an increase of about 15, 32 and 31% with respect the unfilled epoxy for ‘Ep-T3’, ‘Ep-T6’ and ‘Ep-T10’, respectively.

Both scratch test and nano-indentation analysis showed a significant increase of surface mechanical properties by increasing the filler concentration in the photo-cured epoxy/titania nanocomposites. On the basis of the above consideration on dynamic-mechanical analysis, this observed enhancement should be attributed to the presence of rigid filler with higher mechanical properties with respect to the epoxy matrix, but also to an increment of cross-linking density due to the *in situ* generated titania nanoparticles.

Optical properties of the photo-cured films can be deduced by the optical photographs and visible spectra reported in Figure 3.2.2.6 and 3.2.2.7, respectively.

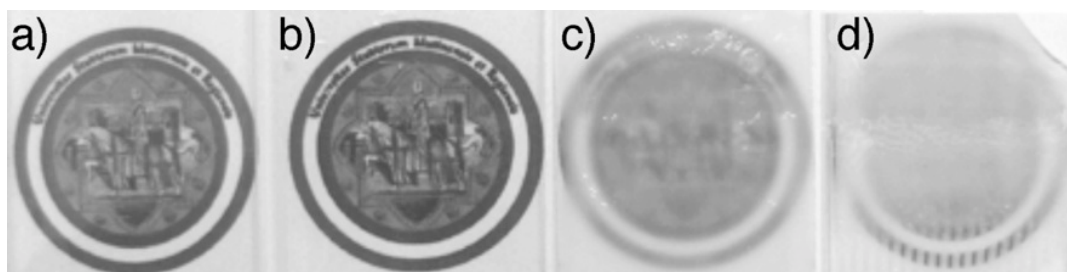


Figure 3.2.2.6 – Photographs of the photo-cured coatings applied onto glass: (a) Ep; (b) Ep-T3; (c) Ep-T6 and (d) Ep-T10

As expected, the pristine epoxy resin 'Ep' appeared fully transparent as shown in Figure 3.2.2.6a according to its amorphous character. The presence of a limited amount of titania nanoparticles didn't influence the transparency of the photo-cured films as shown by 'Ep-T3' sample (Figure 3.2.2.6b). On the contrary, the transparency was significantly inhibited by increasing the filler content ('Ep-T6' and 'Ep-T10' samples, Figures 3.2.2.6c and 3.2.2.6d, respectively) presumably due to scattering phenomena present in the biphasic composite materials.

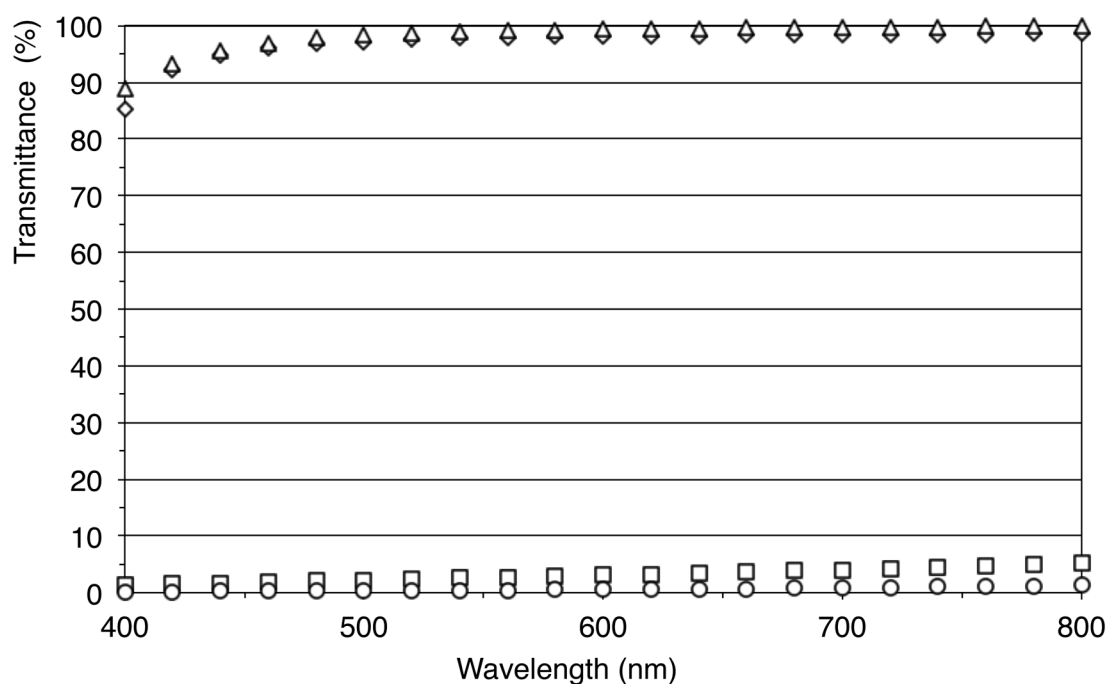


Figure 3.2.2.7 – Visible spectra of (◇) Ep, (△) Ep-T3, (□) Ep-T6 and (○) Ep-T10

The visual analysis was also confirmed by the spectrophotometric analysis carried out in the visible wavelength range (380-800 nm). The transmittance spectra reported in Figure 3.2.2.7 indicates very high transmittance values in the whole visible range for 'Ep' and 'Ep-T3' samples and a dramatic decrement for 'Ep-T6' and 'Ep-T10' samples.

CE, thermally cured

The gravimetric analyses showed actual titania contents (values in Table 3.2.2.3) are rather closed to the nominal ones proving that the employed procedure is an effective alternative to produce composites with respect to the conventional mixing methods.

Composite code	α (%) by Eq. 4	f (wt%)	f_{ORG} (wt%)	$T_{\text{g,DSC}}$ (°C)	$T_{\text{g,DMTA}}$ (°C)	$\tan\delta_{\text{max}}$	$E'_{T=40^\circ\text{C}}$ (Pa)	$E'_{T=T_g+50^\circ\text{C}}$ (Pa)	M_c (g/mol) by Eq. 12
CE_T0	80.9	13.4	13.4	51	95	0.843	6.33E+08	7.85E+05	3600
CE_T3	74.9	11.5	11.8	71	114	0.440	1.78E+09	5.19E+06	660
CE_T5	78.4	8.0	8.3	87	106	0.410	1.89E+09	1.26E+07	260
CE_T10	76.8	6.5	7.0	101	119	0.412	1.26E+09	8.45E+06	430
CE_T5_ex	74.9	25.5	26.7	52	107	0.904	1.65E+09	1.62E+06	1920
CE_T5_ex_C	78.8	18.2	19.0	50	115	0.690	1.63E+09	1.66E+06	2010

Table 3.2.2.3 – Properties of the thermally cured composites: epoxy groups conversion (α), absolute and normalized extractable fractions (f and f_{ORG}), glass transition temperature from DSC ($T_{\text{g,DSC}}$), glass transition temperature from DMTA ($T_{\text{g,DMTA}}$), damping (expressed as maximum value of $\tan\delta$, $\tan\delta_{\text{max}}$), storage modulus measured at $T=40^\circ\text{C}$ and $T=T_g+50^\circ\text{C}$ ($E'_{T=40^\circ\text{C}}$, and $E'_{T=T_g+50^\circ\text{C}}$) and network density (average molecular weight between two adjacent cross-linking points, M_c)

FT-IR analysis was carried out in order to evaluate the conversion degree of epoxy groups (Table 3.2.2.3). A relative high conversion degree was obtained for all samples indicating the efficiency of the curing process based on the cationic ring opening polymerization mechanism thermally initiated by $\text{Yb}(\text{OTf})_3$. Epoxy groups conversion values ranged from 75 to 79% almost independently on the curable investigated formulation, suggesting that the presence of titania did not significantly influence the curing process. These maximum values of epoxy group conversion were presumably limited by the vitrification of network, which inhibited any further progress of the reaction.

Extractable fraction (f) values were determined in order to evaluate the effect of the presence of the titania suspension on the cross-linked structure (see data reported in Table 3.2.2.3). Taking into account that the conversion of epoxy groups

was not quantitative, f values were relative low with values ranging from 7 to 13 for the CE_Tx series. In this case it is interesting to observe that the extractable fraction was always significantly lower than the nominal amount of BzOH present in the formulation (in the range 21-22 wt% depending on the titania content) suggesting the formation of a relatively well developed three-dimensional network even in the case of high content of BzOH. This result suggested that both 'active chain end' and 'activated monomer' mechanisms (see Scheme 3.2.2.1) occurred during the propagation step in the cationic ring-opening polymerization leading to a covalent incorporation of BzOH (and corresponding by-products of NHSG reaction) within epoxy network.

It is also interesting to observe that both f and f_{ORG} values systematically decreased by increasing the amount of titania. In this respect, the presence of *in situ* generated titania particles resulted in a positive contribution to the development of a network structure, presumably due to the formation of a stronger interphase between filler and organic matrix.

The significance of the filler *in situ* generation can be clearly underlined considering the composites CE_T5_ex and CE_T5_ex_C prepared by the *ex situ* synthesized powders T_S25 and T_S25_C (not calcined and calcined, respectively). In this case the epoxy groups conversion values (75-79 %) are very similar to those obtained for the CE_Tx series indicating a negligible effect on the kinetics of epoxy groups reaction. On the contrary, a significantly higher amount of extractable phase was observed for both samples suggesting that the addition of *ex situ* generated particles did not contribute to the development of a cross-linked structure.

FESEM images of the composites permitted to evaluate the distribution and aggregation of titania particles in the matrix. Typical FESEM micrographs of fractured surface epoxy/titania composites (CE_5T, CE_10T and CE_5Tex_C as representative examples) are reported in Figure 3.2.2.8. All samples showed the presence of a dispersed phase rich in titanium, as indicated by EDX analysis (here not reported), attributable to titania.

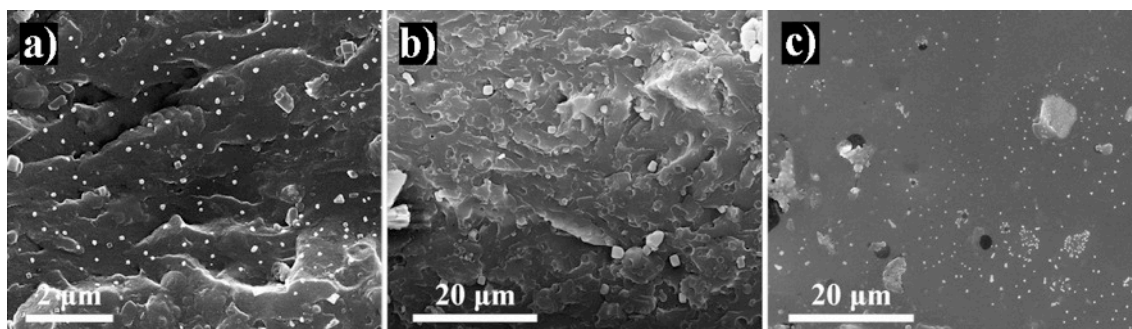


Figure 3.2.2.8 – FESEM micrographs of the CE_5T (a), CE_10T (b) and CE_5Tex_C (c)

The samples prepared by *in situ* generated TiO_2 showed the formation of small aggregates of some titania particles, but presenting anyway very homogeneous filler distribution. The sample CE_5T (Figure 3.2.2.8a) showed an average particles size of 95 ± 22 nm, whereas bigger particles, ranging from 580 nm to 1.3 μm , were detected in the case of CE_10T (Figure 3.2.2.8b), phenomenon that was probably due to the usual tendency of titania nanoparticles to aggregate [20]. The sample prepared incorporating *ex situ* synthesised calcined powder (CE_5Tex_C in Figure 3.2.2.8c) shows that the average particles size increases compared to CE_5T, but the most visible dissimilarity is the less homogeneous filler dispersion and the formation of big aggregates. This is probably due to the calcination that eliminates the organic phase on the particles surface that enhances the interaction between organic and inorganic phase and partially avoids the particles agglomeration improving the dispersion.

Glass transition temperature (T_g), damping (expressed as maximum value of loss factor, $\tan\delta_{\text{max}}$) and storage modulus (E') values obtained by DMTA are reported in Table 3.2.2.3.

The obtained results showed that the dynamic-mechanical properties of composites were significantly affected by the titania content. It is usually expected that, in the case of polymers filled with particles, the incorporation of rigid fillers into a polymeric matrix made difficult the movement of the polymer chains leading to a damping decrement and a shift of T_g values to higher temperatures. Also in the present case, a significant reduction of damping (quantified as $\tan\delta_{\text{max}}$) was observed by increasing the titania concentration in the composites, together with a significant increment in T_g values. The glass transition temperature of unfilled epoxy (95°C)

increased up to 114, 106 and 119°C for CE_T3, CE_T5 and CE_T10, respectively. As already mentioned, such increases in T_g can be attributed to the constrained chain mobility by well-dispersed fillers. A rather similar trend (Table 3.2.2.3) was also observed by DSC analysis that confirmed the increase of T_g above described.

The general increase in T_g and decrease in loss factor $\tan\delta_{\max}$ by increasing the titania content can be also considered as an indirect evidence of the presence of a strong filler-matrix interface. Kim *et al.* [14] reported the preparation and the characterization of epoxy-based composites containing inorganic nanoparticles, functionalized or not functionalized with suitable coupling agents. Kim also explained that composites with weak filler-matrix interface exhibit essentially no modification in T_g and damping with filler contents, opposite to composites with strong filler-matrix interface which show a systematic increase of T_g and decrease of loss factor with filler content. Accordingly, it is interesting to observe that CE_T5_ex (*ex situ* composite with a weaker filler-matrix interface) showed a $\tan\delta_{\max}$ of 0.904, very similar to the value of unfilled resin CE_T0 (0.843) and much higher than the values of *in situ* composites CE_T3, CE_T5 and CE_T10 ($\tan\delta_{\max}$ in the range 0.410-0.440).

The storage moduli E' measured in the glassy state (that is at a temperature of 40 °C) were influenced by the presence and the amount of titania. $E'_{T=40^\circ\text{C}}$ values for composites were always higher than the unfilled one CE_T0 (0.63 GPa) with the maximum value of 1.89 GPa for composite with intermediate filler content (CE_T5). A stronger influence due to the presence of titania was observed in the rubbery state. In this respect, it is very interesting to note that the storage moduli E' measured over the glass transition temperature (at $T_g+50^\circ\text{C}$) increased significantly by increasing the titania content. $E'_{T=T_g+50^\circ\text{C}}$ values of CE_T0 (0.78 MPa) raised up to 5.19, 12.59 and 8.45 MPa for CE_T3, CE_T5 and CE_T10, respectively.

The reduced storage modulus (that is the ratio between the moduli of the composite and of the matrix, respectively) measured in the rubbery region as a function of titania volume fraction is reported in Figure 3.2.2.9. In order to compare the experimental results with data predicted by the well-known models for composites materials, the generalized Kerner equation (Eq. 9). It was applied for the reduced modulus of filled polymers in order to evaluate its dependence on the nanoparticles content.

Data reported for CE_Tx series indicated a very important increment of reduced storage modulus with respect to the values predicted by the generalized Kerner equation (Eq. 9). Taking into account that, in the rubbery region temperature range, the modulus values are mainly governed by the cross-linking density of the network, a considerable increase of this last parameter has to be considered in the presence of *in situ* generated titania. In other words, titania nanoparticles generated by NHSG process acted not only as rigid reinforcing filler but also as cross-linking points, increasing the cross-linking density of the composite material with respect to the pristine epoxy matrix.

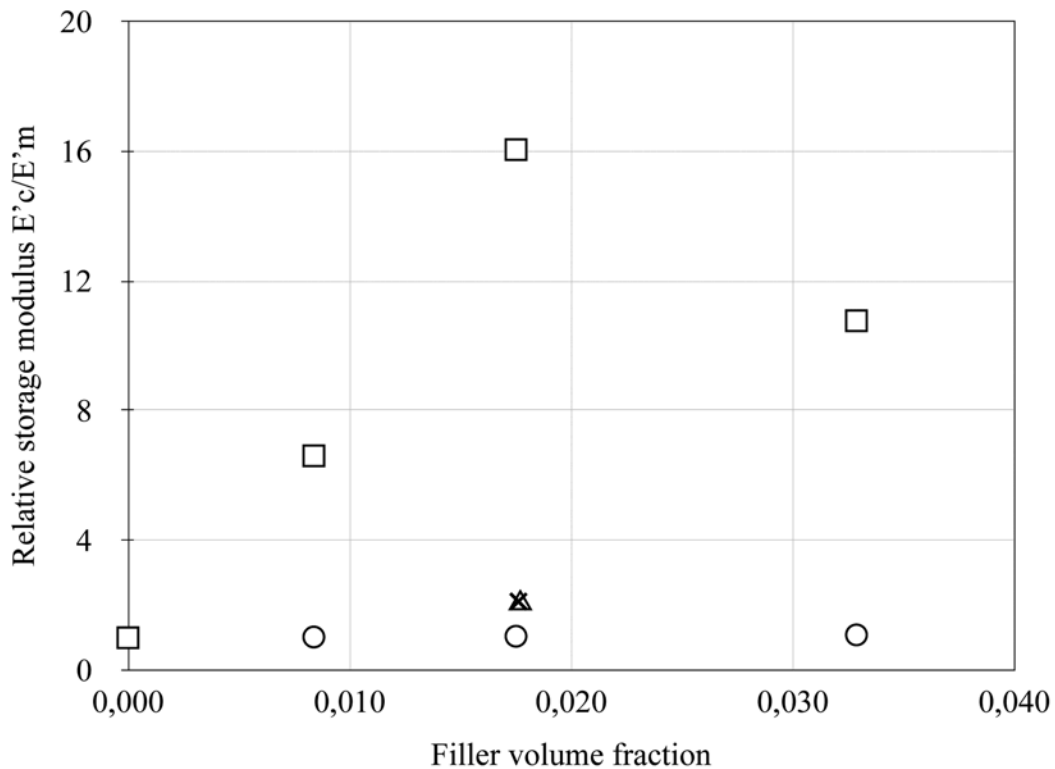


Figure 3.2.2.9 – Relative storage modulus (E') dependence on the filler volume fraction: experimental values of (□) CE_Tx series, (△) CE_T5_ex, (×) CE_T5_ex_C and (○) prediction by generalized Kerner equation (Eq. 9)

Once again, the *ex situ* composites CE_T5_ex and CE_T5_ex_C (in Figure 3.2.2.9, △ and × respectively) showed a completely different behaviour with a reduced storage modulus very similar to the predicted value.

In order to further underline the differences between *in situ* and *ex situ* composites, the storage modulus (E') as a function of the temperature is reported in Figure 3.2.2.10 for CE_T5, CE_T5_ex and CE_T5_ex_C.

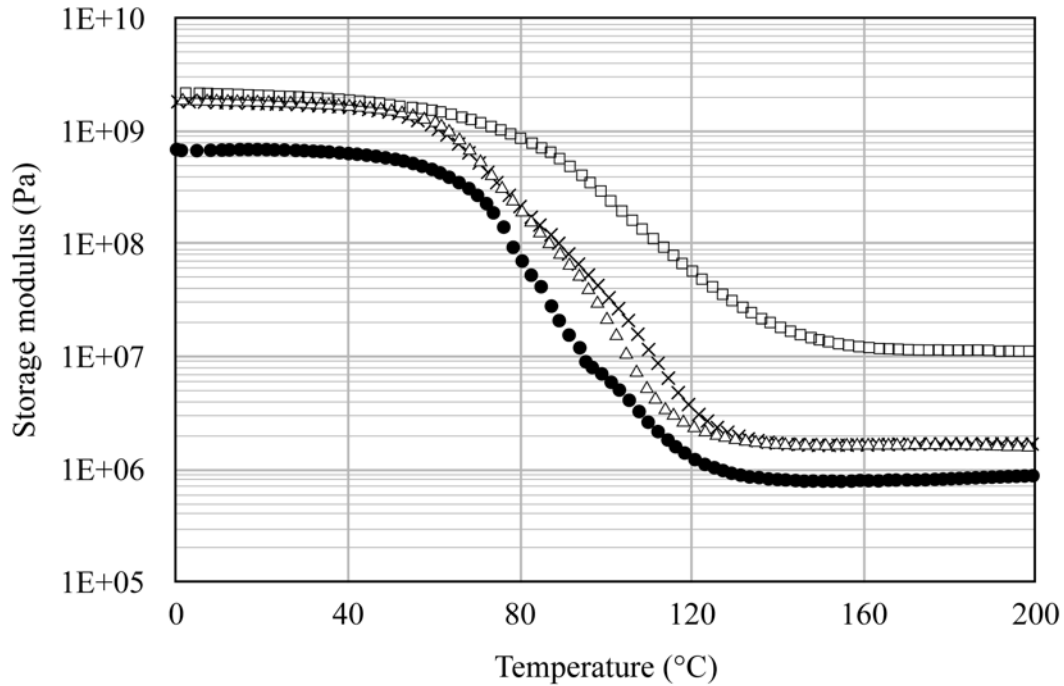


Figure 3.2.2.10 – Storage modulus of (□) CE_T5, (△) CE_T5_ex, (×) CE_T5_ex_C and (●) CE_T0 as a function of the temperature

Data showed a dramatic difference in storage modulus in the rubbery region for *in situ* and *ex situ* composites, even though the amount of filler is rather equal. Remembering once again that the modulus in the rubbery region is mainly determined by the cross-linking density, dynamic-mechanical analysis supported the hypothesis that titania nanoparticles *in situ* generated increased the cross-linking density of the composite with respect to both the unfilled epoxy matrix and the *ex situ* composites.

In order to further investigate this aspect, the network densities (that is the average molecular weight between two adjacent cross-linking points, M_c) were determined in the rubbery region from the storage modulus values at $T_g + 40^\circ\text{C}$ by using the Equation 12.

The calculated values of polymer molecular weight between two cross-linking points (M_c) are reported in Table 3.2.2.3. The network density increases and M_c decreases for CE_Tx series with respect to the unfilled epoxy resin CE_T0. Accordingly to the above discussed data, the *ex situ* composites CE_T5_ex and CE_T5_ex_C showed significantly higher M_c values.

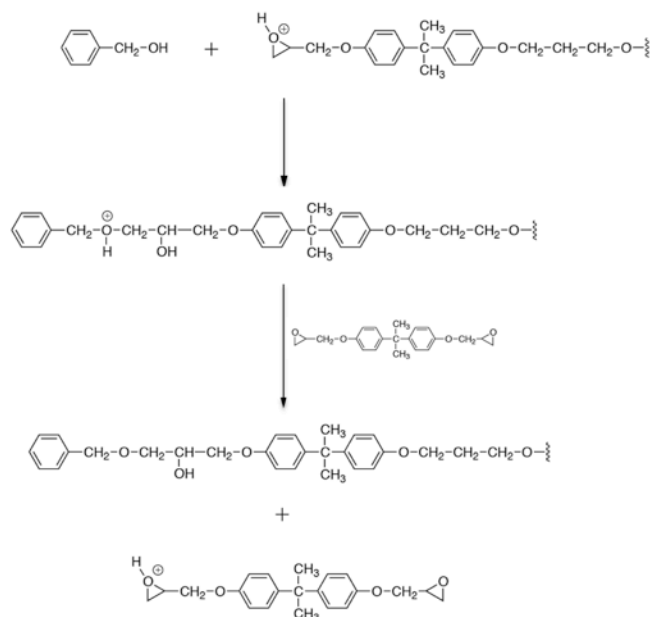
DGEBA, thermally cured

Gravimetric analyses showed actual titania contents (Table 3.2.2.4) are rather closed to the nominal ones proving that the employed procedure is an effective alternative to produce composites overcoming the typical problems related to the conventional mixing methods.

Composite code	G (wt%)	T _{g,DSC} (°C)	T _{g,DMTA} (°C)	tanδ _{max}	E' _{T=40°C} (GPa)	E' _{T=Tg+40°C} (MPa)	Mc (g/mol)	ΔR (nm)
DGEBA-T0	99.0	50	75	1.721	0.458	0.926	12800	-
DGEBA-T3	99.7	67	100	1.436	0.546	2.530	5000	8
DGEBA-T5	99.7	73	113	1.030	0.713	5.014	2600	14
DGEBA-T10	98.8	86	139	0.758	0.549	7.071	2000	12

Table 3.2.2.4 – Properties of the thermally cured composites: gel content (G), glass transition temperature from DSC (T_{g,DSC}), glass transition temperature from DMTA (T_{g,DMTA}), damping (expressed as maximum value of tanδ, tanδ_{max}), storage moduli measured at T=40°C and T=Tg+40°C (E'_{T=40°C} and E'_{T=Tg+40°C}), network density (average molecular weight between two adjacent cross-linking points, Mc) and effective thickness of the particle–matrix interfacial region (ΔR)

Gel content (G) was determined in order to evaluate the effect of the presence of the titania suspension on the cross-linked structure (Table 3.2.2.4). Gel content values are extremely high (equal or higher than 99.0%) for all investigated samples indicating the formation of a fully developed three-dimensional network (with a negligible amount of extractable fraction) even in the case of a relatively high BzOH content. This important result suggested, even in this case, that both ‘active chain end’ and ‘activated monomer’ mechanisms (see Scheme 3.2.2.2) occurred during the propagation step in the cationic ring-opening polymerization leading to a quantitative incorporation of BzOH (and corresponding by-products of NHSG reaction) within epoxy network [21], as indicated by the absence of species extractable in chloroform.



Scheme 3.2.2.2 – Schematic of the ‘Active chain end’ and ‘activated monomer’ mechanisms for the mixture DGEBA/BzOH

FESEM characterization of the composites permitted to evaluate the distribution and aggregation of titania particles in the matrix. Typical FESEM micrographs of epoxy-titania composites fracture surface having titania content of 2.8 and 8.0 phr, respectively, are reported in Figure 3.2.2.11. The fracture surfaces (characteristic also for the other compositions) showed the presence of a homogeneous dispersed phase attributable to a titania rich phase as indicated by EDX analysis (here not reported). Even though the filler is well distributed, FESEM images also showed some particles agglomeration in small titania domains. The sample DGEBA_3T (Figure 3.2.2.11a) showed that the average size of these aggregates is 405 ± 101 nm, whereas bigger agglomerates, ranging from 470 nm to 1.1 μm , were detected in the case of DGEBA-10T (Figure 3.2.2.11b). This phenomenon was probably due to the common strong tendency of titania particles to aggregate that was also reported elsewhere [20]. Anyway, it can be considered a good results, taking into account that homogeneous filler distributions was reached for all samples, avoiding the use of any coupling agent and/or long and complicated dispersion treatments, for samples production.

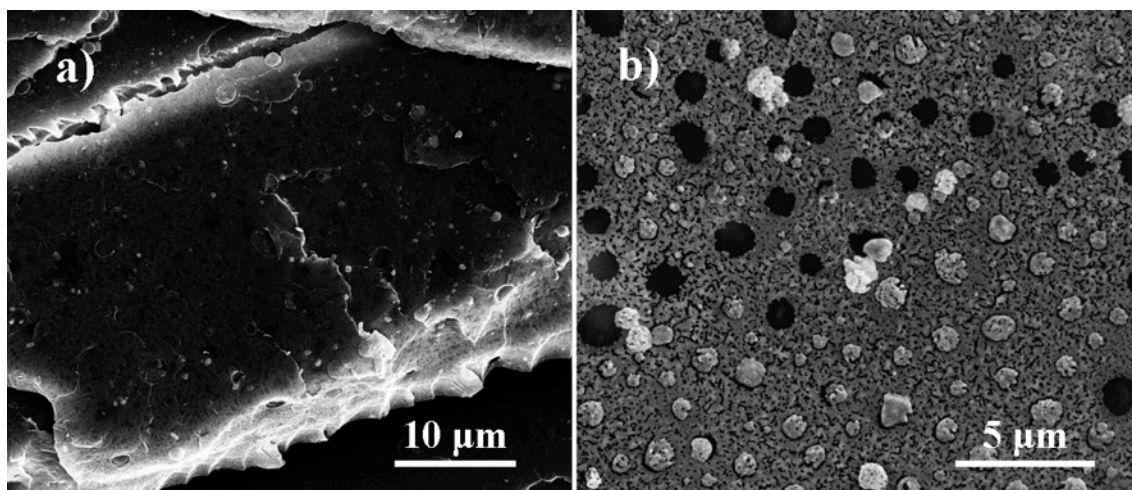


Figure 3.2.2.11 – FESEM micrographs of the fractured surface of DGEBA-3T (a) and DGEBA-10T (b)

Glass transition temperature (T_g), damping (expressed as maximum value of loss factor, $\tan\delta_{\max}$) and storage modulus (E') values of thermally-cured composites obtained by DMTA are reported in Table 3.2.2.4.

The obtained results showed that the dynamic-mechanical properties of composites were significantly affected by the titania content. As expected in the case of polymers filled with particles, the incorporation of rigid fillers into a polymeric matrix made difficult the movement of the polymer chains leading to a damping decrement and a shift of T_g values to higher temperatures. In the present system, as already reported elsewhere [22], a significant reduction of damping (quantified as $\tan\delta_{\max}$) was observed by increasing the titania concentration in the composites, together with a very significant increment in T_g values. The glass transition temperature of unfilled epoxy (75°C) increased up to 100, 113 and 139°C for DGEBA-T3, DGEBA-T5 and DGEBA-T10, respectively. Such increases in T_g can be attributed to the constrained chain mobility by well-dispersed filler.

The general increase in T_g and decrease in loss factor $\tan\delta_{\max}$ by increasing the titania content can be also considered as an indirect evidence of the presence of a strong filler-matrix interface. Kim *at al.* [14] reported the preparation and the characterization of epoxy-based composites containing inorganic nanoparticles functionalized or not functionalized with suitable coupling agents and reported that composites with weak filler-matrix interface exhibit essentially no modification in T_g and damping with filler contents, opposite to composites with strong filler-matrix

interface which show a systematic increase of T_g and decrease of loss factor with filler content.

The storage moduli E' measured in the glassy state were slightly influenced by the presence and the amount of titania. $E'_{T=40^\circ\text{C}}$ values for composites were always higher than that of unfilled DGEBA-T0 (0.458 GPa) with the maximum value of 0.713 GPa for composite with intermediate filler content (DGEBA-T5). A much stronger influence due to the presence of titania was observed in the rubbery state. In this respect, it is very interesting to note that the storage moduli E' measured above the glass transition temperature (that is at a temperature of $T_g + 40^\circ\text{C}$) increased significantly by increasing the titania content. $E'_{T=T_g+40^\circ\text{C}}$ values of DGEBA-T0 (0.926 MPa) raised up to 2.530, 5.014 and 7.071 MPa for DGEBA-T3, DGEBA-T5 and DGEBA-T10, respectively.

The reduced storage modulus (that is the ratio between the moduli of the composite and of the matrix, respectively) measured in the rubbery region as a function of titania volume fraction is reported in Figure 3.2.2.12. In order to compare the experimental results with data predicted with well-known models for composites materials, the generalized Kerner equation [15] (Eq. 9) for the reduced modulus of filled polymers was applied in order to evaluate its dependence on the nanoparticles content.

Data indicated a very important increment of reduced storage modulus with respect to the values predicted by the generalized Kerner equation (Eq. 9). Taking into account that, in the rubbery region temperature range, the modulus values are mainly governed by the cross-linking density of the network, a considerable increase of this last parameter has to be considered in the presence of *in situ* generated titania. In other words, titania nanoparticles generated by NHSG process acted not only as rigid reinforcing filler but also as cross-linking points, increasing the cross-linking density of the composite material with respect to the pristine epoxy matrix.

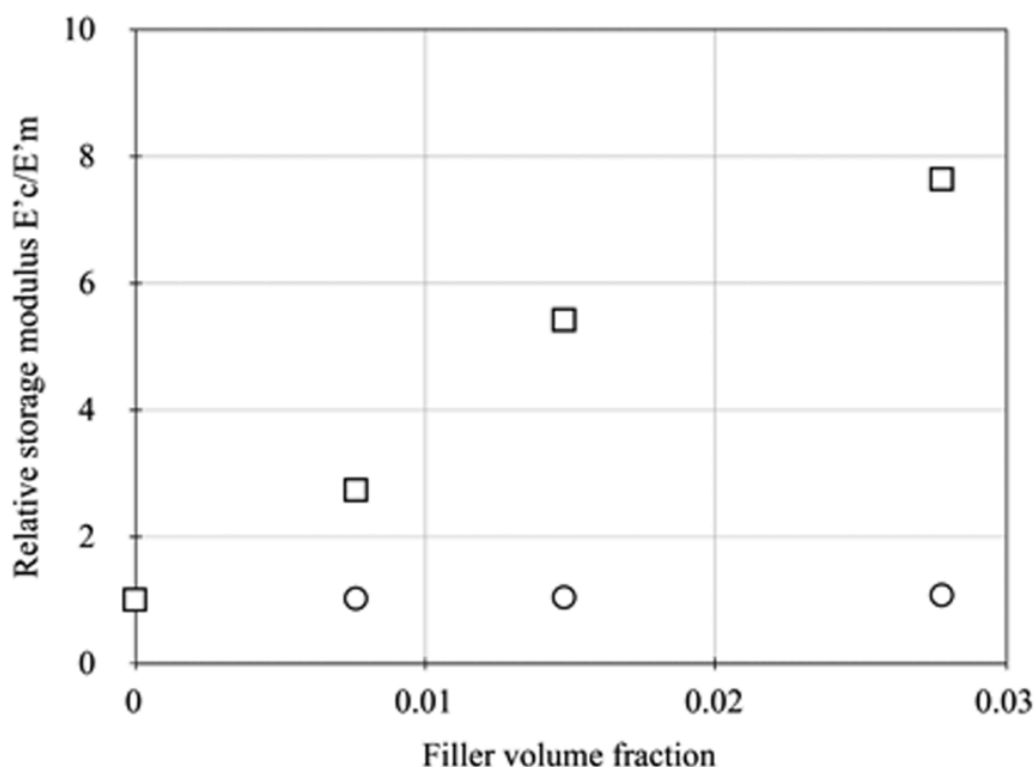


Figure 3.2.2.12 – Relative storage modulus dependence on the titania volume fraction: (□) experimental values and (○) prediction by generalized Kerner equation (Eq.9)

In order to further investigate this aspect, the network densities (that is the average molecular weight between two adjacent cross-linking points, M_c) were determined in the rubbery region from the storage modulus values at $T_g+40^\circ\text{C}$ by using the Eq. 12.

The calculated values of polymer molecular weight between two cross-linking points, M_c , are reported in Table 3.2.2.4. The network density increases and M_c decreases as the titania content increases. According to the dynamic-mechanic behaviour already discussed, the presence of the rigid filler increases the local concentration of the cross-linking points and increases the network density in the composite compared to the neat matrix. As already mentioned, this behaviour could be tentatively explained taking into account that the *in situ* generation of titania and subsequent polymerization of the suspending medium resulted in a very strong filler-matrix interaction with a significant improvement of the cross-linking density due to the titania contribution which in turn incremented the glass transition temperature and the modulus values in the rubbery region.

Thermal properties trend, of the thermally-cured materials by DSC analysis, (see Table 3.2.2.4) is in good agreement with the obtained data by DMTA analysis, showing $T_{g,DSC}$ values of unfilled epoxy DGEBA-T0 (50°C) increasing up to 67, 73 and 86 °C for DGEBA-T3, DGEBA-T5 and DGEBA-T10, respectively.

From the reduced damping values, the thickness of the polymer layer immobilized onto the titania nanoparticles surface was estimated at a temperature below glass transition temperature (35°C) by using Eq. 13 and Eq. 14.

Even if overestimated due to the presence of not negligible amount of organic component, the average diameters of titania crystallites reported in Table 3.1.1.1 were used for the calculation (in particular samples: T_Bz_1, T_Bz_2 and T_Bz_3). The calculated values of the layer thickness ΔR for all the samples are shown in Table 3.2.2.4. A relative thick layer was calculated for the composites (values of ΔR ranging from 8 to 14 nm, that is of the same order of particles' diameter). The values here calculated are of the same order of magnitude of data reported by Friedrich *et al.* [15] for epoxy/alumina nanocomposites prepared by mechanical dispersion of preformed alumina nanoparticles treated with different silane coupling agents. Authors reported values of thickness of the particle-matrix interfacial region in the range 40-60 nm for alumina nanoparticles having diameter of 40 nm.

The relatively high values of the effective thickness (referred to the particles' diameter) of the titania-epoxy interfacial region here reported seem to be in good agreement with the already discussed strong filler-matrix interaction responsible of the significant improvement of the cross-linking density.

Quasi-static mechanical properties were investigated by using nano-indentation analysis due to the limited size of the prepared specimens. Vickers hardness (HV) and indentation modulus (E_{IT}) values are reported in Table 3.2.2.5 in which a very significant increase of surface mechanical properties by increasing the filler concentration can be observed. HV and E_{IT} values increased from 3.3 and 0.6 GPa for unfilled DGEBA-T0 up to maximum values of 19.7 and 3.9 GPa for the composite containing the higher amount of titania (DGEBA-T10).

Composite code	HV (-)	St. dev. (-)	E_{IT} (GPa)	St. dev. (GPa)
DGEBA-T0	3.3	0.2	0.6	0.1
DGEBA-T3	16.6	0.7	3.0	0.2
DGEBA-T5	19.0	3.0	3.6	0.5
DGEBA-T10	19.7	1.5	3.9	0.2

Table 3.2.2.5 – Mechanical properties of the thermally-cured composites obtained by nano-indentation: Vickers hardness (HV) and indentation modulus (E_{IT}) (St. dev.: standard deviation)

On the basis of the above considerations on dynamic-mechanical analysis, this observed enhancement should be attributed to the presence of rigid filler with higher mechanical properties with respect to the epoxy matrix but also to an increment of cross-linking density due to the titania particles produced by NHSG process.

3.2.3 – Composite Based on EPDM rubber

SEM characterization of the composites allowed the evaluation of distribution and aggregation of titania particles in the rubbery matrix. Typical SEM micrographs of unvulcanized rubber with a nominal titania content of 10, 20 and 30 wt% are reported in Figure 3.2.3.1.

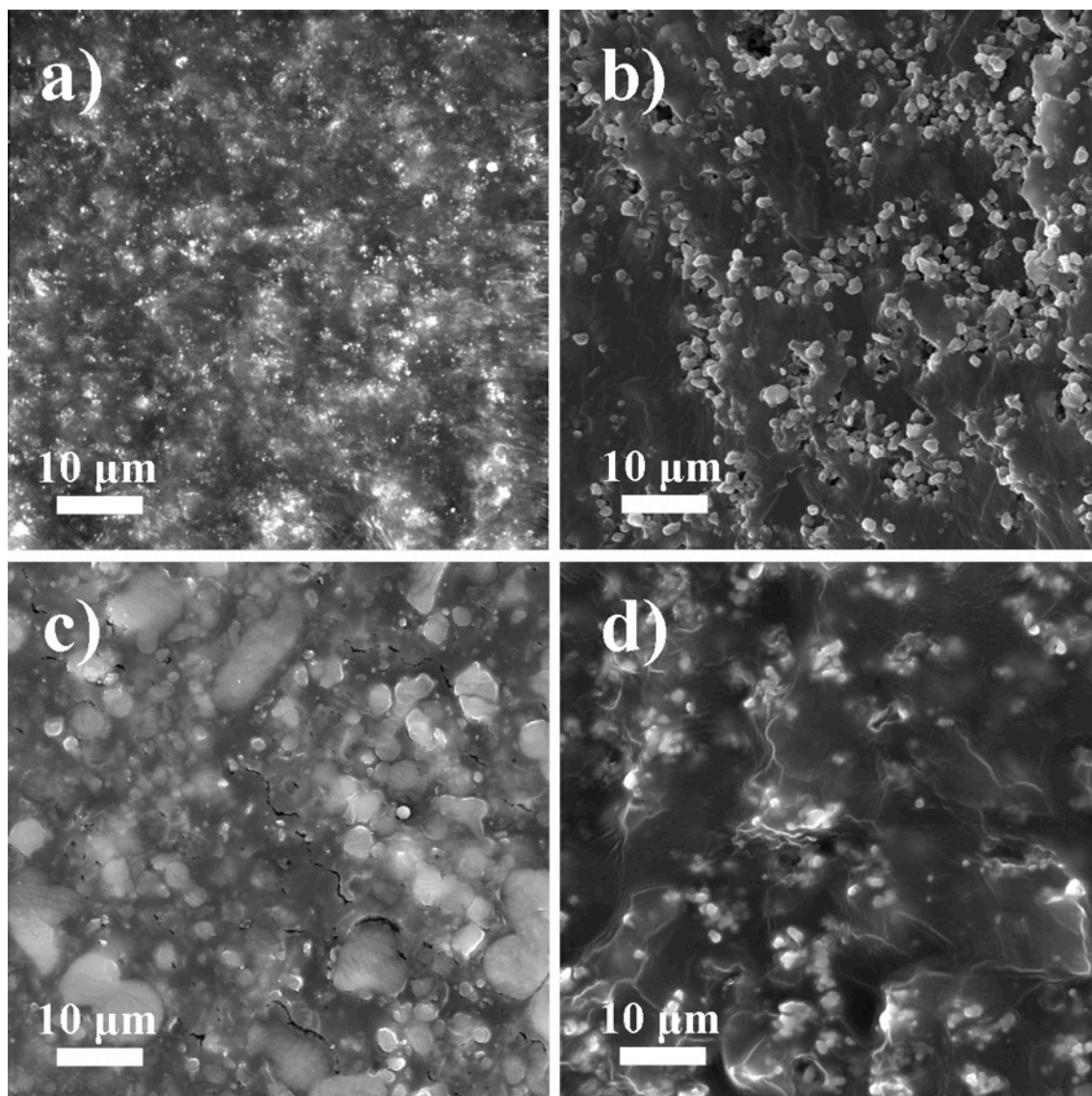


Figure 3.2.3.1 – SEM micrographs of (a) EPDM_10, (b) EPDM_20, (c) EPDM_30, (d) EPDM_20_V

The picture for EPDM_10 in Figure 3.2.3.1a shows a fairly good dispersion of the titania particles in the rubber matrix, although there is also clear evidence of particle agglomeration. The TEM analysis of the titania particles showed that they had

diameters around 6 nm, while the aggregates in the composites seem to have dimensions around 300 nm.

By increasing the titania content (EPDM_20 in Figure 3.2.3.1b), the particle distribution remained good enough, but a significant increase in particle sizes was observed. The average aggregate dimension was around 1.4 μm .

The sample with the highest titania content (EPDM_30 in Figure 3.2.3.1c) showed an increase in the particle size and in size distribution. In particular, large particles having diameters higher than 10-15 μm were present together with smaller particles (about 1 μm in size), meaning that higher filler content causes higher particle aggregation, as already observed and reported by other authors for similar systems [23, 24] and can be tentatively explained taking into account that by increasing the amount of *in situ* formed dispersed phase an increase in the coalescence of the growing particles and of both the average dimensions of the dispersed particles and aggregation are expected.

The SEM micrographs showed no relevant differences between the vulcanized material (EPDM_20_V in Figure 3.2.3.1d) and the unvulcanized materials, meaning that the vulcanization process does not affect the composite morphologies.

TGA was used to determine the actual content of titania and to investigate the thermal oxidative stability of the composites.

Material code	Actual TiO ₂ content (%)	T _{ONSET} (°C)	Material code	Actual TiO ₂ content (%)	T _{ONSET} (°C)
EPDM_0	0.0 (-)	435	EPDM_0_V	0.0 (-)	431
EPDM_10	9.1 (91)	435	EPDM_10_V	9.6 (96)	441
EPDM_20	17.7 (89)	358	EPDM_20_V	18.8 (94)	433
EPDM_30	27.2 (91)	327	EPDM_30_V	28 (93)	375

Table 3.2.3.1 – Thermogravimetric analysis: actual titania content (mass residue at 700°C) and onset temperature (T_{ONSET}) of the main degradation step of EPDM_x and EPDM_x_V composites (the yield in titania is reported in brackets)

The actual filler content values are reported in Table 3.2.3.1 for vulcanized and unvulcanized composites. In all the cases, the actual filler contents were very near to

the expected values, indicating that the NHSG process was appropriate for inducing an almost complete conversion of TiCl_4 to TiO_2 . Other recently reported rubber-matrix composites obtained by *in situ* generation of titania through a hydrolytic sol-gel process showed conversion values of titania precursors (titanium iso-propoxide) in the range 80-84% [11] suggesting a significantly higher reactivity of NHSG with respect to the hydrolytic counterpart. As expected, the vulcanization process carried out at high temperature induced a slight increment in the yield of titania.

Representative TGA curves of unvulcanized EPDM_x are reported in Figure 3.2.3.2 and the TONSET values of the main degradation step are reported in Table 3.2.3.1. The weight losses occurred in three distinct steps. In the first step, the weight loss in the range 50-200 °C was probably due to the evaporation of strongly absorbed solvents and/or condensation by-products of the second step of NHSG reaction. Interestingly, this degradation step was significantly delayed in the case of unfilled EPDM_0. The second step corresponding to the maximum weight loss in the range of 250-500 °C was ascribed to the decomposition of the polymer chain and its onset was strongly affected by the titania content. In the third step, the weight loss observed up to 650 °C was presumably due to the elimination of char residues formed in the previous step.

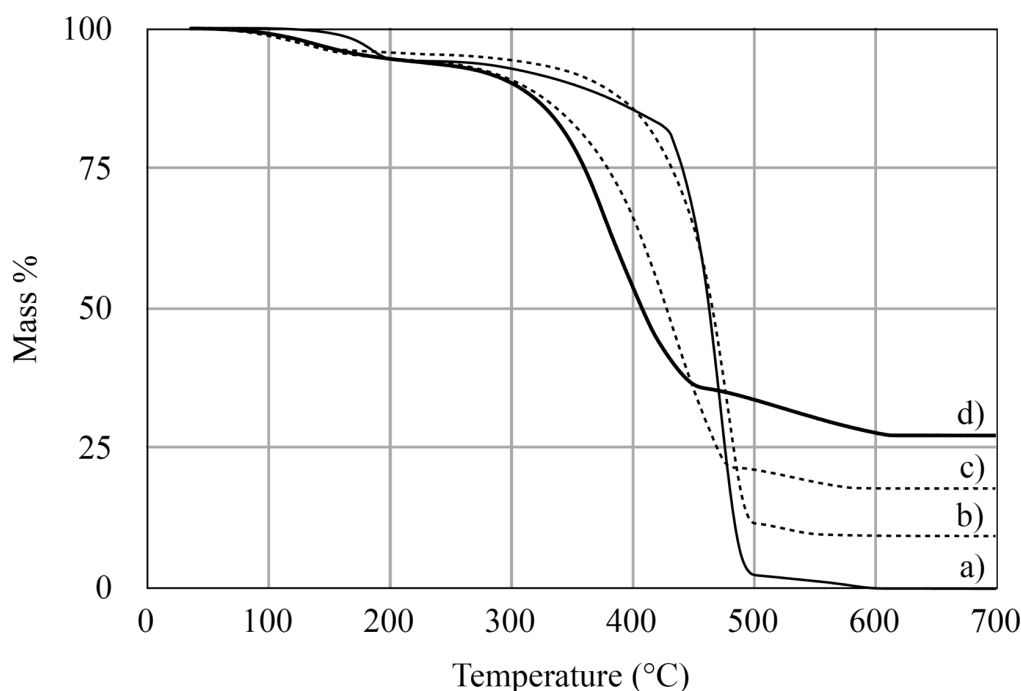


Figure 3.2.3.2 – TG curves of (a) EPDM_0, (b) EPDM_10, (c) EPDM_20, (d) EPDM_30

Comparing the sample containing 10 wt% of filler content with the pristine EPDM, the decomposition temperature did not change for the unvulcanized materials or slightly increased for the vulcanized ones as indicated by the T_{ONSET} values reported in Table 3.2.3.1. The slight increase in resistance to thermal decomposition resulted for the fact that TiO_2 particles were able to sustain high temperature and to retard the heat to diffuse into EPDM matrix. With further increment of filler loadings (20 and 30 wt%), worsening or no further increases in thermal resistance of composites were observed, in accordance to S. Haitao *et al.* [25].

One possibility is that with higher titania content particles aggregated more massively in EPDM matrix, which led to the decline of thermal resistance. Furthermore, this behaviour could probably be attributed to metal-catalyzed oxidative decomposition pathways in the polymer/titania composite, as already observed and discussed for similar materials [26].

The values of q , q_{EPDM} , f and f_{EPDM} in toluene are reported in Table 3.2.3.2. For the unfilled rubber, equilibrium swelling analysis is a well-known method to evaluate the number of effective network chains per volume unit (i.e., the cross-linking density) of an elastomer after vulcanization.

Material code	f (%)	f_{EPDM} (%)	q (-)	q_{EPDM} (-)
EPDM_0_V	0	0	9.4	9.4
EPDM_10_V	29.7	32.6	24.7	27.1
EPDM_20_V	31.7	38.5	20.7	25.2
EPDM_30_V	47.4	65.1	16.7	22.9

Table 3.2.3.2 – Swelling/extraction tests: absolute extractable fraction (f), swelling ratio (q) and values normalized with respect to the EPDM content (f_{EPDM} and q_{EPDM})

In the case of the filled vulcanized rubber, the swelling behaviour depends on complex and different phenomena, such as the crosslinking degree of the rubber matrix, the solvent absorption contribution of the titania phase, the ability of filler particles to act as crosslinking points (i.e., density of polymer-filler attachments), and so on.

Taking into account that conversion of TiCl_4 to TiO_2 can be considered almost quantitative, the extractable fraction in toluene was mainly derived from the uncrosslinked fraction of EPDM. In other words, it could be considered an indicator of the progress of the vulcanization process of EPDM.

In principle, the presence of inorganic fillers should lead to a reduction of the swelling ratio with respect to the unfilled vulcanized rubber, because of the fact that the filler does not absorb toluene during the experiment. In the present case an opposite trend was observed: both values (q and q_{EPDM}) of unfilled rubber are lower than those of filled samples. In particular, the increment of q_{EPDM} (i.e., the swelling ratios referring only to the organic rubber phase) for the filled systems compared to the unfilled ones was attributable to the decreased crosslink density of the rubber phase after vulcanization. This hypothesis is also supported by the observation that f_{EPDM} in toluene increased with increasing titania content (and thus the initial TiCl_4 concentration); this clearly indicates an interfering effect of the sol-gel reaction on the vulcanization process of the rubber. The same behaviour has already been observed for EPDM modified with silica generated *in situ* by a hydrolytic sol-gel process [27].

In order to differentiate the effects due to presence of titania (hydrodynamic effect of a rigid filler) and to the vulcanization of the EPDM matrix (crosslink density), quasi-static and dynamic-mechanical properties were determined before and after the vulcanization step of EPDM-based composites. The results obtained by mechanical characterization (tensile tests) for unvulcanized and vulcanized composites are summarized in Tables 3.2.3.3 and 3.2.3.4 respectively.

The data shown in Table 3.2.3.3 indicate that the presence of titania as rigid filler in the unvulcanized EPDM matrix led to a significant increase in stiffness (both initial and secant moduli) and of the ultimate properties such as stress at break (σ_b). Concerning the low deformation range, the initial modulus increased monotonically by increasing the titania content with an average value for EPDM_30 (8.43 MPa) almost 6 times higher than that of the unfilled unvulcanized EPDM_0 (1.47 MPa). Stiffening and reinforcing effects due to the presence of titania were also observed over a large deformation range with values of secant modulus $E_{\text{sec}, \epsilon=100\%}$, $E_{\text{sec}, \epsilon=200\%}$ and $E_{\text{sec}, \epsilon=300\%}$ and of stress at break σ_b being systematically higher than those of the unfilled rubber. Also for these parameters, a monotonic increase by increasing the

titania content was observed indicating that the concentration of titania particles represents the main parameter for controlling the mechanical properties of these composite materials.

Material code	E_{in} (MPa)	$E_{sec,\epsilon=100\%}$ (MPa)	$E_{sec,\epsilon=200\%}$ (MPa)	$E_{sec,\epsilon=300\%}$ (MPa)	σ_b (MPa)	ϵ_b (%)	R.E. (MPa/wt%)
EPDM_0	1.47 ± 0.09	0.81 ± 0.06	0.47 ± 0.03	0.33 ± 0.02	2.03 ± 0.35	1322 ± 216	-
EPDM_10	2.13 ± 0.10	0.97 ± 0.04	0.56 ± 0.03	0.42 ± 0.02	3.11 ± 0.57	1425 ± 218	0.018
EPDM_20	3.53 ± 0.18	1.40 ± 0.10	0.75 ± 0.08	0.60 ± 0.04	2.82 ± 0.30	854 ± 140	0.033
EPDM_30	8.43 ± 0.18	2.85 ± 0.08	1.67 ± 0.05	1.23 ± 0.04	5.16 ± 0.70	896 ± 182	0.075

Table 3.2.3.3 – Mechanical characterization of unvulcanized composites: initial modulus (E_{in}), secant modulus at an elongation $\epsilon = 100\%$, 200% , 300% ($E_{sec,\epsilon=100\%}$, $E_{sec,\epsilon=200\%}$, $E_{sec,\epsilon=300\%}$), stress at break (σ_b), deformation at break (ϵ_b) and reinforcing efficiency parameter (R.E.)

Comparing the stress at break and deformation at break of the filled composites, it is evident that the material EPDM_10 has the highest value of deformation at break and a good value of stress at break only with 9.1 wt% of titania content, thanks to a good dispersion and the lowest particle aggregation in the rubber matrix.

Das *et al.* [28] proposed a “reinforcing efficiency” (R.E.) parameter to evaluate the reinforcing effect due to the presence of rigid filler with respect to the unfilled rubber matrix. R.E. is defined as the quotient of the difference of the secant moduli at 100% elongation of filled and unfilled vulcanized rubber ($(E_{sec,\epsilon=100\%})_{filled}$ and $(E_{sec,\epsilon=100\%})_{unfilled}$, respectively), with reference to the amount of filler (wt %TiO₂). The reinforcing efficiency is thus defined by:

$$R.E. = \frac{(E_{sec,\epsilon=100\%})_{filled} - (E_{sec,\epsilon=100\%})_{unfilled}}{wt\%TiO_2}$$

Equation 15

R.E. values varied from 0.018 to 0.075, showing the maximum value for the highest titania content (EPDM_30) as already discussed for the above reported mechanical properties. Interestingly, the present values are of the same order of

magnitude as those observed by Das *et al.* [28] (in the range 0.03-0.12) for composite materials prepared by *in situ* hydrolytic sol-gel synthesis to obtain silica particles within triethoxysilyl-grafted EPDM as matrix which ensured a very good interfacial interaction between the silica particles and the rubber. Although this comparison concerns a different filler, can suggest that the generation of titania particles by NHSG in the presence of the rubber was able to enhance the mechanical properties typical of filled systems in the presence of coupling agents, that is a strong filler-matrix interface was created due to the NHSG process.

Concerning the effect of the vulcanization process, the data reported in Table 3.2.3.4 indicate an unexpected generalized slight decrement of properties.

Material code	E_{in} (MPa)	$E_{sec,\epsilon=100\%}$ (MPa)	$E_{sec,\epsilon=200\%}$ (MPa)	$E_{sec,\epsilon=300\%}$ (MPa)	σ_b (MPa)	ϵ_b (%)	R.E. (MPa/wt%)
EPDM_0_V	1.40 ± 0.10	0.89 ± 0.08	0.61 ± 0.03	-	1.12 ± 0.21	171 ± 48	-
EPDM_10_V	1.69 ± 0.16	0.91 ± 0.12	0.53 ± 0.07	0.39 ± 0.04	2.51 ± 0.47	1148 ± 95	0.002
EPDM_20_V	2.56 ± 0.35	1.17 ± 0.12	0.67 ± 0.07	0.49 ± 0.05	2.90 ± 0.13	1144 ± 153	0.015
EPDM_30_V	3.58 ± 0.16	1.42 ± 0.08	0.83 ± 0.03	0.62 ± 0.02	3.90 ± 0.46	1256 ± 167	0.019

Table 3.2.3.4 – Mechanical characterization of vulcanized composites: initial modulus (E_{in}), secant modulus at an elongation $\epsilon = 100\%$, 200% , 300% ($E_{sec,\epsilon=100\%}$, $E_{sec,\epsilon=200\%}$, $E_{sec,\epsilon=300\%}$), stress at break (σ_b), deformation at break (ϵ_b) and reinforcing efficiency parameter (R.E. calculated by Eq. 15)

The values of initial modulus (E_{in}), secant moduli ($E_{sec,\epsilon=100\%}$, $E_{sec,\epsilon=200\%}$, $E_{sec,\epsilon=300\%}$) and stress at break (σ_b) were systematically lower than those determined before vulcanization. This decrease of moduli (strongly remarkable for EPDM_20_V and EPDM_30_V compared with the unvulcanized ones) can be mainly ascribed to some degradative effect due to the vulcanization step at high titania contents. Accordingly, the R.E. parameter also decreased significantly. However, the trend of reinforcement for increased amount of titania was confirmed also in the case of vulcanized composites.

A very significant difference of elongation at break after vulcanization is clearly evident. This behaviour can be explained taking into account that the vulcanization process seems to be inhibited in the presence of titania generated by NHSG process (see swelling/extraction data reported in Table 3.2.3.1). In other words, an efficient vulcanization of EPDM_0_V resulted in a relatively high cross-linking degree (which results in a lower elongation at break), whereas the opposite was seen for EPDM_10_V, EPDM_20_V and EPDM_30_V.

Concerning the initial modulus, the effect due to the inclusion of rigid filler particles is known as hydrodynamic reinforcement and can be quantitatively predicted by using the Smallwood-Guth-Einstein equation [26]:

$$E = E_0(1 + 2.5\phi + 14.1\phi^2) \quad \text{Equation 16}$$

in which ϕ represents the filler volume fraction. Notwithstanding the strict assumptions of this equation (the filler particles are spherical, completely wetted by the rubber and interact only pair-wise), it could be a useful preliminary evaluation of the expected hydrodynamic reinforcement due to the addition of rigid filler. The initial elastic modulus E_{in} of unvulcanized and vulcanized EPDM-based composites predicted by the Smallwood-Guth-Einstein equation (Eq. 16) is reported in Figure 3.2.3.3, together with the experimental data obtained with tensile tests.

Figure 3.2.3.3 clearly shows significantly higher modulus values with respect to the theoretical calculation ones, only based on a hydrodynamic effect. As already pointed out, this effect increased by increasing the titania content and it was particularly important in the case of unvulcanized materials, even if significantly present also after vulcanization. This behaviour (mechanical properties of the rubber are enhanced more than what would be expected from a mere addition of rigid particles to a soft elastomeric matrix) was already observed for EPDM reinforced with silica *in situ* generated by a hydrolytic sol-gel process [27] and it was tentatively explained as an additional contribution arising from the molecular interaction between the rubber and the filler.

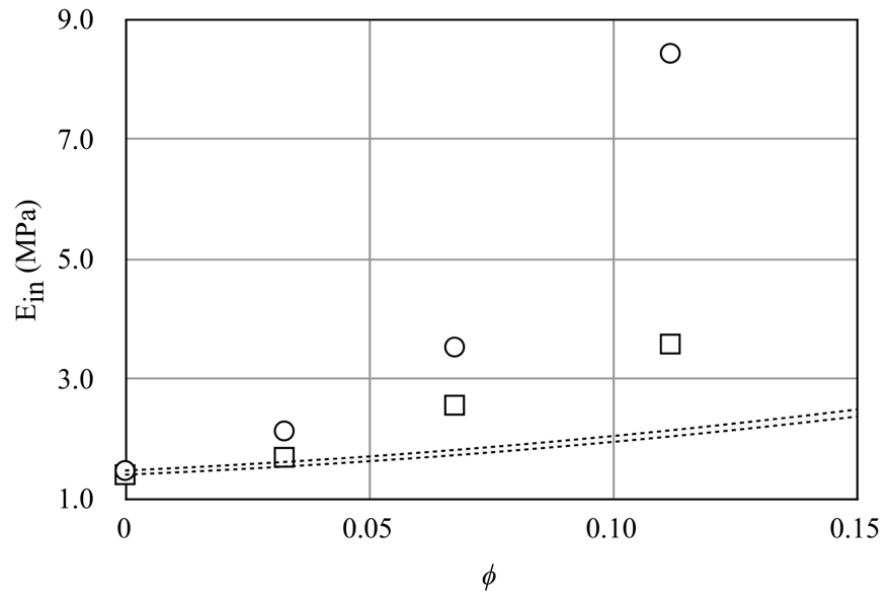
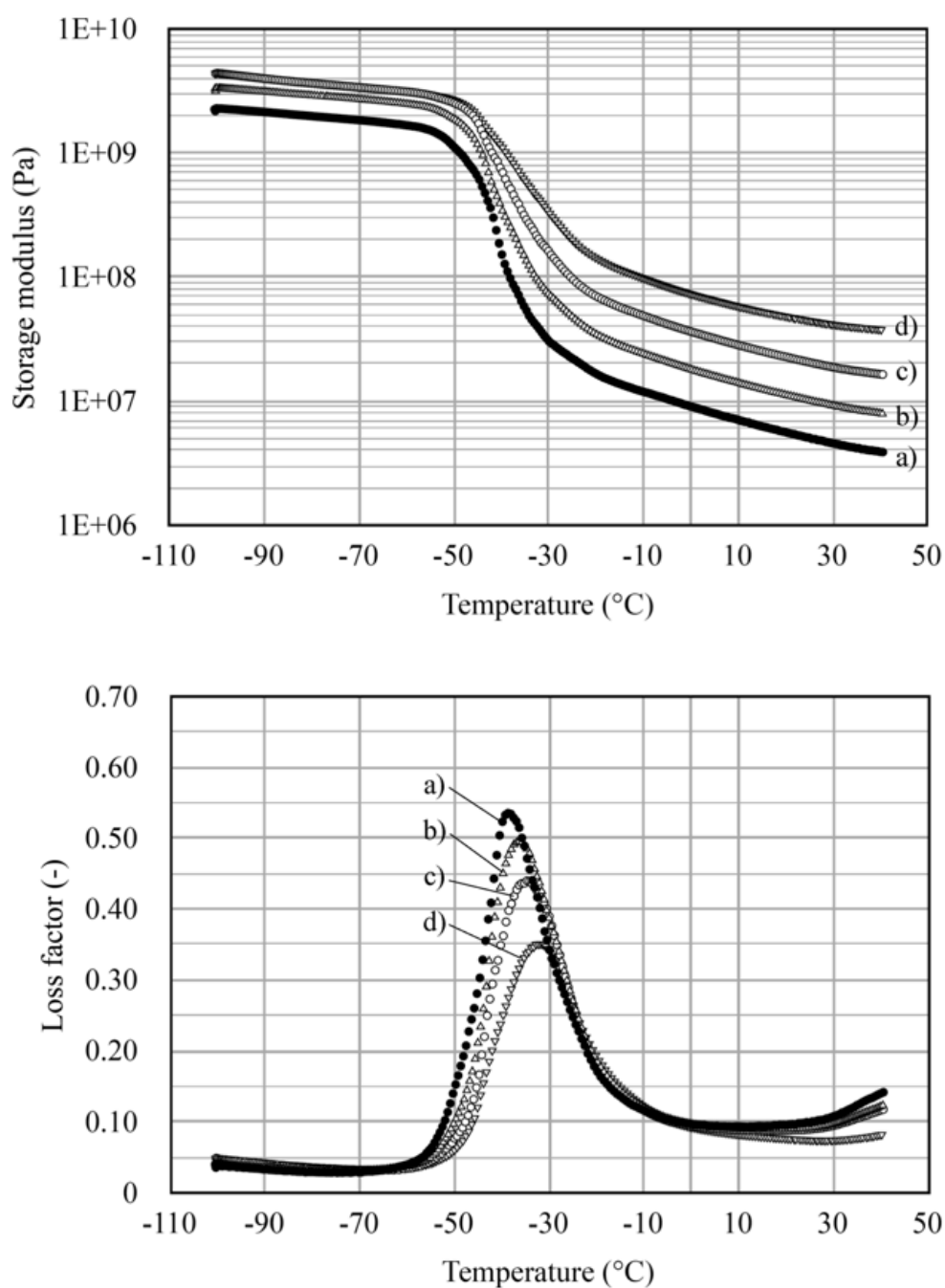


Figure 3.2.3.3 – Initial elastic modulus as a function of filler volume fraction for EPDM_x and EPDM_x_V: predicted values by the Smallwood-Guth-Einstein equation (upper and lower dashed lines, respectively) and experimental data (○ and □, respectively)

Storage modulus (E') and loss factor ($\tan \delta$) as a function of temperature are reported in Figures 3.2.3.4 and 3.2.3.5 for the EPDM_x and EPDM_x_V composites, respectively. The values of storage modulus measured in the glassy region (at a temperature of -70°C , $E'_{-70\text{C}}$) and in the rubbery region (at a temperature of 25°C , $E'_{25\text{C}}$), damping (expressed as maximum value of loss factor, $\tan \delta_{\max}$) and glass transition temperature (T_g , determined as the peak temperature value of the loss factor) are reported in Table 3.2.3.5.

Material code	$E'_{-70^\circ\text{C}}$ (GPa)	$E'_{25^\circ\text{C}}$ (MPa)	$\tan \delta_{\max}$ (-)	T_g ($^\circ\text{C}$)
EPDM_0	1.84 (1.46)	5.07 (3.07)	0.535 (0.610)	-38.7 (-34.1)
EPDM_10	2.70 (2.91)	10.13 (10.33)	0.495 (0.541)	-36.4 (-33.1)
EPDM_20	3.38 (2.53)	20.66 (11.86)	0.440 (0.474)	-34.7 (-31.8)
EPDM_30	3.40 (3.98)	44.49 (22.77)	0.351 (0.458)	-31.8 (-32.6)

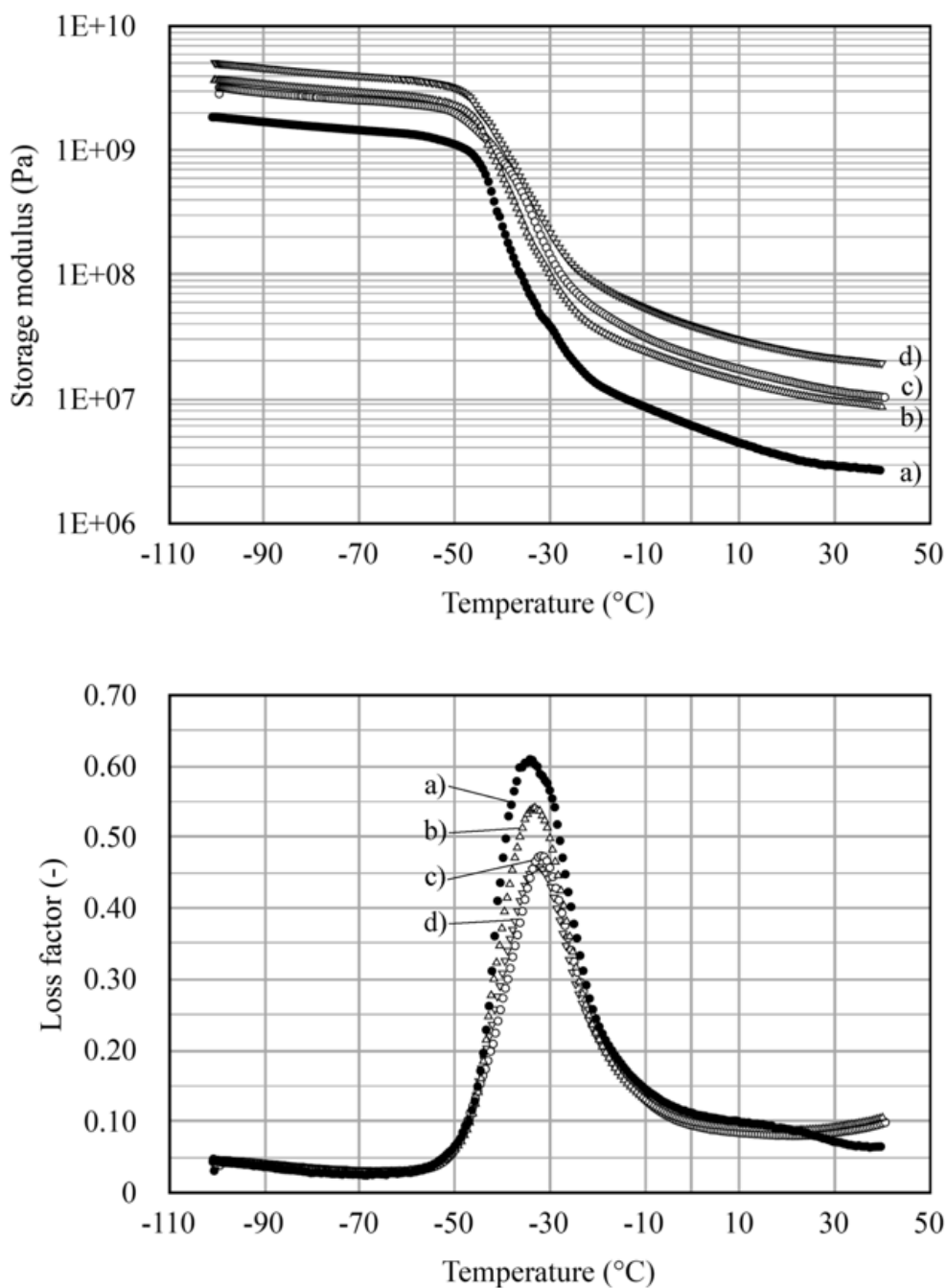
Table 3.2.3.5 – Dynamic-mechanical characterization of composites: storage modulus measured in the glassy region (at -70°C , $E'_{-70\text{C}}$) and in the rubbery region (at 25°C , $E'_{25\text{C}}$), damping (maximum value of $\tan \delta$, $\tan \delta_{\max}$) and glass transition temperature (T_g) (the values after vulcanization are reported in bracket)



Figures 3.2.3.4 – Dynamic-mechanical analysis of unvulcanized composites: storage modulus (E') and loss factor ($\tan\delta$) as a function of temperature for (a) EPDM_0, (b) EPDM_10, (c) EPDM_20, and (d) EPDM_30

The DTMA results show that dynamic-mechanical properties of the vulcanized rubber were significantly affected by the presence and content of titania particles. According to the results obtained with quasi-static tensile properties, the storage modulus values measured in the glassy region ($E'_{-70^\circ\text{C}}$) and in the rubbery region

(E'_{25C}) increased significantly by increasing the titania content in the case of unvulcanized rubber. The same trend is not clearly visible for vulcanized rubbers due to the lower crosslink density of the rubber phase after vulcanization.



Figures 3.2.3.5 – Dynamic-mechanical analysis of vulcanized composites: storage modulus (E') and loss factor ($\tan\delta$) as a function of temperature for (a) EPDM_0_V, (b) EPDM_10_V, (c) EPDM_20_V, and (d) EPDM_30_V

Furthermore, it is usually expected that in particulate filled polymers, the addition of rigid fillers to the polymer matrix restricts the movement of the polymer chains leading to a reduction in damping and a shift in T_g values to higher temperatures [15].

In this study, a significant reduction of damping (here evaluated as the maximum value of the loss factor, $\tan \delta_{\max}$) was observed by increasing the titania content in both unvulcanized and vulcanized samples. The glass transition temperature was slightly affected by the presence of *in situ* generated titania in the case of unvulcanized materials with values monotonically increasing from -38.7 °C for unfilled EPDM (EPDM_0) up to -31.8 °C for the composite with the highest titania content (EPDM_30).

In the case of the vulcanized composites, the increase in T_g by increasing the titania content was less evident and not strictly correlated with the filler concentration. In previous papers, a hindering effect towards the vulcanization process due to the presence of *in situ* generated inorganic oxides (silica) was observed resulting in a reduction in the cross-linking degree of the vulcanized EPDM rubber [27]. Also in the present case the vulcanization of EPDM in the presence of fillers generated by sol-gel processes produced a crosslinked rubber matrix with lower crosslink densities. Taking into account that both the quasi-static and dynamic-mechanical properties of the vulcanized rubber derive from different contributions such as filler amount and crosslink density of the matrix, the lack of strict correlation between filler concentration and ultimate properties can be tentatively attributed to the less efficient vulcanization of the rubber matrix.

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Chapter 4

Conclusions

4. Conclusions

4.1 – Concluding Remarks

Exploiting the non-hydrolytic sol-gel (NHS) chemistry, titanium dioxide (TiO_2) nanoparticles were *in situ* generated within polymers in order to obtain nanostructured hybrid composites.

Four types of polymeric matrices were reinforced/filled with TiO_2 nanoparticles: poly methyl methacrylate (PMMA), two widely used epoxy resins (DGEBA and CE), ethylene-propylene diene monomer rubber (industrially known as EPDM) and polyurethane (study on polyurethane/ TiO_2 is still work in progress as described in “Appendix A”)*.

First of all, a study was carried out on the NHS nanoparticles synthesis, varying the organic solvent, in order to make these types of reactions suitable for the *in situ* filler generation in presence of polymers. TiO_2 nanoparticles were synthesized by NHS reactions, starting from TiCl_4 as precursor and benzyl alcohol, tert-butyl alcohol and polyethylene glycol as oxygen source (TiO_2 nanoparticles synthesis by polyethylene glycol described in “Appendix A”)*. XRD analyses showed that all powders are mainly composed of anatase; the particle size distributions obtained from TEM data ranges from few nanometers to 10 nm demonstrating that the particles dimensions are only slightly affected by the amount of added precursor and by the oxygen donor nature. The powders synthesized by tert-butyl alcohol showed no superficial organic capping and a low crystallinity degree (23%). Whereas, the titania prepared by benzyl alcohol evidenced an organic capping made of uncondensed benzyl group and a higher crystallinity (about 40 %). The morphology of the primary particles was essentially close to spherical for all prepared samples independently on the employed solvent. Moreover, the powders are characterized by high specific surface areas that slightly increase when the amount of the starting oxide-precursor decreases and showed lower density with respect to bulk anatase due to both the presence of amorphous phase and the uncondensed organics chemically bonded to the surface of the particles.

Concerning the composites, the *in situ* filler generation led to homogeneous particles dispersion and remarkable adhesion at the organic/inorganic interphase

independently on the matrix used, as confirmed by the scanning electron microscopy investigations. In addition, the proposed method led to the wanted filler contents proving to be an effective alternative approach for producing hybrid composites and allowing to overcome the typical rheological problems related to the conventional mixing methods.

The dynamic mechanical thermal analyses showed a significant increase of the storage modulus (E') in the rubbery region (temperature range over the glass transition temperature) by increasing the nanoparticles content and independently on the matrix used. This behaviour indicates that the incorporation of nanoparticles is able to increase the stiffness of the pristine polymeric matrices.

The PMMA/TiO₂ based hybrid-composites, unexpectedly, showed very fast photodegradation rate when exposed at ultraviolet light. The incorporation of TiO₂ nanoparticles on one hand is able to improve the mechanical properties of neat PMMA and on the other hand it makes these hybrids excellent disposable material thanks to their fast degradation under sunlight, which can compete with biodegradation procedures nowadays more employed.

By a mechanical point of view, the epoxy resins are the matrices most affected by the presence of TiO₂ nanoparticles. These composites, moreover, showed an increase of Vickers hardness, scratch resistance and a remarkable enhancement of the glass transition temperature by increasing the filler content.

For thermoset-matrix, in the rubbery region, the E' is rather totally governed by the cross-linking density of the polymer. The observed remarkable increase of this parameter, in the case of epoxy/TiO₂ composites, suggests that the *in situ* synthesized particles do not only act as rigid reinforcing filler, constraining the chains mobility, but also as real cross-linking “densifier”. An additional evidence of this result was obtained by comparing the E' of Epoxy/TiO₂ composites obtained by *in situ* filler generation and mechanical dispersion of the same filler (having equal filler content). As expected, the composites prepared by *in situ* synthesis exhibited a higher value of E' . This behaviour strongly supports, once again, the observed remarkable stiffening effect due to the *in situ* generated nanoparticles, with respect to *ex situ* synthesized powder mechanically dispersed.

Finally, EPDM/TiO₂ based hybrid-composites exhibited an improved mechanical behaviour even though the filler particles partially limited the vulcanization process. Quasi-static and dynamic-mechanical characterizations indicated that the presence of titania as rigid filler in both unvulcanized and vulcanized EPDM matrix led to a significant increase in stiffness and stress at break. Whereas, elongation at break improved only up to titania content of 10 wt%, then diminished at higher titania concentrations. The experimental values of modulus were systematically higher than the values theoretically predicted by the classical Smallwood-Guth-Einstein equation and this enhanced stiffness was tentatively attributed to an additional contribution arising from the molecular interaction between the rubber and the filler particles due to its *in situ* generation.

* I have been working on this project since March 2012, in collaboration with Professor Markus Niederberger from ETH (Zurich, Switzerland), as described in the “Appendix A”.

4.2 – Future Perspectives

The proof-of-concept, here presented, indicates that hybrids can be successfully produced by an *in situ* filler generation exploiting a proper NHSG reaction. Indeed, a lot of works have been already performed, but some general aspects are not still well studied and would need further progresses.

For example, the proposed technique can be successfully applied to other polymeric matrices and nanometric inorganic oxides. This would give access to a very large variety of functionalized hybrid-materials with tailored properties for innovative technological applications and especially in the field of the smart-materials.

From another point of view, a further possible future development of this research could be the scale up of the process, taking into account that the proposed approach has not been yet industrially considered in despite of its several advantages. The industrial development should be strongly supported by the academic research that has to drive toward the use of reagents characterized by low toxicity, low price and wide availability in order to make the process, more and more, environmentally friendly and cost effective.

Eventually, the biggest challenge nowadays is to find monomers that can also act as suited oxygen source for the sol-gel reaction, in order to develop a solvent-free and oversimplified process.

Appendix

A

Appendix A

Work in Progress

In according to the challenge discussed in final part of the section 4.2 (Future Perspectives), an innovative non-hydrolytic sol-gel (NHSG) reaction is proposed in this appendix.

Thanks to collaboration between Professor Markus Niederberger (Polytechnic of Zurich, ETH) and Professor Federica Bondioli (University of Parma, Italy) was possible, for the first time to our knowledge, to develop a method for producing polyurethane/TiO₂ nanohybrids. This project meets the scientific challenge, before discussed, in the use of poly ethylene glycols as oxygen source for the sol-gel reaction and contemporaneously monomer for the preparation of polyurethane.

Further noteworthy aspects, of this process, are the low toxicity, low cost and wide availability of the employed oxygen source (poly ethylene glycol) that enable this method to be environmentally friendly and cost effective. In addition, the procedure simplicity and the increased reaction rate, due to the use of microwave-heating method, represent two significant criteria that make this route attractive not only from a scientific point of view, but also from an industrial one.

Unfortunately, only the sol-gel reaction was completed studied, whereas the composites were successfully prepared but just partially characterized. In the following pages the work, which has been carried out until now, is reported.

TiO₂ Synthesized by Using Poly Ethylene Glycols

Materials

Polyethylene glycol (PEG_400, MW = 400 Da average molecular weight), titanium(IV) tetrachloride (TiCl₄), methanol, ethanol, dichloromethane, acetone, diethyl ether, acetonitrile and formic acid were purchased from Sigma Aldrich. All chemicals were high purity reactants and were used as received without any further purification.

Synthesis

The reaction was carried out in a sealed tube reactor (volume 10 mL) and heated by microwave-heating system (CEM - Discover and Explorer SP). A typical preparation was performed as follows: TiCl₄ was added drop wise (amounts reported in Table 1) to 5 mL of PEG at room temperature under vigorous stirring.

TiO ₂ powder code	TiCl ₄ (mL)	PEG_400 (mL)	PEG_400 / TiCl ₄ molar ratio
PEG_15T	0.15	5.0	17.6
PEG_50T	0.50		5.7
PEG_90T	0.90		3.4

Table 1 – Composition of the NHSG reaction batches

The obtained yellow and viscous mixture was kept stirring at room temperature for 30 min until the evolving hydrochloric acid was removed. The heating was carried out by a microwaves apparatus and consisted of: a first step at 80°C (20 W) for 1 min permitting a stabilization of the system pressure and, when it was stabilized, followed by a final heating at 170°C (70 W) for 25 min.

The whitish obtained suspensions were centrifuged at 4000 rpm for 30 min. The samples used for by-products analysis by high performance liquid chromatography equipped with mass spectrometry (HPLC/MS) were prepared by collecting 10 µL of the supernatant added to 1 mL of methanol.

After this first purification step, the synthesized powders were carefully washed and centrifuged (for 15 min at 4000 rpm each time) as follows: twice with 15 mL of dichloromethane, twice with 15 mL of acetone and once with 15 mL of diethyl ether. Each fresh solvent addition was followed by 15 min of sonication in order to completely remove all molecules that are not chemically bonded. Finally, the samples were dried overnight under an aspiration hood at room temperature and for 4 h in an oven at 60°C under vacuum. The obtained powders were coded as PEG_xT (Table 1), where x identifies the precursor amount.

Characterizations

The crystalline phase of the dried TiO₂ particles were analysed with a computer-assisted conventional Bragg-Brentano diffractometer using the Ni-filtered CuK_α monochromatic radiation ($\lambda = 1.5418 \text{ \AA}$) (PANalytical, X'Pert PRO diffractometer). The X-ray diffraction (XRD) patterns were collected at room temperature in a 2θ range of 10-90°, with a scanning rate of $0.005^\circ \cdot \text{s}^{-1}$ and a step size of 0.02° .

Furthermore, the crystallite sizes were estimated from X-ray line broadening measurements by using the TiO₂ (101) diffraction line at 25° (2θ), according to the Scherrer formula (Eq. 1) [1].

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta} \quad \text{Equation 1}$$

where D is the crystallite diameter, λ is the wavelength of the X-ray, θ is the diffraction angle, and β is the full width at half maximum.

The particles morphologies were examined by transmission electron microscopy, JEM 2010 TEM (Jeol), operating at 200 kV. A drop of the so-obtained reaction mixture was diluted in ethanol (2 mL) and sonicated (15 min); the final suspension was centrifuged for 1 min. A drop of the supernatant was placed on a copper grid (Carbon Film 200 Mesh Cu, Agar Scientific) followed by drying at 40°C. Moreover, the obtained images were analyzed and processed by ImageJ open-source software in order to determine the average particles size.

The specific surface area (SSA) and density of the powders were determined by the Brunauer-Emmett-Teller (BET) method (Gemini 2380 apparatus, Micromeritics)

and by a picnometer (Accupic 1330 apparatus, Micromeritics), respectively. The samples were carefully dried using the previously described procedure at the end of the “TiO₂ synthesis” section.

The amount of organics covalently linked to the particles surface was evaluated by thermal gravimetric analysis equipped with differential thermal analysis (TGA/sDTA 851E, Mettler Toledo). The measurements were performed in nitrogen flow (50 mL·min⁻¹) at a heating rate of 10°C·min⁻¹ from 30 to 1000°C.

The surface-adsorbed organic species were qualitatively analyzed by Fourier transform infrared spectroscopy (Perkin-Elmer 2000 FT-IR spectrometer) from 4000 to 500 cm⁻¹, in attenuated total reflectance (ATR) mode equipped with a ZnSe crystal.

BY-PRODUCTS CHARACTERIZATION

In order to detect the NHSG reaction by-products, chromatographic separation was performed by using a high performance liquid chromatography (HPLC/MS) Agilent Technologies Serie 1200 equipped with a Zorbax SBC18 column (300×2.1 mm ID, 3.5 µm PS, 80 Å pores size, Agilent Technologies).

Elution was carried out at a flow rate of 0.20 mL·min⁻¹ at 25°C, using a solvent gradient consisting of a linear increase from 0 to 100% of acetonitrile (solvent B) in water (solvent A) in a background of 0.1% (wt/wt) formic acid in order to improve the ionization in the mass spectrometer. The elution gradient employed for the separation is reported in Table 2, which was followed by 100% solvent B for 2 min in order to wash the column.

Time (min)	% (V/V) Acetonitrile (solvent B)
2	5
8	100
12	100

Table 2 – Schematized gradient of elution

The mass detection was performed by positive ion mass spectrometry using a quadrupole ion trap mass analyzer (6310A Ion Trap LC-MS, Agilent Technologies) equipped with an electro spray ionization (ESI, capillary voltage 3500V, nebulizer pressure 25psi, temperature drying gas 300°C, drying gas flow 9 L·min⁻¹).

The prepared solutions, as above described, were filtered by an ultrafine filter in order to remove possible agglomerates and particles. Due to the high concentrations of the analytes, the solutions were diluted 200 times (5 μ L in 1 mL of methanol) and 2 μ L of the final solutions were injected and eluted by a solvent gradient for 22 minutes.

Results and Discussion

The XRD patterns of the synthesized powders are reported in Figure 1, showing that all powders have the same crystal structure. All the peaks were attributed to crystalline titanium dioxide in anatase form (JCPDS reference code: 00-021-1272).

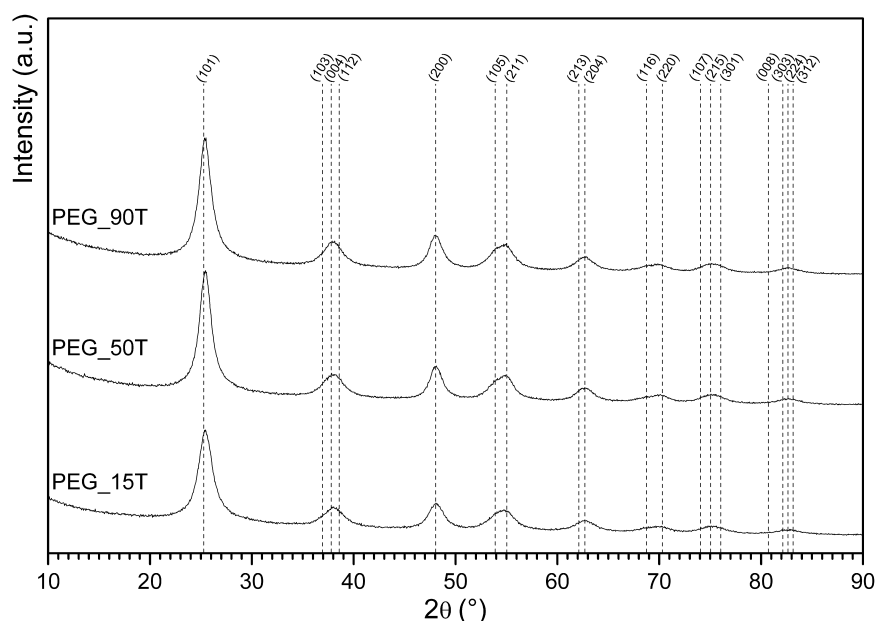


Figure 1 – XRD patterns of the synthesized powders. The (101) reflection at 25° (2θ) was used for determining the average crystallite size by Eq. 1

Moreover, the broad reflections indicate that all synthesized powders are characterized by nanometric crystallites. In particular, the average crystallite size, as determined by Scherrer equation (Eq.1), is around 10 nm independent of the PEG₄₀₀/TiCl₄ molar ratio (Table 3).

Sample Code	Average diameter by TEM images (nm)	Average diameter by Eq. 1 (nm)	SSA ($\text{m}^2\cdot\text{g}^{-1}$)	Mass Loss by TGA (%)	Density ($\text{g}\cdot\text{cm}^{-3}$)
PEG_15T	4 $\pm$ 1	9	192.4 $\pm$ 1.2	26	2.46 $\pm$ 0.03
PEG_50T	6 $\pm$ 2	10	176.2 $\pm$ 1.2	25	2.50 $\pm$ 0.01
PEG_90T	8 $\pm$ 2	10	143.1 $\pm$ 1.1	22	2.58 $\pm$ 0.01

Table 3 – Summary of the data obtained for the washed and dried powders

The shape and dimensions of the primary particles were also evaluated by TEM. The obtained images of the prepared samples (Figure 2) show that the synthesized powders are nanostructured and very well dispersed without any evidence of agglomeration. The particles have a rather uniform shape and sizes in the range from 4 to 8 nm, in good agreement with the results obtained by Scherrer's equation. In particular, the micrographs (Figure 2) demonstrate that PEG_400/TiCl₄ molar ratio does not affect the morphology of the nanoparticles showing, for all samples, a value of roundness factor that ranges from 0.82 to 0.86. The average grains size was slightly increased by increasing the starting precursor amount with respect to PEG, as reported in Table 3.

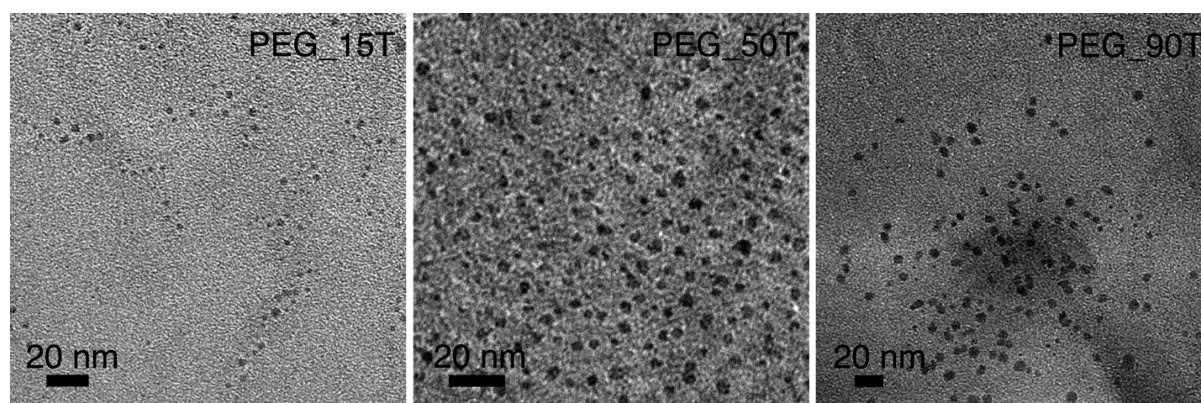


Figure 2 – TEM micrographs of the synthesized powders

As expected for powders having particle dimensions as small as shown by TEM micrographs, very high SSAs were measured. The values range from a maximum of 192 $\text{m}^2\cdot\text{g}^{-1}$ for PEG_15T to a minimum of 143 $\text{m}^2\cdot\text{g}^{-1}$ PEG_90T (Table 3), showing a slight decrease with PEG_400/TiCl₄ molar ratio. By analysing the data in Table 3 it

becomes evident that the particles dimension (by TEM) and SSA are inversely proportional showing a common size effect on the surface area.

TGA was carried out to evaluate the presence of organic substances strongly adsorbed and/or covalently bonded to the TiO₂ particles. The obtained results of mass loss showed the presence of a significant amount of organic species with values of 22, 25 and 26% for PEG_90T, PEG_50T and PEG_15T, respectively (Table 3).

Consistently with the results of TGA, the experimental density values (ρ_{exp}) of the powders (Table 3) are relatively low if compared to the literature value of 3.9 g·cm⁻³ [2] corresponding to pure anatase. This difference can be considered as deriving from a sort of hybrid materials composed of TiO₂ and organic substances covering the surface of the inorganic particles.

REACTION MECHANISMS

In order to better understand the involved reaction mechanisms, the by-products generated by NHSG were detected. Four samples were analysed: unreacted PEG_400 and methanol as reference, PEG_15T and PEG_90T. The relevant part of the chromatograms is between 0 and 11 min retention time, whereas over 11 min only insignificant impurities, deriving from column residuals, were detected. For each peak the mass spectrum (here not reported) was collected in order to evaluate the molecular weight of the generated molecules.

Figure 3 shows that the as-purchased PEG_400 is composed of nine fractions characterized by the general formula HO-(CH₂CH₂-O-)_xH where x ranges from 4 to 12. It is possible to notice, that the main fractions have x that ranges from 6 (at 3.7 min) to 10 (at 8.6 min). Moreover, fractions characterized by x equal to 4, 5, 11 and 12 can be considered minor components and the latter two (detected only in traces) are hidden under the peak tail at about 9 min of retention time.

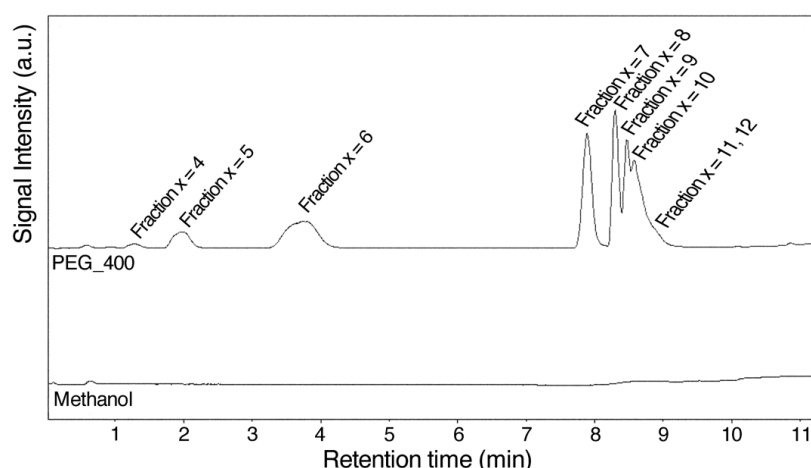


Figure 3 – Unreacted PEG_400 and methanol chromatograms, as reference

The solutions obtained by NHSG reactions showed between 0 and 8 min a chromatogram similar (Figure 4) to PEG_400, whereas in the region between 8.5 and 10 min of retention time, three different peaks were detected. Both samples PEG_15T and PEG_90T showed similar peaks with different intensity, due to the decrease of the PEG fractions and the increase of by-products. Concerning the peaks in the second part of the chromatogram, mass spectroscopy showed the presence of two main types of by-products: mono-chloride and bi-chloride molecules obtained by substitution of PEG's hydroxyl groups. The substitution occurs randomly on all PEG fractions, but obviously the most concentrated fractions are the ones mainly involved in the reaction. This evidence can also explain why not all fractions led to related by-products, as expected.

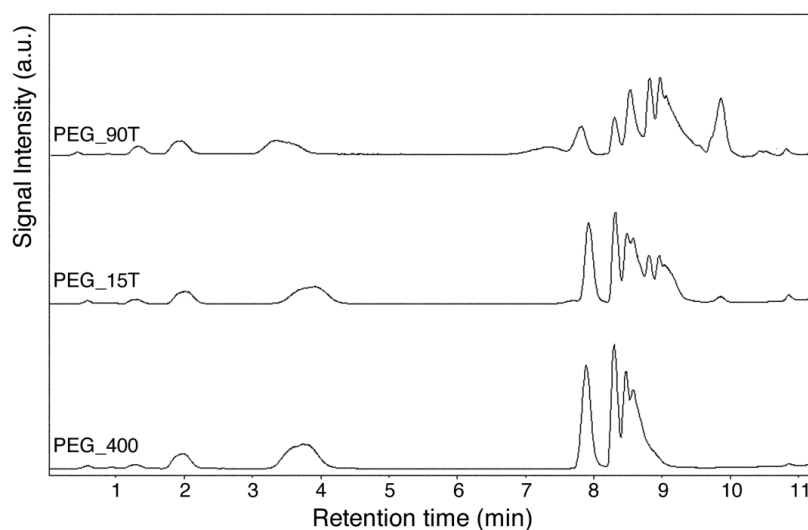
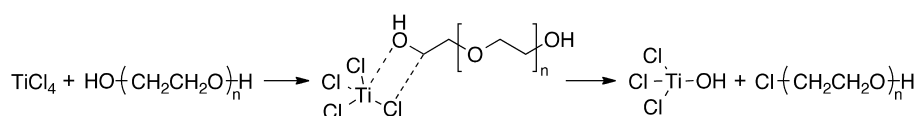


Figure 4 – Unreacted PEG_400, PEG_15T and PEG_90T chromatograms

Mono-chloride species were detected under the large band between 9 and 9.25 min. These species can be summarized as $\text{Cl}-(\text{CH}_2\text{CH}_2-\text{O})_x\text{H}$ where x mainly ranges from 6 to 10, being these latter five fractions the most concentrated, hence the most statistically involved in the reaction. A distribution of masses that perfectly matches the bi-chloride species ($\text{Cl}-(\text{CH}_2\text{CH}_2-\text{O})_x\text{CH}_2\text{CH}_2\text{Cl}$, with x between 5 and 9) were detected under the isolated peak at about 9.85 min. In addition, this peak increases its intensity with the added amount of precursor, suggesting that not only PEG fractions participate as oxygen donor in this reaction, but also the yielded mono-chloride species can still react by using the second hydroxyl group, generating the detected bi-chloride molecules.

These results suggest that the main mechanism involved during the alcoholysis step is a uni-molecular nucleophilic substitution ($\text{S}_{\text{N}}1$), where PEG exchanges the terminal OH^- groups with Cl^- of TiCl_4 . Comparable mechanisms were already observed by Vioux in [3] and Trentler *et al.* [4]. The proposed mechanism can be summarized as follows:



Scheme 1 – Summarized uni-molecular nucleophilic substitution ($\text{S}_{\text{N}}1$)

In order to better investigate the nature of the organic phase on the particle surfaces and the involved reaction mechanism, FT-IR analysis was performed. The presence of organic residual bonded on the particles surface, as determined by TGA, was confirmed. In Figure 5 the spectra of the powders and the spectrum of the PEG_400, are compared. The spectra of the powders do not present any significant differences; centered at 3250 cm^{-1} is clearly visible the common $-\text{OH}$ stretching band and its related weak peak close to 1630 cm^{-1} , due to $-\text{OH}$ bending vibration, was also observed [5, 6]. These results are in good agreement with the suggested mechanism that leads to the formation of $-\text{OH}$ on the titanium atoms, which do not completely condense on the particles surface leading to the formation of the so-called “titanols”.

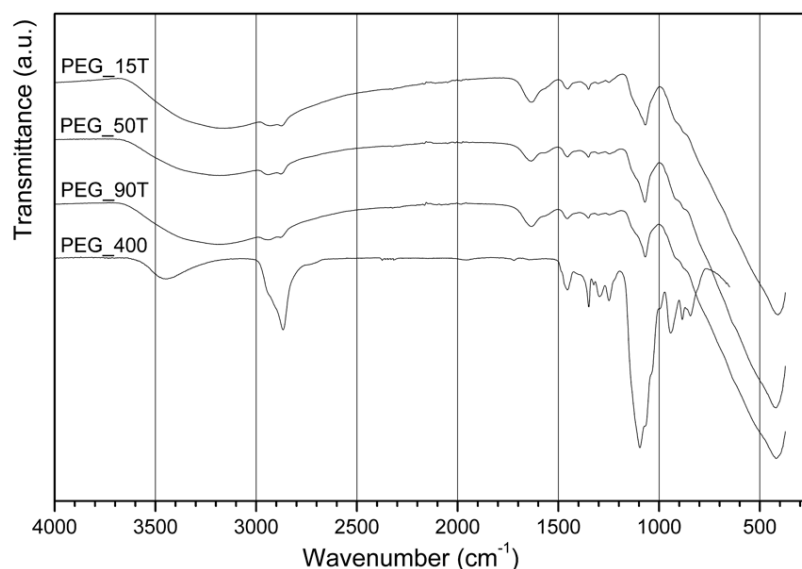
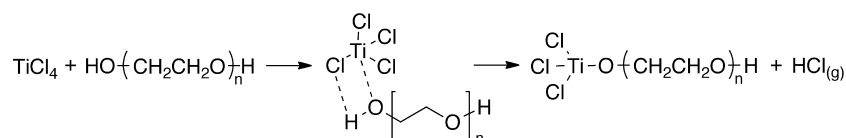


Figure 5 – FT-IR curves performed in ATR mode on the synthesized powders and PEG_400 as reference

The shoulder at 2900 cm^{-1} (CH_2 stretching), the weak peaks located in the range $1500 - 1200\text{ cm}^{-1}$ (CH_2 bending) and the peak at 1070 cm^{-1} (C-O stretching) fit rather precisely to the spectrum of PEG_400 [5, 6]. Considering that each powder was carefully washed by using sonication and three sorts of solvents and eventually well dried, this means that some residual PEG chains are chemically bonded to the surface. This result suggests that, during the alcoholysis step, not only the before described mechanism occurs but two simultaneous mechanisms are involved. In order to justify the formation of hydrochloric acid (yielded during the TiCl_4 addition) and the presence of PEG chains on the particles surface, a bi-molecular nucleophilic substitution mechanism ($\text{S}_{\text{N}}2$) can be supposed. This is usually the main mechanism when the involved species are primary alcohol (as PEG's terminal hydroxyl groups can be considered) and a strong nucleophile as in this case. A comparable behavior was also observed by Gerrard *et al.* in [7] and Mutin *et al.* in [8] for a similar reaction between alcohols and SiCl_4 . This second mechanism can be schematized as follows:



Scheme 2 – Schematized bi-molecular nucleophilic substitution ($\text{S}_{\text{N}}2$)

Probably during the condensation step, PEG chains do not completely condense as proved by the absence, in the chromatograms, of the long-chain by-products that should have been produced by the ether elimination. On the basis of this evidence, it is possible to assume that the first mechanism is mainly responsible for the oxide formation (i.e., oxygen source), whereas the second one is mainly responsible for the surface functionalization (i.e., stabilizing agent). The role of PEG as a capping agent on the particles surface, as observed by FT-IR, results in very small particle dimensions and prevention of agglomeration.

Polyurethane/TiO₂ Prepared by *in situ* Non-Hydrolytic Sol-Gel Reaction

Materials

Polyethylene glycol (PEG_200, MW = 200 Da average molecular weight), titanium(IV) tetrachloride (TiCl₄), 4,4'-methylene diphenyl diisocyanate (MDI), dimethylformamide (DMF) were purchased from Sigma Aldrich. All chemicals were high purity reactants and were used as received without any further purification.

Preparation

Polyurethane (PU)/TiO₂ composites with nominal TiO₂ contents of 1, 3 and 5 wt% were prepared by a thermal activation polymerization of the titania suspensions in PEG (prepared as described above in the previous section) and MDI [9]. The TiO₂/PEG suspensions as obtained were carefully blended (by magnetic stirrer) to a solution of MDI previously dissolved in 15 mL of DMF. The added amount of MDI was calculated in order to obtain a molar ratio MDI/PEG equal to 1 (reagents amounts in Table 4).

Composite code	TiO ₂ content (wt%)	TiCl ₄ (mL)	PEG_200 (mL)	MDI (g)	DMF (mL)
PU_0	-	-	5.0	7.0	15
PU_1T	1	0.15			
PU_3T	3	0.50			
PU_5T	5	0.90			

Table 4 – Samples descriptions and related used reagents quantities

The so obtained suspension was left stirring at room temperature for 30 min and consequently heated to 90°C for 2 h and 30 min followed by stirring at room temperature for further 3 h to complete the reaction. The mixtures were concentrated by rotary evaporation at 65°C and dynamic vacuum, in order to remove both non-desirable by-products yielded from the sol-gel reaction (hydrochloric acid) and DMF (about 20% of the initial volume).

The obtained viscous suspensions were casted in a silicon mould and slowly dried under hood for one days and at 70°C for two days in an electric oven. When the samples were dry the temperature was increased to 150°C under dynamic vacuum for further 2 h. Another set of specimen was prepared by coating the viscous suspensions onto microscope slides, made of quartz, by using a wire-wound applicator (film thickness of about 12 μm). The solvent was evaporated by using the same procedure explained for bulk samples.

Characterizations

The actual titania content was evaluated by gravimetric analysis (starting sample mass about 0.5 g), calculating the amount of residual titania after a treatment at high temperature in an electric furnace (Optolab – FS5). The treatment was carried out at 500°C for 4 hours, up to constant mass was reached.

Results and Discussion

The actual titania contents are 1.0, 3.0 and 4.7 for PU_1T, PU_3T and PU_5T respectively. They match rather perfectly the nominal ones, confirming the effectiveness of the used method.

Figure 6 showed the samples coated on a quartz microscope glass. The transparency of the prepared coating is very high even for the sample characterized by 5 wt% of TiO_2 . It has to be considered a very good result, if compared to the samples prepared with epoxy resins (section 3.2.2 “CE UV cured”) in which the transparency remarkably decreased over the 2.7 wt% (2.8 phr).

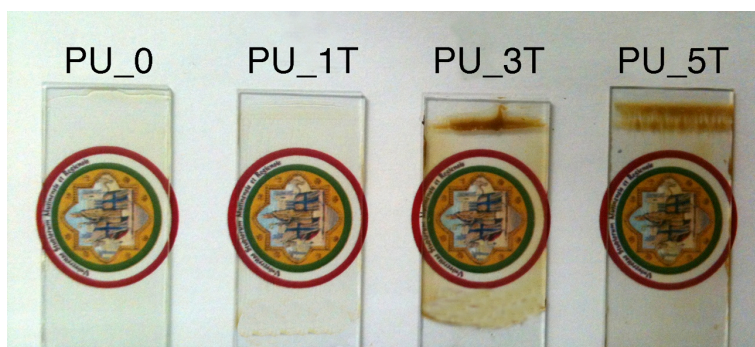


Figure 6 – Photographs of the polymerized coatings applied on quartz

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Appendix

B

List of Papers

D. Morselli, M. Messori, F. Bondioli, *"Poly(methyl methacrylate)-TiO₂ nanocomposite obtained by non-hydrolytic sol-gel synthesis"*, Journal of Materials Science, 46, (2011), 6609–6617

D. Morselli, F. Bondioli, M. Sangermano, M. Messori, *"Photo-cured epoxy networks reinforced with TiO₂ in-situ generated by means of non-hydrolytic sol-gel process"*, Polymer, 53, (2012), 283-290

D. Morselli, F. Bondioli, M. Fiorini, M. Messori, *"Poly(methyl methacrylate)-TiO₂ nanocomposites obtained by non-hydrolytic sol-gel synthesis: the innovative tert-butyl alcohol route"*, Journal of Materials Science, 47, (2012), 7009-7012

D. Morselli, F. Bondioli, A. S. Luyt, T. H. Mokhothu, M. Messori *"Preparation and characterization of EPDM rubber modified with in situ generated silica"*, Journal of Applied Polymer Science, 128, (2012), 2525–2532

K. Paderni, D. Morselli, F. Bondioli, A. S. Luyt, T. H. Mokhothu, M. Messori, *"EPDM rubber reinforced with titania generated by non-hydrolytic sol-gel process"*, in press on Polymer Engineering and Science, (2013)

D. Morselli; F. Bondioli; M. Sangermano; I. Roppolo; M. Messori *"Thermally cured epoxy networks reinforced with TiO₂ generated by non-hydrolytic sol-gel process"*, in press on Journal of Applied Polymer Science, (2014)

D. Morselli; M. Niederberger; I. Bilecka; F. Bondioli *"Double role of polyethylene glycol in the microwaves assisted non-hydrolytic synthesis of nanometric TiO₂: Oxygen source and stabilizing agent"*, Submitted to Chemistry-A European Journal, (2014)

D. Morselli; F. Bondioli; M. Sangermano; I. Roppolo; M. Messori "*Epoxy networks reinforced with TiO_2 generated by non-hydrolytic sol-gel process: a comparison between in situ and ex situ syntheses to obtain filled polymers*", Submitted to Polymer, (2014)

Appendix

C

Attended Congresses

F. Bondioli, M. Messori, D. Morselli, *“Non-aqueous sol-gel for the preparation of poly(methyl methacrylate)/titania hybrids”*, 2nd International Conference on Multifunctional, Hybrid and Nanomaterials ‘Hybrid Materials 2011’, Strasbourg, France, 6th – 10th March 2011 (POSTER)

D. Morselli, M. Messori, F. Bondioli, *“The benzyl alcohol route: an innovative approach towards polymer-matrix nanocomposites”*, 8th INSTM National Meeting on Materials Science and Technology, Aci Castello, Italy, 26th – 29th June 2011 (SPEAKER)

D. Morselli, M. Messori, M. Sangermano, F. Bondioli, *“Non-hydrolytic sol-gel process to obtain Epoxy/Titania nano-hybrid material”* 4th ECNP Young Researchers Conference, Lyon, France, 7th – 10th November 2011 (SPEAKER)

D. Morselli, M. Messori, F. Bondioli, *“EPDM/SiO₂ nanocomposites obtained by in situ generation of silica”* 2nd MACROGIOVANI 2012, Milan, Italy, 13th February 2012 (SPEAKER)

D. Morselli, M. Messori, F. Bondioli, *“EPDM/SiO₂ nanocomposites obtained by in situ generation of silica”* 5th ECNP Young Scientist Conference, Prague, Italy, 22nd – 29th April 2012 (SPEAKER)

D. Morselli, N. Florini, F. Bondioli, *“Synthesis of metal oxides by means of non-hydrolytic sol-gel reaction”* 4th ICC4 International Congress on Ceramics, Chicago, Illinois, USA, 15th – 19th July 2012 (INTERACTIVE POSTER – SHORT PRESENTATION)

Travel Grant Awarded, sponsored by Corning Incorporated, for attending to the ICC4

D. Morselli, F. Bondioli, M. Sangermano, M. Messori, *“Photo-cured epoxy networks reinforced with titania in situ generated by means of non-hydrolytic sol-gel process”* 2nd ESPS European Symposium of Photopolymer Science, Torino, Italia, 4th – 7th September 2012 (POSTER)

D. Morselli, F. Bondioli, M. Messori, *“EPDM rubber reinforced by in situ generated silica”*
XI AIMAT National Congress, Gaeta, Italy, 16th – 19th September 2012 (POSTER)

D. Morselli, M. Messori, F. Bondioli, *“Epoxy/Titania Nano-Composite Obtained by Combining Non-Hydrolytic Sol-Gel Process and Cationic Polymerisation”* 3rd MACROGIOVANI 2013, Milan, Italy, 11st February 2013 (SPEAKER)

D. Morselli, M. Messori, F. Bondioli, *“Epoxy/Titania Hybrid Material Nanostructured Obtained by Joining Non-Hydrolytic Sol-Gel Process and Cationic Polymerisation”*, 3rd International Conference on Multifunctional, Hybrid and Nanomaterials ‘Hybrid Materials 2013’, Sorrento (Na), Italia, 3rd – 7th March 2013 (POSTER)

D. Morselli, M. Messori, F. Bondioli, *“Non-hydrolytic sol-gel synthesis for nano-structured polymer-based composites”*, IX INSTM CONFERENCE, Bari, 30th June – 3rd July 2013 (SPEAKER)

D. Morselli, M. Messori, F. Bondioli, *“Nano-structured composites prepared by in situ Sol-Gel synthesis”*, XVII International Sol-Gel Conference, Madrid, Spain, 25th – 30th August 2013 (SPEAKER)

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