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Epoxy resin/TiO_2 nanocomposites prepared by the *Reactive Suspension Method*: dynamic-mechanical properties and their prediction through adjusted Kerner equation

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Abstract

This work reports a study on the mechanical properties of epoxy resin/TiO_2 nanocomposites obtained according to the *Reactive Suspension Method*. In particular, after the chemical-physics characterization of both inorganic and organic components, the dynamic-mechanical properties of the composite materials have been studied. The resulting experimental data have been compared to theoretical predictions obtained by the established Kerner equation. Interestingly, the experimental storage modulus in the rubbery state was significantly higher than the theoretical expected one. The observed discrepancy has been rationalized taking into account that the synthesized TiO_2 nanoparticles are covalently bonded to the polymer chains as shown by solid state NMR analyses. Therefore, the inorganic nanoparticles act as additional cross-linking points, which is the main parameter that governs the storage modulus in the rubbery state. On the basis of the collected data and considering that the Kerner equation does not take into account any type filler-matrix chemical interaction, an adjustment of one parameter that composes the equation has been proposed in order to have a better fitting of the experimental results. The proposed approach has been also tested on our previously published studies to find a correlation between the filler-matrix interaction and the modified equation parameter.

Keywords: Polymer nanocomposite, titanium dioxide, non-aqueous sol-gel, *in situ*, reactive suspension method, storage modulus, Kerner equation

1. Introduction

Since the last decade of the 20th century the field of the polymer/inorganic particles composites has been having an increasing interest, thanks to the possibility to obtain materials with tailored properties and their customization for specific applications.[Kumar, Macromolecules 50 (2017) 714–731] It is well-known that mechanical properties and thermal/chemical stability of polymers can be modified by the addition of inorganic nanoparticles (NPs).[Nano Materials Science 1 (2019) 2–30] Among them, both metal or non-metal oxides represent the most studied reinforcing materials nowadays available, which allow to tune mechanical strength,[POLYM. ENG. SCI., 54 (2014) 2544–2552] hardness,[Polymer 53 (2012) 283-290] viscoelastic behavior [Composites Science and Technology 71 (2011) 1039–1045] and glass transition temperature.[Composites Science and Technology 71 (2011) 1039–1045] The NPs dispersion plays the most important role in order to achieve a homogeneous nanocomposites characterized by the expected properties. Nevertheless, the filler dispersion is still the main problem related to the conventional procedures based on the mechanical and/or ultrasound mixing of inorganic NPs in melted polymers or in polymeric solutions. In several cases, it has been observed that oxide NPs prepared by flame pyrolysis or colloidal syntheses cannot be effectively redispersed in polymers by conventional mixing methods, due to their strong tendency to form micrometrics or even larger aggregates.[Pol Eng Sci 55 (2015) 1689] In this regard, NPs surface modification through suitable coupling agents is a widely used approach that can improve the compatibility between the two counterparts, but it requires multi-steps wet-chemical procedures and the use of a large amount hazardous solvents.[Progress in Polymer Science 38 (2013) 1232-1261] A simple alternative approach to overcome this problem is the *"Reactive Suspension Method"*,[Colloid Polym Sci 295 (2017) 695-701] which is based on an *in situ* synthesis of NPs into the desired polymeric matrix. Specifically, in our previous studies, such innovative procedure has been proposed for preparing nanocomposites by combining a non-hydrolytic sol-gel for the synthesis of titanium dioxide (TiO_2) NPs and a cationic polymerization [Polymer 53 (2012) 283-290; J Appl Pol Sci 131 (2014) 40470; Pol Eng Sci 55 (2015) 1689] that leads to the formation of a three-dimensional hybrid network with very low extractable fraction. In fact, the suspending medium (typically an alcohol) is covalently linked to the polymeric network according to the activated-monomer mechanism, which takes place during the propagation step in the cationic ring-opening polymerization.[J Appl Polym Sci 111 (2009) 2822] The homogeneous TiO_2 NPs dispersion and distribution result in an unexpected very high reinforcing and stiffening effect. This has been rationalized taking into consideration two aspects: the presence of inorganic fillers that can constrain the chains mobility and, most importantly, a higher cross-linking density with respect to the pristine epoxy matrix.[Polymer 53 (2012) 283-290] Such an interesting result suggests that the TiO_2 NPs act not only as rigid filler embedded in a polymeric matrix, as assumed by the Kerner's theory,[R. F. Landel, L. E. Nielsen, Mechanical Properties of Polymers and Composites, 2nd Edition (1993) CRC Press] but also as actual cross-linking points.[Pol Eng Sci 55 (2015) 1689] This has been directly observed using Solid-State Nuclear Magnetic Resonance (MAS NMR) analyses, which have shown TiO_2 NPs linked to the polymeric network through hydrogen bonds between polymer carboxyl groups and titanols (Ti–OH) on the particle surface.[Colloid Polym Sci 295 (2017) 695-701] A step forward has been done by our group, developing a solvent-free one-step synthesis of TiO_2 NPs taking advantage of both particles surface modification and the *in situ* synthesis approaches.[J Nanopart Res 16 (2014) 2645] In detail, the developed new synthesis leads to TiO_2 NPs functionalized with poly(ethylene glycol) (PEG) hydroxyl-terminated chains, which can be polymerized by the above-mentioned activated-monomer mechanism (second step of the *Reactive Suspension Method*). This results in TiO_2 NPs covalently bonded to the polymeric network, with a significant increase of the cross-linking density leading also to an enhancement of the stiffness of the resulting material, especially in the rubbery state temperature range. We have noticed that these stiffness variations cannot be accurately predicted by the existing theories, which do not properly consider both filler size and interactions at the filler/matrix interface.[Polymer 53 (2012) 283-290; Polymer Engineering and Science 54 (2014) 2544-2552; Polymer Engineering and Science 55 (2015) 1689-1697; J. Appl. Polym. Sci. 128 (2013) 2525–2532] These two parameters are key factors that importantly affect the composite mechanical properties. Similar conclusions have been also reported by Fu et al.,[Compos Part B-Eng 39 (2008) 933-961] who concluded that strength and toughness are mainly influenced by the particle/matrix adhesion, expanding the former study by Ou et al. [J Pol Sci Part B: Pol Phys 36 (1998) 789-795] who highlighted that the existing theories have strong limitations when the investigated composites involve nanosized filler. Fu et al. further support this idea reporting that the stiffness of a composite material is difficultly predictable *a priori* when the filler reaches a critical particle size, known as ''nano-effect".[Compos Part B-Eng 39 (6):933-961]

Kerner equation is still the most widely employed method in order to predict the mechanical reinforcement of a filler dispersed in a polymeric matrix. Despite the reasonable results for micrometric-sized fillers that do not present strong interactions at the filler/matrix interphase, Kerner equation underestimates the effect on the storage modulus when a nanofiller is involved in the studied system.[Polym Eng Sci 55 (2015) 1689-1697] This displacement may even increase, if the filler is functionalized on its surfaces with groups which can chemically or physically interact with the available groups on the polymeric chains.[Polym Eng Sci 55 (2015) 1689-1697; Colloid Polym Sci 295 (2017) 695-701]. For this reason, Kerner equation needs to be adjusted in order to better fit experimental data of hybrid nanocomposites (NPs and polymeric phase bonded with different types of interactions) that by now represents the large majority of the studied composite materials.

In the present study, we prepare covalently bonded TiO_2/epoxy resin composites with different filler content produced by the previously established *Reactive Suspension Method*. The experimental dynamic mechanical data are then compared with the predictions calculated by the well-known Kerner equation. The observed discrepancy between experimental and theoretical data is then rationalized to understand how the Kerner equation can be adjusted to better fit the experimental results of systems composed of nanosized and covalently bonded fillers. Furthermore, we also extend the proposed approach to similar system previously reported that present different types of interactions at the filler/matrix interphase.

2. Experimental

2.1 Materials

3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate epoxy resin (CE), titanium(IV) chloride ($TiCl_4$), polyethylene glycol (PEG, average molecular weight 200 Da), propylene carbonate (PC), ytterbium(III) trifluoromethanesulfonate hydrate ($Yb(OTf)_3$), chloroform (≥99.5%), dichloromethane (≥99.8%), acetone (≥99.9%), ethanol (≥99.8%) and diethyl ether (≥99%) were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

2.2 TiO_2 synthesis

According to the previously reported synthetic procedure,[J Nanopart Res 16 (2014) 2645] a given amount of $TiCl_4$ was added drop wise to PEG (Table 1) in a sealed tube reactor (volume 12 mL) at room temperature under vigorous stirring for 15 min. Next, the system was heated by microwaves assisted heating system (CEM – Discover SP) as follows: first step at 80°C (20 W) for 1 min in order to stabilize the inner reactor pressure and a second heating at 170°C (70 W) for 25 min for activating the reaction. A portion of the obtained stable whitish suspensions were used for composites preparation according to *Reactive Suspension Method* [Polym Eng Sci 55 (2015) 1689-1697] (detailed procedure in section 2.3). The rest of the suspensions were centrifuged at 8000 rpm for 15 min (Sorvall ST 8 benchtop centrifuge, Thermo Scientific), in order to separate the NPs for their characterization. The NPs were then carefully washed twice using dichloromethane, twice by acetone and once by diethyl ether, sonicating for 10 min each time that fresh solvent was added. Finally, powders were dried at

60°C for 5 h under dynamic vacuum. The prepared suspensions and corresponding powders were coded as S1, S3 and S5.

Table 1. Composition of the reaction mixtures to synthesize TiO_2 NPs suspensions.

Sample	$TiCl_4$ (mL)	PEG (mL)
S1	0.14	3.56
S3	0.41	
S5	0.69	

2.3 TiO_2/epoxy resin nanocomposites preparation

According to the *Reactive Suspension Method*,[Polym Eng Sci 55 (2015) 1689-1697] thermally curable formulations were prepared by mixing the previously prepared TiO_2 NPs suspensions with a given amount of CE resin and $Yb(OTf)_3$/PC solution (0.4 g·mL^{-1}) as thermal cationic initiator (Table 2). The mixing was carried out using a T18 Ultra-Turrax® Ika disperser for 5 min and ultrasonic bath for further 5 min. The so-prepared formulations were cast into silicone molds (cavity dimensions of 4×1×0.4 cm^3) and degassed by dynamic vacuum to avoid bubbles formation during the curing step. The formulations were placed in an oven for 15 min at 120°C and for further 15 min at 160°C to activate the curing. The cured nanocomposites were coded as EpC_T*X*, where *X* is the nominal TiO_2 NPs content expressed as weight percentage (wt.%).

Table 2. Composition details of the thermally curable formulations used to prepare nanocomposite materials.

Sample	CE (g)	TiO_2 suspension	$Yb(OTf)_3$/PC solution (mL)
EpC	5.00	1.78 mL of PEG	0,13
EpC_T1		1.78 mL of S1	
EpC_T3		1.78 mL of S3	
EpC_T5		1.78 mL of S5	

2.4 TiO_2 characterization

X-ray diffraction (XRD) investigations were used in order to confirm the crystalline phase of the inorganic NPs. The measurements were performed on a conventional Bragg-Brentano diffractometer (X'Pert PRO, Panalytical) using the Ni-filtered CuKα monochromatic radiation (λ = 1.5418 Å) (XPert PRO, Panalytical) to identify the crystalline phase of the synthesized NPs. The XRD patterns were collected at room temperature in a 2θ range of 10 – 90°, with a scanning rate of $0.05° \cdot s^{-1}$ and a step size of 0.1°.

Size and morphology of the synthesized NPs were investigated by a high-resolution scanning electron microscope (HRSEM, JEOL JSM 7500FA) equipped with a cold field emission gun, applying an accelerating voltage of 15 kV. Approximately 5 mg of NPs were dispersed into 1 mL of ethanol by 5 min of ultrasonic bath. Next, 5 µL of the prepared suspension was dropped on a silicon wafer attached by carbon tab on a stub and left drying for few minutes. The obtained images were analyzed by Fiji open-source software to evaluate the average particles size and particles size distribution. The elemental mapping by energy-dispersive X-ray spectroscopy (EDS) was recorded using the same instrument but applying an acceleration voltage of 25 kV.

The organic functionalization of the TiO_2 particles was studied by Magic Angle Spinning (MAS) nuclear magnetic resonance (NMR). The spectra were acquired at 300 K using an AVANCE III HD 600 Bruker spectrometer equipped with a 2.5 mm H/X CPMAS probe operating at 600.13 and 150.90 MHz for ^1H and ^{13}C, respectively. Samples were packed into 2.5 mm zirconia rotors and spun at the magic angle. ^1H-NMR spectra were obtained at 33±1 kHz MAS rate, using DEPTH sequence18 in order to remove baseline distortions, at 125 kHz spectral width, 10 s relaxation delay, 2.3 µs 90° pulse, 4k data points, and 32 scans. The empty rotor ^1H spectrum was subtracted to compensate for background effects. Cross-Polarization-MAS (CP-MAS) ^{13}C-NMR spectra were obtained at 16 kHz MAS rate, using the standard Bruker CP sequence with 139 kHz spectral width, 1 s relaxation delay, 2.3 µs 90° 1 H pulse, radio frequency field strength of about 62 kHz for Hartmann−Hahn match, 0.2 ms contact time, 4k data points, and 28k−32k scans. All chemical shifts were referenced by adjusting the spectrometer field to the value corresponding to 38.48 ppm chemical shift for the deshielded line of the adamantane ^{13}C-NMR signal.[Clays Clay Miner. 65 (2017) 220– 233, DOI: 10.1346/CCMN.2017.064065]

The NPs functionalization was also analyzed by Fourier-transform infrared (FTIR) spectroscopy. The analysis was carried out using an FT-IR VERTEX 80 spectrometer (Bruker) in attenuated total reflectance (ATR) mode from 4000 to 500 cm^{-1} (32 scans and resolution of 4 cm^{-1}), equipped with a diamond crystal. Moreover, the organic fraction that functionalized the particle surface was quantified on samples of approx. 200 mg by gravimetric analysis, measuring the percentage weight loss after a treatment at 500°C for 2 hours in a lab furnace.

The density (ρ) of the TiO_2 NPs were evaluated on approx. 1 g of each sample by a pycnometer Accupic 1330 (Micromeritics) using helium.

2.5 TiO_2/epoxy resin composites characterization

The TiO_2 NPs contents in the nanocomposites were determined by gravimetric analysis on approx. 800 mg of each sample. The weight of the samples was evaluated before and after a thermal degradation of the polymer at 500°C for 4 hours in a lab furnace. The filler volume fractions were calculated using the determined NPs contents and the densities of the composites experimentally determined by pycnometer, following the same procedure described above in the section 2.4.

The FTIR investigations were carried out the epoxy groups conversion (α) using the same instrumental parameters reported in section 2.4. α was determined from the intensity of the signal at 794 cm^{-1}, which is associated to asymmetric stretching of the EpC epoxy group. Such a signal was normalized with respect to the signal corresponding to the stretching of carbonyl groups of EpC (1726 cm^{-1}).[POLYM. ENG.SCI., 55 (2015) 1689–1697; Macromolecules 40 (2007) 8827-8829] α (%) was calculated by the following equation:

$$\alpha\ (\%) = [1 - (A_t/A_0)] \cdot 100$$ Equation 1

where A_0 and A_t are the normalized areas of the epoxy group signal (at 794 cm^{-1}) before and after the curing step, respectively.

Extraction tests were carried out to evaluate the extractable fraction *(f)* non-covalently bonded in the 3D hybrid polymeric network. Approximately 300 mg of each sample was wrapped in a filter paper and immersed in 30 mL of chloroform at room temperature for 24 hours under gentle stirring. The samples were then dried at 60°C under dynamic vacuum up to constant mass was reached. The *f* values were normalized to the actual polymeric phase content.[J. Appl. Polym. Sci. 128 (2013) 2525-2532] f percentages were calculated by the following equation:

$$f = [(m_0 - m_e)/m_0]/w_{ORG} \cdot 100$$ Equation 2

where m_0 and m_e are the mass of the sample before and after the extraction test, respectively. w_{ORG} is the weight of organic phase present in the composite materials.

HRSEM investigations (JEOL JSM 7500FA) were used to evaluate NPs distribution in the nanocomposites. The prepared samples were fractured in liquid nitrogen and the cross-sections were analyzed by applying an accelerating voltage of 10 kV. The cross-sections were previously coated with gold (thickness 10 nm) by an electro-deposition method to impart electrical conduction. The recorded images were analyzed by Fiji open-source software in order to obtain the particle size distribution.

MAS-NMR experiments were performed on TiO_2/epoxy resin composites using the same procedure described for NPs in section 2.4.

Dynamic-mechanical analyses (DMA) were carried out on a DMA Q800 (TA Instruments) in single-cantilever configuration applying a deformation of 0.05% and a frequency of 1 Hz. The storage modulus *(E′)* and loss factor (tanδ) were measured from -50 to 150°C with a heating ramp of 3°C·min^{-1}. The glass transition temperature ($T_{g,DMA}$) was assumed as the maximum of the loss factor curve.

The average molecular weight between two adjacent cross-linking points (M_C) were calculated using the following equation [Journal of Applied Polymer Science 89 (2003) 3774-3785] from E' values in the rubbery region (at T_g + 50°C):

$$E'_{90°C} = 3 \cdot q \cdot n \cdot RT = 3 \cdot q \cdot (\rho / M_c) \cdot RT \qquad \text{Equation 3}$$

where, q is the front factor (typically equal to 1), n is the apparent cross-linking density, R is the gas constant (8.314 J·K^{-1}·mol^{-1}), T is the absolute temperature and ρ is the density of the material.[Vassileva, Journal of Applied Polymer Science 89 (2003) 3774-3785]

3. Results and discussion

XRD measurements presented in Figure 1a show that the synthesized TiO_2 NPs are characterized by the two main diffractions of the anatase pattern (JCPDS file 00-021-1272). In particular, both signals at 25° and 48° (2θ) associated to (101) and (200) crystalline planes, are very broaden meaningful of a nanostructured crystallinity that is typically obtained when non-hydrolytic sol-gel chemistry is used for the synthesis.[J Nanopart Res 16 (2014) 2645, Acc. Chem. Res. 40 (2007) 793-800] As shown in Figure 1b and related inset, the particles present an irregular spherical shape with an average dimension of 168 ± 61 nm (particle size distribution in Figure S1 and data in Table S1). The related EDS elements mapping (Figure S2a, S2b and S2c) show that the particles are composed of TiO_2, thus confirming the XRD results (Figure 1a).

The used synthetic approach typically leads to TiO_2 NPs with surface functionalized with PEG chains.[J Nanopart Res 16 (2014) 2645] This organic fraction was quantified by gravimetric analysis and qualitatively investigated by FTIR and ^{1}H MAS -NMR. In particular, gravimetric analysis showed that the organic content is approximately 65% for all samples (Table S1). According to this, the measured TiO_2 density (ρ_{exp}) ranges from 2.0 to 2.5 g·cm^{-3} (Table S1), which are significantly lower than the reference value of 3.9 g·cm^{-3} for bare TiO_2.[CRC handbook] These values are deriving from the hybrid material composed of TiO_2 and PEG chains that functionalize the particles surface. From a qualitative point of view, both MAS NMR analyses (Figure 1c and 1d) and FTIR results (Figure S3), clearly show the presence of PEG chains on the TiO_2 surface. In detail, ^{1}H MAS-NMR spectra of PEG-functionalized

TiO_2 NPs (in Figure 1c) show two narrow signals at 3.64 and 4.46 ppm assigned to the ^1H of methylene group of the terminal monomeric unit of PEG. In comparison to the typical broad signal centered at 4 ppm and representative to all CH_2 groups of free non-bonded PEG [RSC Adv. 9 (2019) 15657, DOI: 10.1039/c9ra01848d], the less mobility of the CH_2 groups of bonded PEG leads to two distinct signals for terminal CH_2. Moving from S1 to S3 and S5, a decrease in the resolution of these signals can be observed due to a reduced mobility. Modifications are also visible in the broad resonance from 2 to 10 ppm relative to inner CH_2 of PEG and unreacted OH titanols.

Figure 1d reports the ^{13}C MAS-NMR spectra in of PEG-modified TiO_2 NPs. Specifically, the signals at 64 ppm ($-O-CH_2-\boldsymbol{C}H_2-OH$) and at 73-75 ppm ($-O-\boldsymbol{C}H_2-CH_2-OH$ and the inner ethylene glycol unit $-O-\boldsymbol{C}H_2-\boldsymbol{C}H_2-O-$) are in agreement with what was previously observed elsewhere.[RSC Adv. 9 (2019) 15657, DOI: 10.1039/C9RA01848D; International Journal of Biological Macromolecules 118 (2018) 783–791, DOI: 10.1016/j.ijbiomac.2018.06.142] With respect to free PEG, the observed signals are broader due to the reduced mobility derived from the formation of the covalent bond between PEG and TiO_2 NPs. By the comparison of S1 with S3 and S5 CP spectra, small modifications are also detectable; in particular more evident variations are visible moving from S1 to S3 than from S3 to S5.

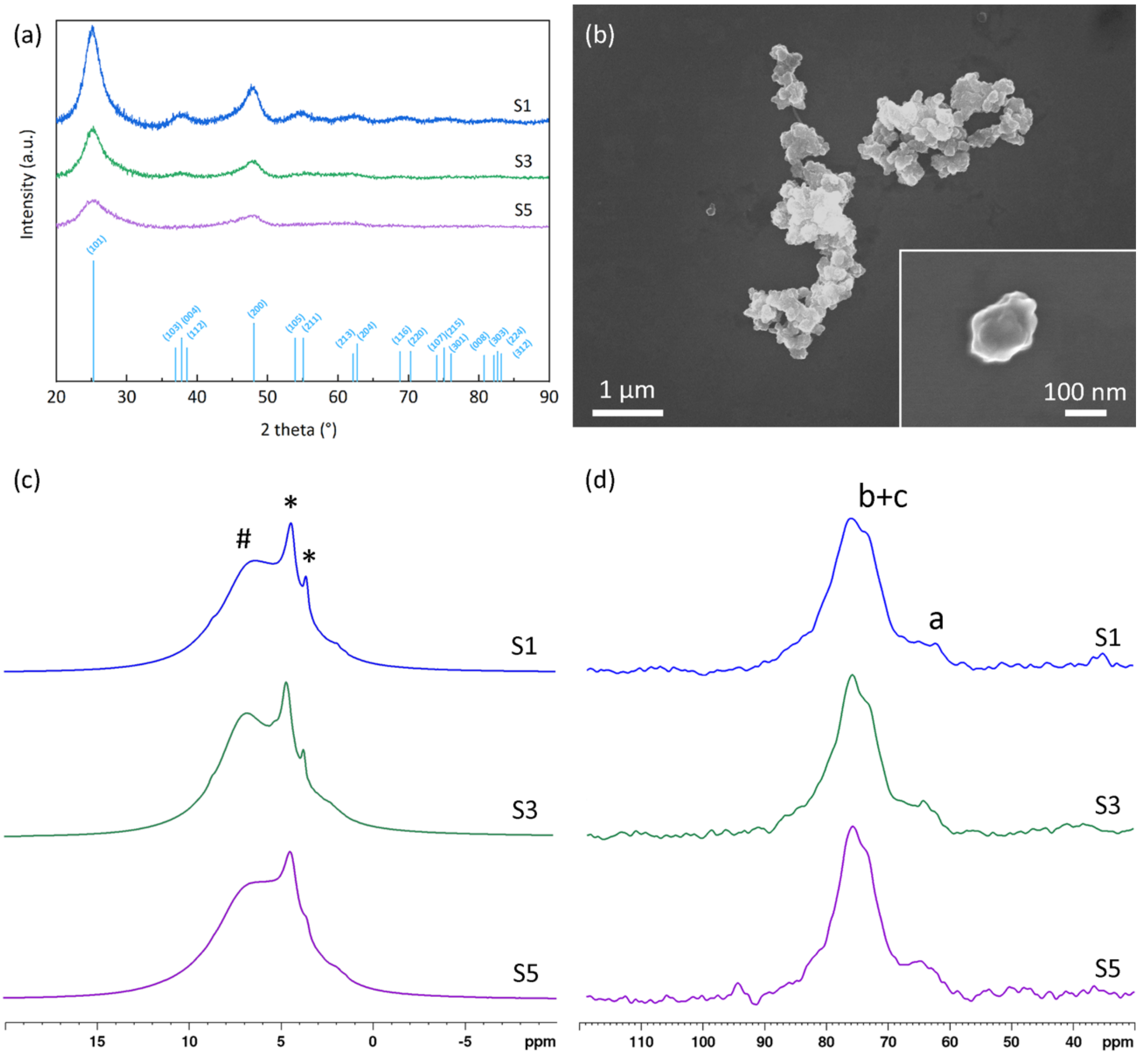


Figure 1. (a) XRD diffractograms of the synthesized NPs and (b) representative HRSEM image of the synthesized TiO_2 NPs recovered by suspension S3. (c) ^{1}H MAS-NMR and (d) ^{13}C MAS-NMR spectra of synthesized TiO_2 NPs. (In figure 1c * indicates signals at 3.64 and 4.46 ppm and # indicates the broad resonance from 2 to 10 ppm; in figure 1d “a” indicates signals at 64 ppm and “b+c” indicates the signal at 73-75 ppm).

EpC/TiO_2 composites are characterized by homogeneous dispersion and distribution of the filler as depicted by HRSEM images reported in Figure 2. As a consequence, also the transparency of formulations coated and cured on quartz glasses, is only slightly affected even when the NPs content increases up to 5 wt.% (Figure S4).

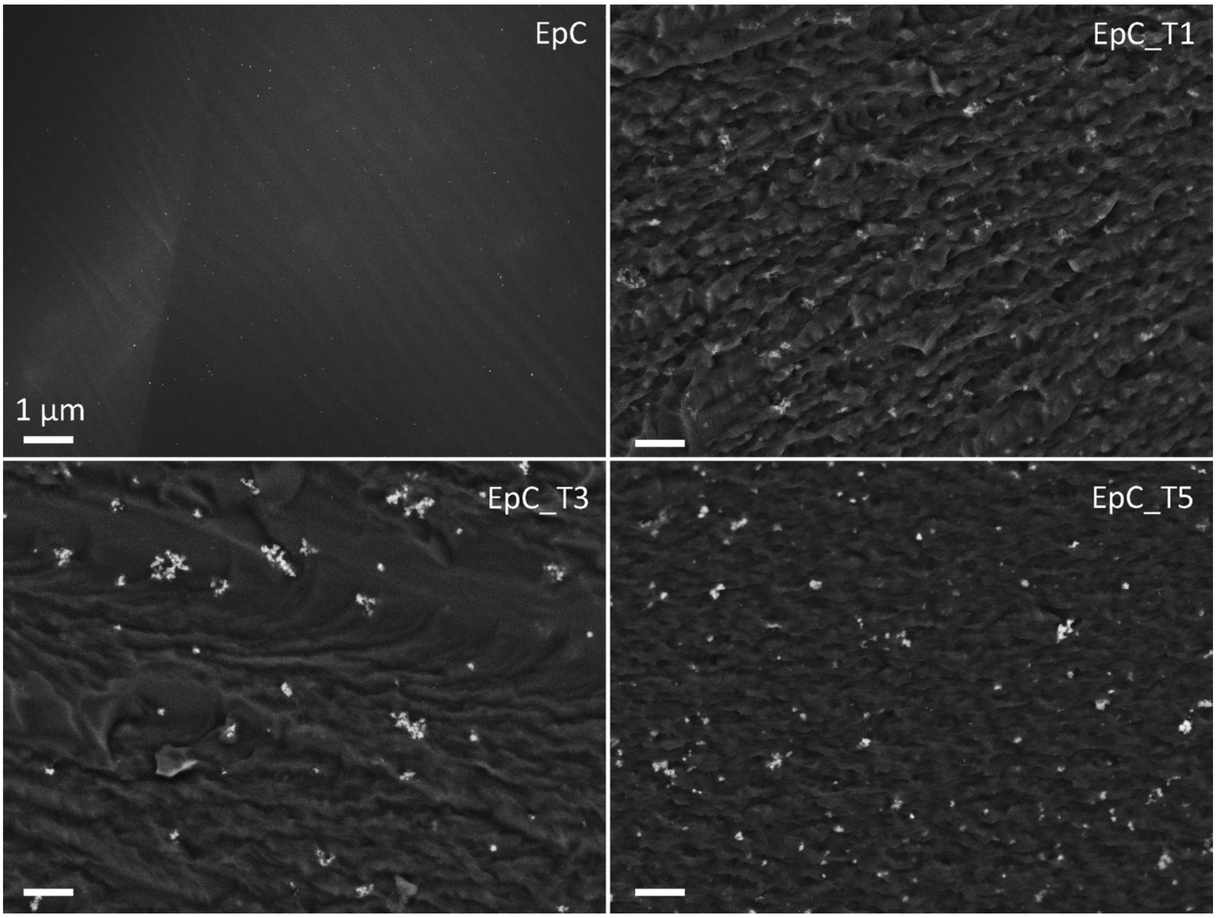


Figure 2. Cross-section HRSEM images (backscattered electrons) of the neat EpC resin and the composite materials with different content of TiO_2 NPs (scale bar indicates 1μm).

The inorganic NPs contents were measured by gravimetric analyses, which show the consistency between nominal and actual values (Table S2) confirming the effectiveness of the proposed method. The conversion of the epoxy groups *(α)* was determined by the peak at 794 cm^{-1} in the FTIR spectra presented in Figure S5a. α values are for the EpC and associated composites of approx. 77% (Figure S5b and Table S2), suggesting that the presence of TiO_2 NPs do not significantly affect the curing process. The maximum values of α is presumably limited by the network vitrification, which inhibits the progress of the polymerization reaction, as previously observed in similar systems.[Polymer 53 (2012) 283-290]

Extractable fraction *(f)* was determined to evaluate the effect of the TiO_2 suspension on the cross-linked polymeric network. Despite the conversion of epoxy groups is not quantitative, *f* is particularly low with values that range from 12 to 14% (Table S2). It is also interesting to observe that also *f* is not significantly affected by the different TiO_2 content, thus confirming that the inorganic NPs do not prevent the development 3D polymeric network and suggesting the formation of a strong interaction between filler and organic matrix. In addition, *f* is significantly lower than the nominal amount of PEG present in the formulation (approx. 28 wt%) in all sample, indicating that the formation of a covalently bonded three-dimensional network is achieved. Such result strongly supports that both “active chain end” and “activated monomer” mechanisms (Figure 3a) occur during the propagation step of the cationic ring-opening polymerization [J Appl Polym Sci 111 (2009) 2822], thus leading to the covalent bonding of PEG hydroxyl groups within epoxy network. Moreover, the free hydroxyl terminal groups of PEG chains on TiO_2 surface can also react according to the above-mentioned mechanisms, leading to the formation of an organic/inorganic covalently bonded hybrid network. In particular, the signal at 4.2 ppm of the ^1H MAS-NMR spectra (Figure 3b) is attributed to CH_2 groups (both inner or terminal) of PEG chains, which instead are not detected in the ^1H MAS-NMR spectrum of neat CE reported in Figure S6b. In addition, increasing the TiO_2 NPs content in the EpC, the spectra lose resolution in the whole ppm range (Figure 3b), probably due to the less mobility of the terminal monomeric units of PEG that bond the inorganic phase, as also evident in Figure 1c for TiO_2 particles S3 and S5. The ^{13}C MAS-NMR spectra, in Figure 3c, confirm the covalent bond between PEG-functionalized NPs and CE epoxy resin: modifications are visible in all the compositions at 40 and 70 ppm with respect to neat CE resin (^{13}C MAS-NMR spectrum of neat CE is reported in Figure S6c).

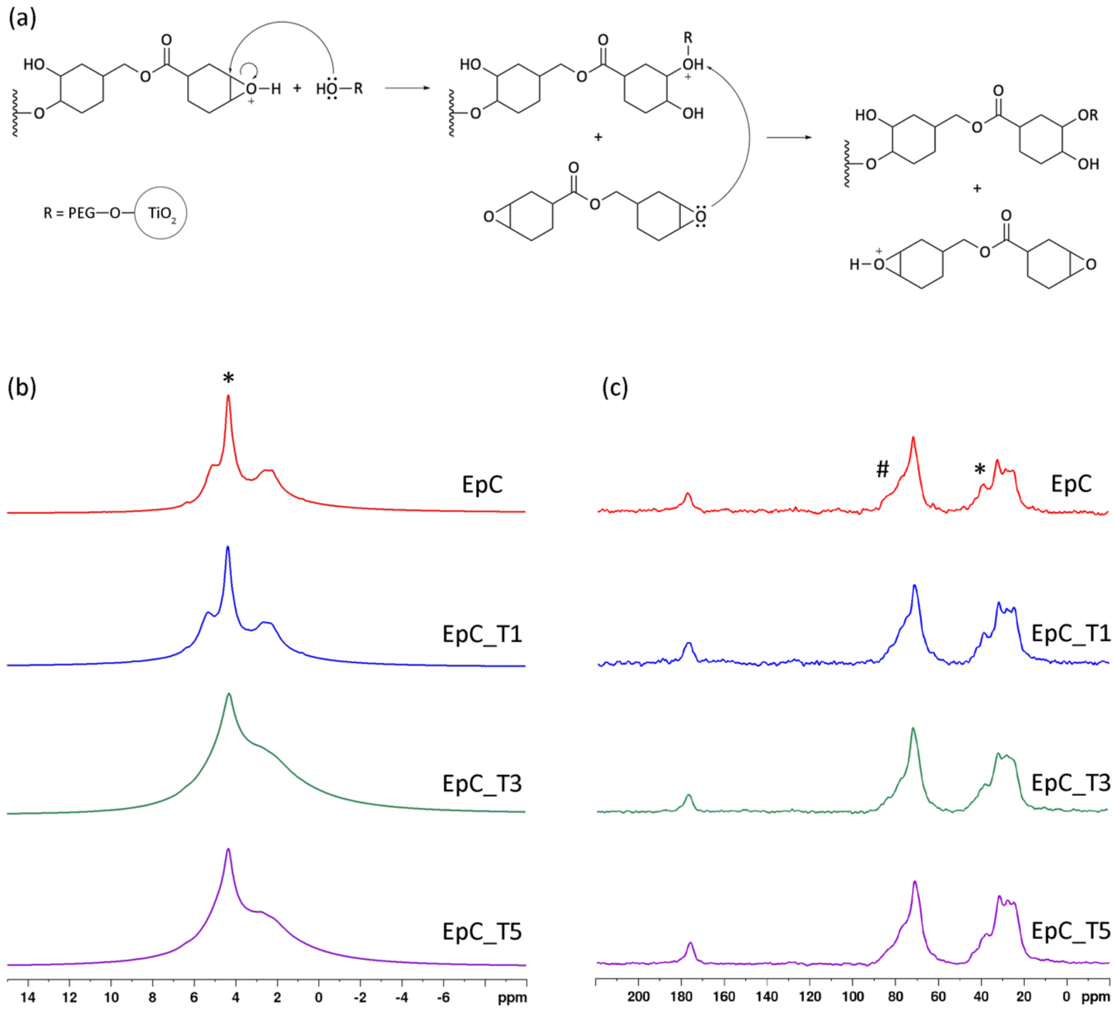


Figure 3. (a) "Active chain end" and "activated monomer" mechanisms, which take place in the propagation step of the polymerization process in presence of hydroxyl groups. (b) ^{1}H MAS-NMR and (c) ^{13}C MAS-NMR spectra of the neat EpC and associated composite samples with different TiO$_2$ content. (In figure 3b * indicates the signal at 4.2 ppm; in figure 3c # indicates the signal at 40 ppm; in figure 3c * indicates the signal at 70 ppm)

The presence of interactions between the inorganic NPs and the polymeric network affects the dynamic mechanical properties, especially in the temperature region above T$_g$ (rubbery region).[Polymer 53 (2012) 283-290; POLYM. ENG.SCI., 55 (2015) 1689–1697; J. Appl. Polym. Sci. 131 (2014) 40470] As shown by Figure 4a, in the glassy state (below T$_g$) storage modulus *(E′)* is slightly influenced by the presence and content of filler NPs (data in Table S2). On the other hand, *E′* is significantly affected by the NPs in the rubbery state (T$_g$ + 50°C), where *E′* value of neat EpC (0.458 MPa) is increased to 0.874, 1.379 and 2.176 MPa for EpC_T1, EpC_T3 and EpC_T5, respectively. It is known that, in this temperature range, *E′* is mainly governed by the cross-linking density since the weak chain-chain interactions become negligible if compared to the covalent bond's strength. Comparing the measured E' with the Kerner predictions, depicted in Figure 4b, it is clear that the prepared samples have a E' significantly higher then expected. Specifically, the measured E' values were then converted to reduced storage moduli (E'/E'_0) and plotted as a function of TiO_2 volume fraction. The predicted E'/E'_0 values were calculated from generalized Kerner equation, following reported: [Nielsen and Landel, Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker Inc., 1994]

$$E'/E'_0 = (1 + A \cdot B \cdot \varphi_i)/(1 - B \cdot \psi \cdot \varphi_i) \qquad \text{Equation 4}$$

where E' and E'_0 are the storage moduli of composite and unfilled epoxy, respectively. φ_i represents the filler content expressed as volume fraction. The constant A, in the case of spherical filler particles and for any Poisson's ratio (v) of the matrix, is defined as: [Nielsen and Landel, Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker Inc., 1994]

$$A = (7 - 5v)/(8 - 10v) \qquad \text{Equation 5}$$

The constant B depends on the filler and matrix moduli ratio (E'_f and E'_0, respectively) and it can be approximated to 1 for very large moduli ratios as also in our case. B is defined as:[Nielsen and Landel, Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker Inc., 1994]

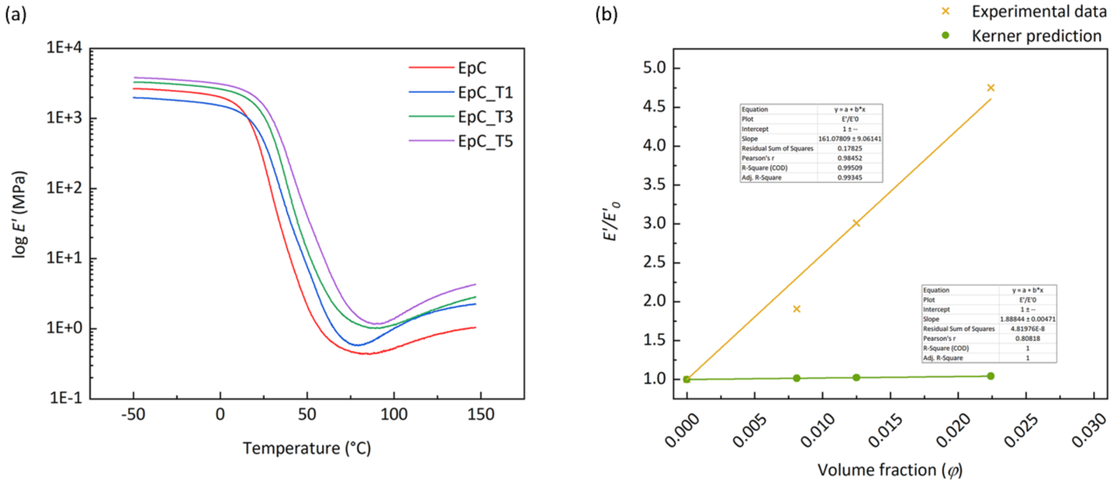
$$B = (E'_f/E'_0 - 1)/(E'_f/E'_0 + \mathrm{A}) \qquad \text{Equation 6}$$

The term ψ depends on the maximum packing fraction of the filler particles (ϕ_m) according to the following empirical equation [Nielsen and Landel, Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker Inc., 1994]:

$$\psi = 1 + [(1 - \phi_m)/\phi_m^2 \cdot \varphi_i] \qquad \text{Equation 7}$$

in which φ_i is the filler volume fraction and ϕ_m is the maximum packing fraction which is a constant that defines the filler packing configuration. According to Nielsen and Landel book,[Nielsen and Landel, Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker Inc., 1994] v of the matrix and ϕ_m are equal to 0.5 (epoxy in the rubbery state) and to 0.601 (random loose packing), respectively.

As shown in Figure 4b, the Kerner prediction does not fit the experimental data similarly to what was observed in other previous studies.[J. Appl. Polym. Sci. 131 (2014) 40470; Polymer 53 (2012) 283-290; POLYM. ENG.SCI., 55 (2015) 1689–1697, Compos Part B-Eng 39 (2008) 933-961] In detail, experimental E'/E'_0 values are significantly higher with respect to the values calculated by the generalized Kerner equation (Eq. 4). It is noteworthy that Kerner theory only considers that the increase of E'/E'_0, with respect to the unfilled matrix, is due to the presence of homogeneous dispersed rigid particles, which constrain the polymeric chains mobility. It was reported that the deviation from Kerner predictions becomes evident reducing the filler particles size [Composites: Part B 39 (2008) 933–961] and/or introducing interactions, such as bonds, between the polymer and filler.[POLYM. ENG.SCI., 55 (2015) 1689–1697; Colloid Polym Sci 295 (2017) 695-701] As mentioned above, in the rubbery region, *E′* is mainly governed by the cross-linking density of the polymeric network, therefore a considerable increase of this parameter has to be attributed to the presence of these NPs. In other words, the formed TiO_2 NPs act not only as rigid reinforcing filler suspended in a very high viscous fluid as considered by Kerner theory, but also as cross-linking points thus over increasing the *E′* values in the composite materials.



Equation	y = a + b*x
Plot	E'/E'0
Intercept	1 ± --
Slope	161.07809 ± 9.06141
Residual Sum of Squares	0.17825
Pearson's r	0.98452
R-Square (COD)	0.99509
Adj. R-Square	0.99345

Equation	y = a + b*x
Plot	E'/E'0
Intercept	1 ± --
Slope	1.88844 ± 0.00471
Residual Sum of Squares	4.81976E-8
Pearson's r	0.80818
R-Square (COD)	1
Adj. R-Square	1

Figure 4. (a) Dynamic mechanical thermal analysis of the prepared materials. Storage modulus *(E′)* as a function of the temperature. (b) Reduced storage modulus *(E′/E′₀)* as a function of the TiO_2 volume fraction (φ). (×) experimental values and (•) prediction calculated by generalized Kerner equation (Eq. 4).

Figure 4b clearly shows that the slope of the linear fitting is the main difference between the two set of data. Therefore, redefining one of the constants that composes the generalized Kerner equation (Eq. 4), a better fitting of the experimental data can be obtained. In particular, we noticed that the ratio between the slopes of experimental and predicted data returns a value of ψ, which if entered in the Kerner equation (Eq. 4) allows to obtain a satisfactory fitting of the experimental data. From this new value of ψ is then possible to retro-calculate a new value of ϕ_m (from Eq.7) that now acquires a meaning not only associated to the filler packing, but also to the filler-matrix interaction. For this set of samples, the calculated ϕ_m is X.XXXX, which is of one order of magnitude lower than the tabulated values, which typically range from 0.370 to 0.907.[Nielsen and Landel, Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker Inc., 1994] Considering that MAS NMR investigations (Figure 3b and 3c) show the presence of covalent bonds between the organic and inorganic components, the calculated value of ϕ_m can be used in the case of random loose packing and covalently bonded nanometric spherical filler.

The TiO_2 NPs act as cross-linking densifier bonding several polymeric chains. This is further supported by the decrease of the average molecular weight between two adjacent cross-linking points (M_C) calculated by Eq. 3, which indicates an increased cross-linking density (Table S2). Although the Eq. 3 was initially developed for single phase materials,[Journal of Materials Science 26 (1991) 2348-2352] it has been shown that provides reliable results also for composite systems.[Journal of Applied Polymer Science 89 (2003) 3774-3785] Moreover, if M_C values are only compared within the same set of samples, this assumption becomes even more reasonable. As expected, M_C values decreases from 2.39E+4 $g \cdot mol^{-1}$ for bare EpC down to 8.10E+3, 1.09E+4 and 5.17E+3 $g \cdot mol^{-1}$ for the composites EpC_T1, EpC_T3 and EpC_T5, respectively. Such result further confirms that the discordance between experimental data and Kerner predictions (Figure 4b) can be attributed to the presence of interactions (such as covalent bonds) at the filler/polymer interphase, which are not taken into account by the generalized Kerner equation.

In our previous works, we showed that the formation of non-covalent interactions [Polymer 53 (2012) 283-290; POLYM. ENG.SCI., 55 (2015) 1689–1697, J Appl Polym Sci 131 (2014) 40470] or H-bond [Colloid Polym Sci 295 (2017) 695-701] between polymer chains functional groups and the surface of the inorganic particles can also lead to a deviation from the Kerner predictions. For this reason, the above reported approach was also extended to our previous studies [POLYM. ENG.SCI., 55 (2015) 1689–1697] in order to define a suitable value of ϕ_m also for different type of filler-matrix interactions. Figure 5a (adapted from [POLYM. ENG.SCI., 55 (2015) 1689–1697]) reports both experimental and predicted E'/E'_0 values as a function of the TiO_2 volume fraction presented where H-bonds are the main contribution to filler-matrix interaction. For this system a ϕ_m value of X.XXXX ensures a suitable fitting of the experimental data.

Figure 5b (adapted from [J Appl Polym Sci 131 (2014) 40470]) shows the comparison of E'/E'_0 experimental data and related Kerner prediction for bisphenol A diglycidyl ether (DGEBA) resin reinforced with TiO_2. In this case, no carbonyl group is present in the polymeric network, thus it can be assumed that only Van der Waals forces play a role at the organic-inorganic interface. For this system, a suitable fitting of the experimental data can be obtained entering in the Kerner equation a ϕ_m of X.XXXX.

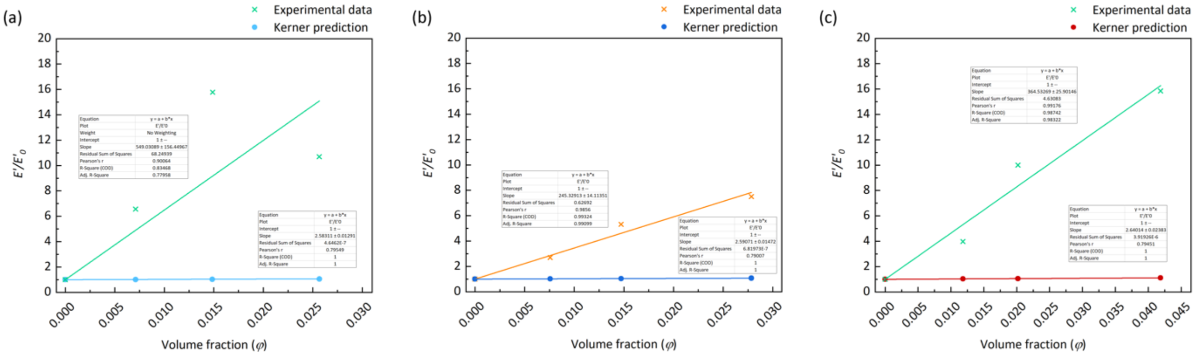


Figure 5. Reduced storage modulus *(E′/E′₀)* as a function of the TiO_2 volume fraction (φ). (×) experimental values and (•) prediction of generalized Kerner equation (Eq. 4). Redrawn from (a) [POLYM. ENG.SCI., 55 (2015) 1689–1697], (b) [J Appl Polym Sci 131 (2014) 40470] and (c) [Polymer 53 (2012) 283-290].

4. Conclusions

In this study the preparation of TiO_2 nanoparticles/epoxy resin composites, by means of the *Reactive Suspension Method* is reported. The dynamic-mechanical properties of the prepared composite samples were characterized and compared with the Kerner equation predictions, showing a significant underestimation of the experimental storage modulus in the temperatures range above glass transition temperature (rubbery region). Such behavior was rationalized considering that the synthesiszed TiO_2 particles are able to act not only as a rigid filler but also as a cross-linking densifier, leading to an increase of cross-linking density. This result was supported by MAS NMR analysis that show the formation of covalent bonds at the organic-inorganic interphase. Since Kerner equation has shown to have several limitations when the incorporated filler is characterized by nanometric size and/or has interactions with the polymer, we propose a simple empirical method for adjusting the equation. In particular, we found out that the parameter ψ of the Kerner equation can be modified in order to have a more accurate fitting of the experimental data. In addition this approach has been extend to other two/three previous studies that present samples with a different type of polymer-nanoparticles interactions. This allowed to find out new ψ values that can be used to predict dynamic-mechanical properties of polymer-based composites characterized by nanosized fillers with different type of polymer-nanoparticles interactions at the interphase. Finally, this work open up a new approach to successfully predict dynamic-mechanical properties and to extend the applicability of the Kerner equation to nanosized fillers bonded with different interactions to a polymeric matrix.

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Supporting Information

Particle size distribution of TiO_2 particles (sample S3), energy-dispersive X-ray spectroscopy (EDS) characterization on TiO_2 particles, FTIR spectra of TiO_2 particles, UV-visible-NIR spectra of composites, FTIR spectra of the formulation before curing and after curing, ^{1}H MAS-NMR and (c) ^{13}C MAS-NMR spectra of CE and tables that summarize the obtained results are reported in the supporting information file.

Graphical Abstract

FIGURE

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