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Cover Letter

Prof. Dean Webster

North Dakota State University

Fargo, North Dakota, USA

Madrid, June 16th 2015

Dear Prof. Webster,

We send our manuscript entilted "Mechanical characterization of sol-gel epoxy-silylated hyperbranched poly(ethyleneimine) coatings by means of Depth Sensing Indentation methods", to be considered for publication in Progress in Organic Coatings.

As it has been reported previously, some of the studied hybrid coatings showed the capacity of self-repairing. In our opinion, the new experimental results of the depth sensing indentation tests allow to obtain a very detailed and precise description of the anelastic recovery of the coatings, behavior that has been explained in terms of their composition.

Looking forward to hearing from you, I remain.

Yours sincerely,

Prof. Vicente Lorenzo

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Mechanical characterization of sol-gel epoxy-silylated hyperbranched poly(ethyleneimine) coatings by means of Depth Sensing Indentation methods

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Abstract

A series of hybrid epoxy-silica coatings were prepared from a synthesized hyperbranched poly(ethyleneimine) with ethoxysilyl groups at the chain ends and diglycidylether of bisphenol A in different proportions. The curing procedure was based in a first sol-gel reaction performed at 80 °C in a humid chamber followed by the anionic homopolymerization of epoxides initiated by 1-methylimidazole in an oven at 180 °C. The prepared coatings were characterized mechanically by means of Depth Sensing Indentation technique. The influence of physical ageing on indentation hardness has been evaluated. The kinetic of the delayed depth recovery has been analyzed using the phenomenological so-called Kohlrausch-Williams-Watts relaxation function. It has been found that silylated hyperbranched poly(ethyleneimine) improves simultaneously the mechanical coating performance and the elastic recovery.

Keywords: Sol-gel, hybrids, hyperbranched, epoxy coatings, indentation, mechanical properties

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1. Introduction

The interest in hybrid organic/inorganic epoxy materials in coatings applications is continuously growing because of their improved characteristics in reference to epoxy thermosets such as: surface hardness, solvent resistance, barrier properties, optical appearance and corrosion resistance and even they can present self-healing and fire retardancy abilities among others [1][2]. Such characteristics make them highly suitable not only in the automotive and aeronautic industry, but also in packaging, membranes, electronics and flame retardant coatings [3],[4],[5],[6].

Although the addition of inorganic fillers to epoxy thermosets seems to be the easiest way to reinforce epoxy coatings, the generation of inorganic silica particles by the sol-gel procedure is advantageous because of the smaller sizes of the inorganic particles and the greater dispersion achieved in the organic matrix that improves the interaction among organic and inorganic domains, leading to a greater reinforcement of the coating[7],[8]. In addition, the smaller size of the silicon particles enhances the transparency of this type of materials. Another advantage of sol-gel/epoxy formulations is that they are easily applied because of its lower viscosity in reference to formulations containing nanosilica particles, being this advantage decisive in coatings applications[5].

Organoalkoxysilanes have been used to reduce the tendency of macroscopic phase separation, often caused by the thermodynamic incompatibility of the components. Thus, the formation of covalent bonds between organic and inorganic parts is essential to avoid this separation. Organoalkoxysilanes have reactive functional groups similar in nature to both organic and inorganic materials constituting the hybrid and they are known as coupling agents. They usually react in the presence of tetraethylorthosilicate (TEOS) to create silica particles by sol-gel condensation in the presence of water or humidity. Nazir et al.[7] prepared hybrid epoxy-silica polymer films based on diglycidylether of bisphenol A resin (DGEBA) and diamine curing agent and a silica reinforcing phase. They obtained materials with the highest glass transition and degradation temperatures in the presence of a coupling agent containing amino and triethyoxysilyl groups, which enhanced the organic- inorganic interphase compatibility without affecting the optical transparency of hybrid polymer films.

It has been reported that hyperbranched polymers improve the dispersion of the inorganic particles in epoxy matrices[9],[10]. Nanometric silica struc-

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tures were confirmed using silyl terminated polyesters in sol-gel processes in photocationic polymerization of epoxy monomers[11] .

In a previous work[12], we explored the use of a multifunctional organoalkoxysilane compound (PEI-Si) obtained by functionalization of hyperbranched poly(ethyleneimine) (PEI) in the NH groups. This multifunctional coupling agent can be easily prepared by reacting commercial PEI and 3-(triethoxysilyl)propyl isocyanate (TESPI). This compound was added to a DGEBA formulation in different proportions with 1-methylimidazole as anionic homopolymerization initiator. Highly transparent coatings were prepared on glass surfaces by a two-step procedure. The first step was the sol-gel process, performed in a humid chamber at 80 °C and the second was an anionic thermal curing of epoxides in an oven at 180 °C. This procedure allowed us to get a series of homogeneous hybrid films, with the formation of cage-like POSS structures, which were confirmed by ^{29}Si-NMR spectroscopy[13].

The films obtained were rated by scratch measurements, which demonstrated that the highest resistance to penetration during scratching was reached for formulations with intermediate PEI-Si content (DGEBA/PEI-Si 70/30 and 50/50 w/w %). However, the elastic recovery after scratching increased with the proportion of PEI-Si in the formulation. Moreover, the coatings with the highest content of the silylated polymer (DGEBA/PEI-Si 20/80 w/w %) showed a self-repairing character[12].

According to these results, it seems interesting to go deeper in the mechanical characterization of these materials, to predict the performance of these coatings once applied. The prepared coatings have been characterized mechanically by means of Depth Sensing Indentation (DSI) technique, since the two-step sol-gel/epoxy curing preparation procedure does not allow obtaining bulk-materials in the size and shape necessary to perform other traditional mechanical methods such as stress-strain tests[3]. DSI technique was also selected because it has been reported that the concurrent analysis of the results of DSI and scratch tests is a sound approach to the mechanical characterization of coating-substrate systems[14]. Even more, the results in the literature prove that DSI is an adequate experimental technique to evaluate the mechanical properties of nanocomposites with polymeric matrices[15]. Hence, the aim of this work is to deepen the understanding of the mechanical behavior of these nanostructured DGEBA/PEI-Si hybrid coatings by means of DSI experiments.

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2. Experimental

2.1. Materials

Poly(ethyleneimine) (PEI) Lupasol® FG (PEI800, 800 g/mol, BASF) was dried under vacuum before use. 3-(Triethoxysilyl)propyl isocyanate (TESPI) and 1-methylimidazole (1- MI) were purchased from Sigma-Aldrich and used without further purification. Chloroform was purchased from Scharlab, dried under $CaCl_2$ and distilled before use. Diglycidylether of bisphenol A (DGEBA) Araldite GY 240 (EEW = 182 g/eq) was provided by Huntsman. Ammonium dihydrogen phosphate from Acros Organics was used for the controlled humidity chamber .

2.2. Preparation of triethoxysilyl modified hyperbranched poly(ethyleneimine) (PEI-Si)

The synthetic procedure and the characterization were performed as described previously by reaction of PEI and TESPI in chloroform at 0 °C 12 (Figure 1)
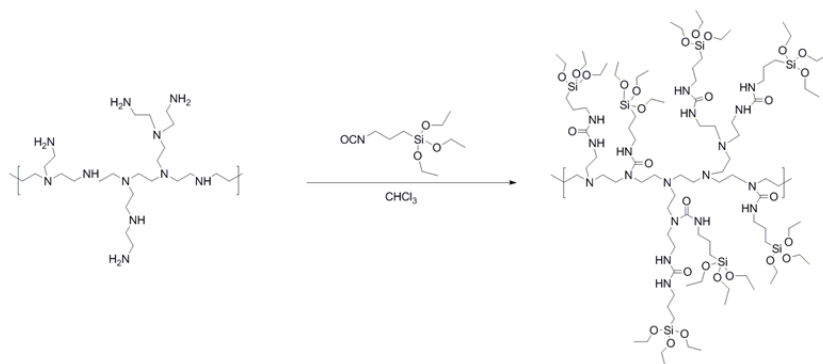
Figure 1: Synthetic procedure used in the preparation of PEI-Si

2.3. Sample preparation

The PEI-Si was added to the DGEBA epoxy resin at a content of 20, 30, 50 and 80 wt % and a 2% in wt. in reference to the DGEBA of 1-MI was added and stirred mechanically until the mixture became clear. The notation used in this paper (FXYZ) reflects the composition of the formulation, being X the parts per hundred of 1-MI in reference to DGEBA and Y and Z representing the weight proportion of DGEBA and PEI-Si, respectively. As an example,

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100.4 g of formulation F228 contain 20 g of DGEBA, 80 g of PEI-Si and 0.4 g of 1-MI.

The formulations were coated on glass slides by means of a wire-wound applicator. The sol-gel process was carried out by thermal treatment at 80 °C for one day in a controlled high humid atmosphere (95-98% relative humidity controlled by a saturated solution of aqueous $NH_4H_2PO_4$) and was followed by a thermal curing process at 180 °C during 2 h in an oven.

2.4. Instrumented indentation experiments

Samples were stored at room temperature in the laboratory during more than 45 days before being measured. As it will be explain later, this delay is necessary to relax the materials.

A Shimadzu DUH 211S Ultra-Microhardness Tester was used to carry out DSI measurements at room temperature (21.5 ± 1.5 °C). The tester was equipped with a Berkovich type indenter. The system was calibrated with a fused silica specimen in order to determine the area function of the indenter and the frame compliance of the equipment. After placing the samples on the stage of the indenter, they were allowed to reach thermal equilibrium with the equipment for half an hour in order to avoid the difficulties due to the thermal drift. A force, P_{max}, of 10 mN was applied with a loading rate, dP/dt, of 1.4632 mN/s in the first stage of the indentation process. After reaching P_{max}, this load was hold for 5 s before unloading. The applied force was then released from P_{max} to its minimum value, P_{min}, 0.02 mN with an unloading rate of -1.4632 mN/s. The force P_{min} remained constant for 5 s and then the sample was finally unloaded. The hardness and elastic modulus data calculated are the result of an average of at least 6 indentation experiments analyzed with the Oliver and Pharr method[16].

3. Results and discussion

In a previous paper the discussion on the preparation of the films by sol-gel condensation followed by homopolymerization of epoxides is detailed[12]. Also, the thermal characterization, TEM inspection and scratch tests are deeply described. The materials were highly transparent due to the formation of nanometric cage-like silicon structures (POSS) because of the trifunctionality of the silylated hyperbranched (PEI-Si). The formation of these cage-like structures was confirmed by ^{29}Si-NMR spectroscopy. No aggregation was observed and the scratch performance attained was maximum for formulations

with an intermediate content of PEI-Si (DGEBA/PEI-Si 50/50 and 70/30 w/w %). This is because of the proper combination of soft structures coming from PEI, rigid homopolymerized DGEBA and POSS nanoparticles acting as reinforcement and crosslinking points. However, the most striking feature was the self-repairing capacity of the film obtained from DGEBA/PEI-Si 20/80 formulation, probably due to the highest elasticity of this material. To go deeper in the mechanical characterization of this type of materials, we investigated them by depth sensing indentation (DSI). This method which monitors the penetration of an indenter into the material surface during the application and release of a load, allows the mechanical characterization of materials, especially of the thin coatings.

First of all, we will discuss about the need of a dwell time in the laboratory before accomplishing the DSI measurements of these epoxy-based materials. It is well established that amorphous materials experiment structural relaxation if they are maintained below their glass transition temperature, T_g [17],[18]. During this process, that is also known as physical ageing, the mechanical and thermal properties of the material change approaching their relaxed values. As hybrid materials that are being studied are amorphous thermosetting polymeric systems with a T_g above room temperature[12], they will experiment physical ageing while they are stored in the laboratory. In order to minimize the effect the ageing time, t_a, variable on the results of the DSI experiments, the samples were relaxed at room temperature before measuring their mechanical properties.

The kinetics of the relaxation can be determined by monitoring the dependence of certain physical properties of the system on the ageing time. To study the kinetics of the physical ageing of our hybrid materials, the indentation hardnesses, H_{it}, of the different specimens were determined after different storage times at room temperature. The dependences of H_{it} on dwelling time for the neat specimen and for the sample with the highest PEI-Si content are illustrated in Figure 2. As can be seen, H_{it} increases significantly at the initial part of the storage period and remains unchanged after being maintained for six weeks in the laboratory. Figure 2 also shows that the relative increase in H_{it} of these materials due to the structural relaxation is close to 10% of the initial value.

It can be argued that some previous results showed that the physical ageing at room temperature of DGEBA epoxy resins, measured by means of DSC techniques, extends beyond 45 days[19]. However, other experimental evidences point to the fact that the kinetics of the ageing measured by
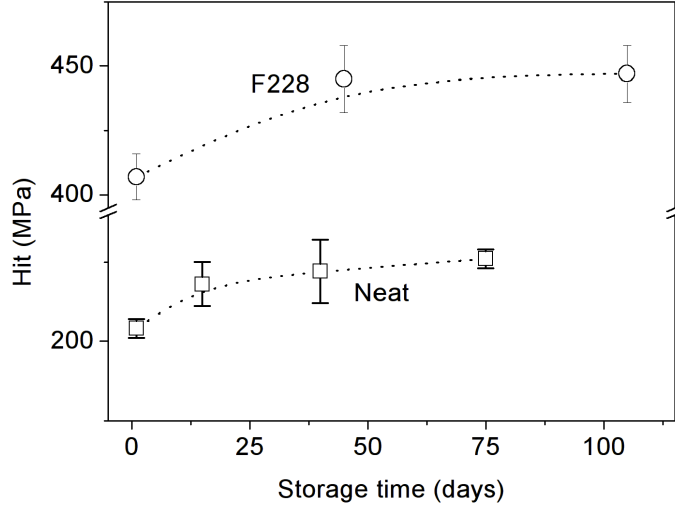
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Figure 2: Indentation hardness, H_{it}, as a function of storage time of the neat and the F228 hybrid material.

means of mechanical tests is different to that obtained from thermal tests because of differences in the sensitivity of the properties to the molecular changes associated with physical aging[20]. Even more, it has been reported that relaxation times of some polybibenzoates obtained from hardness measurements are shorter than those obtained from DSC measurements[21]. In any case, the extent of physical aging should be experimentally determined, since the aging time strongly depends on the chemical structure, the degree of crosslinking achieved and on the aging temperature[22]. Hence, the results collected in Figure 2, suggest that the mechanical properties of these materials, which can be derived from DSI experiments, remain independent of t_a if they are stored for more than 45 days at room temperature.

After storage at room temperature, each sample was indented at least six times and the Martens hardnesses, HM115 and HMs, the indentation hardness, H_{it}, the reduced modulus, E*, the indentation creep, c_{it}, and the elastic part of the indentation work, η_{it}, were obtained from the depth-force curves. The determination of H_{it} and E* was accomplished by means of the Oliver-Pharr method[16]. The uncertainties of all these mechanical parameters, which were evaluated as the 95% confidence interval for the mean, remains lower than 5% of the average values in most cases.

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After these initial calculations, the contact stiffnesses, S, were recalculated by using the creep factor, C, that was proposed by Feng and Ngan[23] to take into consideration either the anelastic or viscoelastic character of the mechanical behavior of polymers. These corrections can be important for the analysis of the indentations of polymeric based materials since it has been shown that the ratio C/S can reach values as high as 0.6 depending on the loading program[24]. The magnitude of the corrections of the reduced modulus and indentation hardness of our hybrid samples ranged from 1 to 3% of the uncorrected values when tested under the loading program that has been described previously. As the corrections related to the mechanical time dependent behavior of these hybrid materials were lower than the uncertainty of the measurements, the corrections were disregarded and the uncorrected values have been reported. It is not surprising that these corrections are negligible because it has been previously shown that this is also the fact for DSI measurements on other polymeric based systems including PLA homopolymers[24], bisphenol A polycarbonate matrix nanocomposites[25] and poly(propylene)-co-poly(1-heptene) copolymers[26] which were tested under load programs analogous to that of this work.

DSI measurements provide information about the combined modulus, E^*, of the tested materials, that, for a polymeric based system, is closely related to indentation modulus, E_{it}, and can be approximated by means of the following expression:

$$E_{it} \approx (1 - \nu^2)E^* \tag{1}$$

where ν accounts for the Poisson ratio[25]. The indentation moduli of the hybrid materials were calculated using equation 1, after hypothesizing that the value of ν is 0.35 for all the specimens, an average value for DGEBA epoxy resins and epoxy matrix composites with filler contents ranging from 0 to 50% and aging times below 200 days[27]. This assumption can be justified after calculating the derivative of the last equation that yields:

$$\frac{\Delta E_{it}}{E_{it}} \approx \frac{2\nu^2}{1 - \nu^2}\frac{\Delta \nu}{\nu} \approx \frac{1}{4}\frac{\Delta \nu}{\nu}. \tag{2}$$

Hence, this result allows one to conclude that the error in estimating E_{it} from E^* value is relatively small compared to that made measuring ν of the indented materials.

Some of the depth-force curves that were obtained in the DSI experiments have been plotted in Figure 3. These curves show that the maximum

indentation depth reached was 1.6 μm, which is much less than the thickness of the coatings (between 100 and 200 μm), i.e., that the ratio of the thickness to the penetration depth is, at least, greater than 60 in all the experiments. Thus, it can be admitted that the results of these DSI experiments are not affected by the substrate and, consequently, are representative of the mechanical properties of the specimens[28].
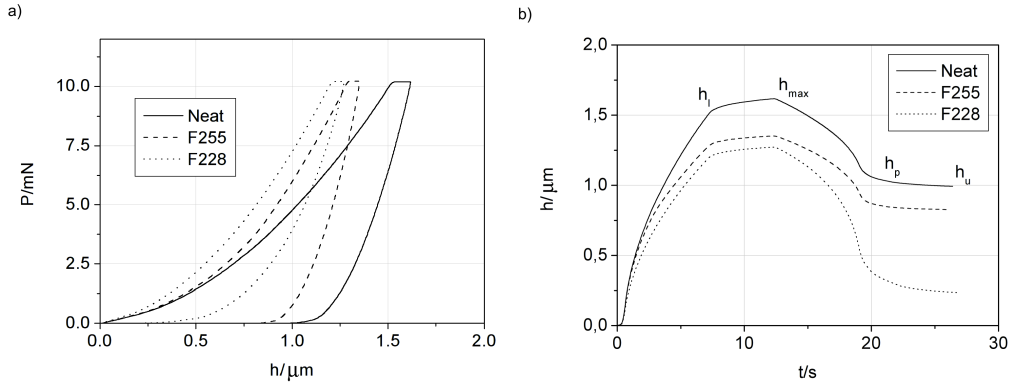
Figure 3: Load-indentation depth (a) and depth-time (b) curves for the neat coating, and for the F255 and F228 hybrid materials.

Examination of Figure 3 shows that the P-h curves of the different samples are clearly distinct. This observation seems to point out to the fact that the PEI-Si percentage in the initial formulation modulates the mechanical properties of these hybrid materials. In order to get a deeper understanding of the relationships between the structure of these hybrids and their mechanical response, the dependences of the different parameters that can be derived from the depth-force curves on the inorganic phase content are going to be analyzed. The values of some of the mechanical parameters that can be obtained from the analysis of the DSI depth-force curves are collected in Table 1.

The data in Table 1 relative to the different hardnesses show that H_{it} increases moderately for PEI-Si content lower than 50% and experiments a significant increment if PEI-Si rises from 50 to 80%, whereas HM115 and HMs displays a minor increment when the inorganic phase content is raised. To understand the meaning of these facts, it is important to consider the distinct character of indentation and Martens hardnesses: whereas the former is related to resistance to the permanent deformation, the latter is a mea-

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	PEI-Si (%)	HM115 (MPa)	HMs (MPa)	H_{it} (MPa)	E_{it} (GPa)	c_{it} (%)	η_{it} (%)
Neat	0	138±4	145±4	226±3	3.41±0.04	6.2±0.3	29.4±0.9
F282	20	151±4	151±4	241±8	3.38±0.05	5.9±0.2	33.3±1.1
F273	30	148±5	151±5	241±9	3.34±0.10	5.7±0.2	33.6±0.6
F255	50	184±8	204±20	294±15	4.12±0.29	5.2±0.4	35.1±3.0
F228	80	230±4	214±7	447±11	3.84±0.05	5.8±0.2	50.8±0.6

Table 1: Composition and results of DSI measurements of the different formulations studied (HM115 and HMs: Martens hardness and Martens hardness determined from the slope of the loading curve, respectively, H_{it}: indentation hardness, E_{it}: indentation modulus, c_{it}: indentation creep factor, η_{it}: elastic part of the indentation work).

surement of the resistance to both permanent and recoverable deformations. Hence, these results seem to suggest that inorganic nanoparticles improve the resistance of the epoxy matrix to either permanent or recoverable deformation. It is also interesting to discuss the differences between H_{it} and HM115 or HMs that are significantly higher for F228 sample than for the others. Consequently, these results seem to indicate that the ratio of the recoverable deformation to the total one (permanent + recoverable) is more important for the coating with the highest POSS content.

The conclusion of the last paragraph can be confirmed by examining the dependence of the elastic part of the indentation work, η_{it}, on the inorganic phase content. The values of η_{it}, that is defined as the ratio of the elastic work recovered during unloading to the total work done during the loading, have been gathered in Table 1. According to these results, η_{it} increases slightly from 29.4 to 35.1 if %PEI-Si rises from 0 to 50 and η_{it} ratio rises abruptly from 35.1 to 50.8 for inorganic phase contents above 50%, i.e., average slope changes from a value close to 0.1 for $0 \leq$ %PEI-Si $\leq$ 50 to 0.5 for $50 \leq$ %PEI-Si $\leq$ 80.

Hence, the analysis of the dependence of η_{it} on %PEI-Si appears to indicate again that the instantaneous elastic recovery of the F228 specimen is significantly higher than that of the hybrid materials with lower POSS content. This statement confirms the conclusion that was drawn after analyzing the results of the scratch tests on these hybrid materials that were previously reported[12]. It has been found that the residual scratch depth, R_d, a magnitude related to the instantaneous elastic recovery after scratching, decreases from, approximately, 15 to below 1 μm if the inorganic phase

percent increases from 0 to 80. Since the maximum penetration, P_d, is about 50 μm for both neat and F228 samples, the ratio of R_d to P_d falls from a value close to 0.3 for the neat resin to a value below 0.02 for the sample with the highest PEI-Si fraction. The higher instantaneous elastic recovery of the F228 formulation can be tentatively attributed to the soft and elastic character of the flexible hyperbranched PEI, in spite of having higher content of inorganic phase. It should be taken into account that POSS particles only represent about 14% to the total F228 sample weight, but they act as crosslinking points of the PEI structure.

At this point it might be interesting to consider the dependence of indentation modulus, E_{it}, on the composition of these hybrid coatings. It can be seen from Table 1 that this value is maximum for PEI-Si contents close to 50%. This detail seems to be contrary to the expectations since it can be thought that the dependences of E_{it} and H_{it} on composition should display the same trend as suggest some reported results[29]. In order to understand the reason of the observed behavior, it is important to bear in mind that E_{it} and H_{it} measure different aspects of the mechanical response of the material. Whereas E_{it} is related to the recoverable deformation, H_{it} is linked to the permanent deformation. Thus, it can be anticipated that the ratio of both magnitudes should be dependent on η_{it}. In fact, it has been proved by means of dimensional analysis that the ratio of H_{it} to the reduced modulus, E^*, is related to η_{it} by means of the following expression that can be applied to ideal elastic-plastic materials[30]:

$$\eta_{it} \approx 5\frac{H_{it}}{E^*} \qquad (3)$$

Although this model cannot be applied to polymeric systems in strict sense, it can be expected a qualitative agreement as a consequence of the nature of the arguments. The examination of data in Table 1 and Figure 4 allows concluding that this assumption seems to be correct since the H_{it} /E_{it} ratio of the hybrid materials rises linearly if η_{it} increases.

In addition, a more detailed analysis of these results proves that the ratio of η_{it} to H_{it} /E^* for these hybrid materials is 4.5 $\pm$ 0.5, a value that is very close to the slope of the straight line that describes the behaviour of ideal elastic-plastic materials. Hence, the empirical relationships E_{it}(F255) > E_{it}(F228) and H_{it}(F255) < H_{it}(F228) can be explained because the elastic recovery of F228 is higher than those of the hybrid materials with less inorganic content.
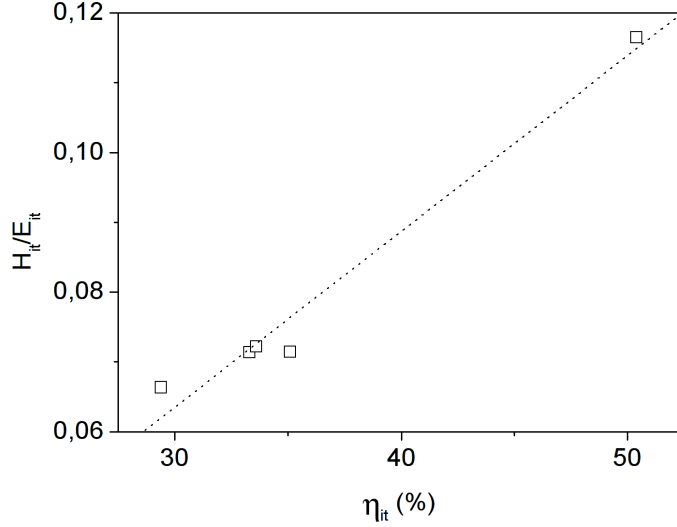
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Figure 4: H_{it} /E_{it} ratio variation against η_{it} it of the hybrid materials.

DSI experiments also allow obtaining information about some of the time dependent mechanical behavior of polymeric based systems. Two aspects of the viscoelastic, anelastic or viscoplastic behavior of polymers that can be explored by analyzing the results of instrumented indentation are creep and elastic recovery. In order to study these phenomena, the dependence of the indentation depth, h, on time, t, should be considered. The h-t curves for the neat sample and some of the hybrid materials, that are depicted in Figure 3-b, shows four clearly distinguishable stages: loading, creep, unloading and delayed elastic recovery that are limited by penetration depths that have been labeled h_l, h_{max}, h_p and h_u, respectively.

During the holding period that follows the loading stage of the instrumented indentation experiments, depth increases from the h_l to h_{max}. Indentation creep, c_{it}, can be defined as the ratio of the increase of the indentation depth during the holding period to h_l:

$$c_{it} = \frac{h_{max} - h_l}{h_l} \tag{4}$$

The values of this ratio for the hybrid materials, collected in Table 1, are close to 6%. It can be thought that the easiness for the creep of all the samples is similar because of the closeness in their c_{it} values. At this point,

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it is important to understand that c_{it} is evaluated under the action of the same P_{max} load for all the samples but the contact pressure is not the same. In fact, HM115 and HMs, which are defined as the average contact pressure under the action of P_{max}, increase as the inorganic phase fraction raises. Hence, it can be concluded that POSS nanoparticles not only reinforce the coatings but also increase the resistance to creep of the epoxidic matrix.

The elastic recovery of these materials can be considered as the combination of an instantaneous and a delayed contribution. The relative importance of both components of depth recovery in DSI experiments can be evaluated by considering the indentation depths at the end of the P_{max} holding period, h_{max}, at the end of the unloading process, h_p, and at the end of P_{min} holding period, h_u. The instantaneous elastic depth recovery, IER, can be related to:

$$IER = 1 - \frac{h_p}{h_{max}} \tag{5}$$

whereas the relative significance of the delayed anelastic depth recovery, DER, can be estimated by means of:

$$DER = 1 - \frac{h_u}{h_p} \tag{6}$$

Figure 5, which illustrates the dependence of the instantaneous elastic indentation depth recovery on composition of the hybrid materials, shows that IER gently increases from 35 to 45 % if the PEI-Si fraction rises from 0 to 50% and climb to 75% if the PEI-Si content rises from 50 to 80%, a trend that parallels that of η_{it} on inorganic phase fraction.

Figure 5 also shows that the DER is a monotonically increasing function of the PEI-Si content and that the slope of the DER curve after 5 s vs. PEI-Si content display an abrupt increment for PEI-Si fraction greater than 50%. Hence, these results seem to confirm the previous ones about depth recovery obtained by considering the differences between the Martens and indentation hardness or the elastic part of the indentation work. All these parameters agree to the soft and elastic character of the flexible hyperbranched PEI, put in evidence in a previous work[12]. In this work it was observed that the glass transition temperature, T_g, of all PEI-Si/DGEBA hybrids decreases over 90 °C respect to the neat formulation.

A more detailed description of the recovery of the indentations can be obtained if the dependence on time of the indentation depth during the holding
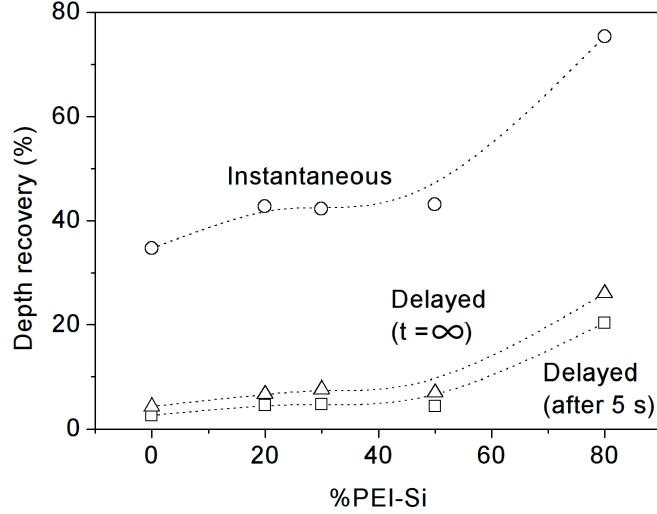
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Figure 5: Instantaneous and delayed elastic depth recoveries of hybrid coatings as a function of the %PEI-Si in the formulation.

period under the action of minimum load, P_{min}, is considered (delayed elastic recovery). Figure 3-b shows the dependence of the fractional depth recovery of the indentations (DER) under the action of the minimum force. It can be seen that the indentation depth on F228 sample recovers more and more rapidly than the indentations on the others specimens. These qualitative appreciations can be confirmed quantitatively if the time dependence of the DER on time is analyzed by using some well-stated phenomenological models.

It has been reported[31],[32] that the kinetics of the indentation depth recovery under zero stress, h(t), can be described by means of the expression:

$$h(t) = h_p - \Delta h(1 - \exp(-t/\tau)) \tag{7}$$

where t and τ are the time ellapsed after releasing the indenter and the retardation time, respectively, h_p is the depth at the beginning of recovery process and Δh is related the asymptotic DER of the indentation. This functional dependence has been proposed by analogy to the Burgers model that predicts an exponential strain recovery under zero stress for viscoelastic materials[31]. Curve fitting of the experimental results about DER as measured in DSI tests proves that the experimental dependence of delayed depth

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recovery on time can be described by using equation 7 to a first approximation. However, some differences between the model and the experimental results can be found. These differences are a consequence of the implicit assumption that the delayed elastic recovery can be explained in terms of only one retardation time. It has been shown that it is possible to obtain a very precise description of creep and DER as measured by means of DSI experiments by using generalized Maxwell models or Prony series[33],[34]. An alternative model to improve the results of fitting can be derived from the empirical Kohlrausch- Williams-Watts (KWW) relaxation function[35]:

$$h(t) = h_p - \Delta h(1 - \exp(-(t/\tau_{eff})^{\beta}))$$ (8)

being β the stretching exponent ($0 < \beta \leq 1$) and τ_{eff}, the effective relaxation time. This function is preferred to the generalized Maxwell models because of it provides a very precise description of the experimental results, the number of unknown parameters of the model is relatively reduced and it has been demonstrated that KWW function can be used satisfactorily for the analysis of relaxation processes of different kind in glassy materials.

After analyzing the dependence on time of the data about the DER of these hybrid materials by means of equation 8, it has been found that β ranges from 0.75 to 0.79 with 95% confidence intervals for the average value between 0.02 and 0.06. Hence, it appears that the width of the relaxation spectra does not depend on the POSS content. On the contrary, it has been found that the differences in the τ_{eff} of the hybrid materials are significant. Figure illustrates the variation of the effective relaxation time with the PEI-Si percentage in the initial formulation.

Provided that β seems to be independent on the composition, the inverse of τ_{eff} allows quantifying the kinetics of the relaxation, the results appear to indicate that the depth recovery of the hybrid materials is faster for the samples with the highest nanoparticle content. According to equation 8, the asymptotic DER equals the ratio $\Delta h/h_p$. The exam of figure 6, that shows the dependence of this ratio on the composition for the hybrid materials, seems to point to the fact that the DER of the hybrid materials increases as the POSS content raises. In fact, the value of the DER of the F228 specimen is more than threefold that of the neat epoxy. Hence, this analysis proves that the indentation depth on F228 sample recovers not only more than the indentations on the samples with lower PEI-Si contents but also recovers faster than the other specimens.
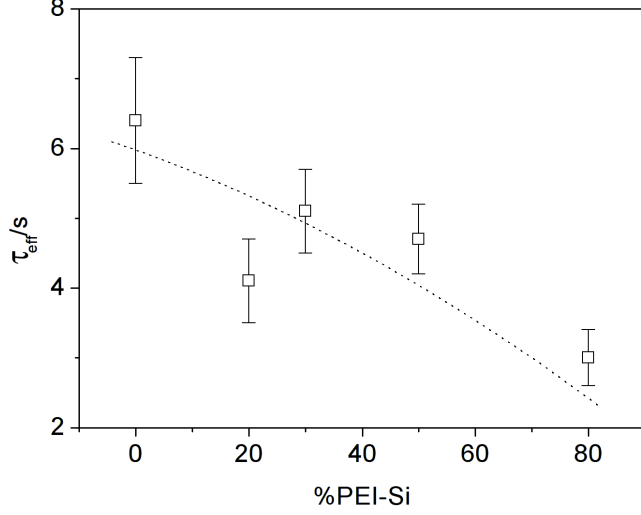
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Figure 6: Dependence of the effective relaxation time, τ_{eff}, for the delayed elastic recovery on PEI-Si contents in the initial formulation.

Anyway, one should not conclude too much from the absolute values extracted from these models: they must be considered only as tools to perform an empirical fit and to have a relative perception of the relaxation kinetics. In fact, these models are purely phenomenological with very little physical significance. They are only useful to give some quantitative description of time dependence of some aspects of DSI experiments[36]. The limitations of these models can be illustrated by the facts that the frequency of maximum of $\tan \delta$ obtained from creep DSI experiments approximately equals the inverse of the holding time[37] or that the retardation time for the DER of high density polyethylene is very close to the duration of the DER experiment[31],[32]. Despite the lack of physical meaning of the parameters of these models, they are useful for ordering different materials[32] or they can be used for estimating the corrections due to the time dependent mechanical behavior of polymers[24],[25].

4. Conclusions

Some of the mechanical properties of epoxy-silylated hyperbranched poly (ethyleneimine) hybrid coatings have been determined by means of Depth

Sensing Indentation measurements. The results have been compared with those of the scratch tests that were accomplished previously in order to get a deeper understanding of the capacity of self-repairing that seems to show the formulation with the higher inorganic phase proportion.

It has been found that the resistances to either permanent or recoverable deformation of the coatings as measured by the indentation and Martens hardnesses increase if the PEI-Si content raises. This increment relative to the hardnesses of the DGEBA epoxidic resin can be explained in terms of the reinforcement effect of POSS nanostructures that are finely dispersed in the organic matrix.

The analysis of the two last stages of the DSI experiments allows to obtain a detailed quantitative description of the recovery of the indentations of the hybrid coatings. The results prove that both the instantaneous and the asymptotic delayed depth recoveries increase significantly if the PEI-Si content rises. Moreover, the fraction of the recovered elastic energy to the total deformation work, η_{it}, follows the same increasing trend. Not only the magnitude of the depth recovery can be analyzed by means of DSI experiments but the kinetics of the recovery can also be studied. The data indicate that the time dependent depth recovery of the hybrid coatings accelerates as the fraction of the PEI-Si increases. This anelastic self-repairing behaviour can be explained as a consequence of the increment of the volumetric fraction of the soft and flexible hyperbranched PEI coupling agent.

In conclusion, the findings of this study have provided some evidence that confirms that the mechanical properties of these hybrid coatings can be tailored for optimizing their performance. It has been proved that the DSI is an adequate experimental technique for characterizing the mechanical behaviour and that the fine dispersion of POSS particles formed from sol-gel condensation of silylated hyperbranched poly(ethyleneimine) improves simultaneously both the resistance to damage and recovery capacity of these coatings.

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References:

[1] O. Becker, G. P. Simon, K. Dusek, Epoxy Layered Silicate Nanocomposites, in: Inorganic Polymeric Nanocomposites and Membranes, number 179 in Advances in Polymer Science, Springer Berlin Heidelberg, 2005, pp. 29–82.

[2] S. Pavlidou, C. D. Papaspyrides, A review on polymerlayered silicate nanocomposites, Progress in Polymer Science 33 (2008) 1119–1198.

[3] F. Mammeri, E. L. Bourhis, L. Rozes, C. Sanchez, Mechanical properties of hybrid organicinorganic materials, J. Mater. Chem. 15 (2005) 3787–3811.

[4] J. J. Chruściel, E. Leśniak, Modification of epoxy resins with functional silanes, polysiloxanes, silsesquioxanes, silica and silicates, Progress in Polymer Science 41 (2015) 67–121.

[5] D. Wang, G. P. Bierwagen, Solgel coatings on metals for corrosion protection, Progress in Organic Coatings 64 (2009) 327–338.

[6] R. Pfaendner, Nanocomposites: Industrial opportunity or challenge?, Polymer Degradation and Stability 95 (2010) 369–373.

[7] T. Nazir, A. Afzal, H. M. Siddiqi, Z. Ahmad, M. Dumon, Thermally and mechanically superior hybrid epoxysilica polymer films via solgel method, Progress in Organic Coatings 69 (2010) 100–106.

[8] S. Ponyrko, L. Kobera, J. Brus, L. Matějka, Epoxy-silica hybrids by nonaqueous solgel process, Polymer 54 (2013) 6271–6282.

[9] M. Sangermano, H. El Sayed, B. Voit, Ethoxysilyl-modified hyperbranched polyesters as mulitfunctional coupling agents for epoxy-silica hybrid coatings, Polymer 52 (2011) 2103–2109.

[10] V. Geiser, Y. Leterrier, J.-A. E. Månson, Low-Stress Hyperbranched Polymer/Silica Nanostructures Produced by UV Curing, Sol/Gel Processing and Nanoimprint Lithography, Macromol. Mater. Eng. 297 (2012) 155–166.

18

[11] M. Sangermano, M. Messori, M. Martín Gallego, G. Rizza, B. Voit, Scratch resistant tough nanocomposite epoxy coatings based on hyperbranched polyesters, Polymer 50 (2009) 5647–5652.

[12] C. Acebo, X. Fernández-Francos, M. Messori, X. Ramis, A. Serra, Novel epoxy-silica hybrid coatings by using ethoxysilyl-modified hyperbranched poly(ethyleneimine) with improved scratch resistance, Polymer 55 (2014) 5028–5035.

[13] L. Matějka, O. Dukh, J. Brus, W. J. Simonsick Jr, B. Meissner, Cage-like structure formation during solgel polymerization of glycidyloxypropyltrimethoxysilane, Journal of Non-Crystalline Solids 270 (2000) 34–47.

[14] J. Malzbender, J. M. J. den Toonder, A. R. Balkenende, G. de With, Measuring mechanical properties of coatings: a methodology applied to nano-particle-filled solgel coatings on glass, Materials Science and Engineering: R: Reports 36 (2002) 47–103.

[15] A. M. Díez-Pascual, M. A. Gómez-Fatou, F. Ania, A. Flores, Nanoindentation in polymer nanocomposites, Progress in Materials Science 67 (2015) 1–94.

[16] W. Oliver, G. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, Journal of Materials Research 7 (1992) 1564–1583.

[17] L. C. E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier Scientific Publishing Company, 1978.

[18] D. Cangialosi, V. M. Boucher, A. Alegra, J. Colmenero, Physical aging in polymers and polymer nanocomposites: recent results and open questions, Soft Matter 9 (2013) 8619–8630.

[19] S. Montserrat, P. Cortés, Y. Calventus, J. Hutchinson, The use of DSC to characterize structural relaxation in thermosetting polymers, Journal of Thermal Analysis and Calorimetry 49 (1997) 79–85.

[20] S. L. Simon, Aging, Physical, in: Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc., 2002.

[21] E. Pérez, J. M. Pereña, R. Benavente, A. Bello, V. Lorenzo, Micro-hardness and DSC measurements on liquid crystalline poly(diethylene glycolp,p-bibenzoate) as a function of the ageing time, Polymer Bulletin 29 (1992) 233–237.

[22] S. Montserrat, Physical aging studies in epoxy resins. I. Kinetics of the enthalpy relaxation process in a fully cured epoxy resin, J. Polym. Sci. B Polym. Phys. 32 (1994) 509–522.

[23] G. Feng, A. H. W. Ngan, Effects of Creep and Thermal Drift on Modulus Measurement Using Depth-sensing Indentation, Journal of Materials Research 17 (2002) 660–668.

[24] S. C. Cifuentes, E. Frutos, R. Benavente, J. L. González-Carrasco, V. Lorenzo, Strain rate effect on semi-crystalline PLLA mechanical properties measured by instrumented indentation tests, European Polymer Journal 59 (2014) 239–246.

[25] V. Lorenzo, M. U. de la Orden, C. Muoz, C. Serrano, J. Martínez Urreaga, Mechanical characterisation of virgin and recovered polycarbonate based nanocomposites by means of Depth Sensing Indentation measurements, European Polymer Journal 55 (2014) 1–8.

[26] A. García-Peñas, J. M. Gómez-Elvira, V. Lorenzo, E. Pérez, M. L. Cerrada, Synthesis, molecular characterization, evaluation of polymorphic behavior and indentation response in isotactic poly(propylene-co-1-heptene) copolymers, European Polymer Journal 64 (2015) 52–61.

[27] J. C. Smith, Experimental values for the elastic constants of a particulate-filled glassy polymer, Journal of Research of the NBS-A. Physics and Chemistry 80A (1976) 45–49.

[28] A. C. Fischer-Cripps, Nanoindentation, Springer, New York, 3rd edition, 2011.

[29] G. Constantinides, C. A. Tweedie, D. M. Holbrook, P. Barragan, J. F. Smith, K. J. Van Vliet1, Quantifying deformation and energy dissipation of polymeric surfaces under localized impact, Materials Science and Engineering: A 489 (2008) 403–412.

20

[30] Y.-T. Cheng, C.-M. Cheng, Scaling, dimensional analysis, and indentation measurements, Materials Science and Engineering: R: Reports 44 (2004) 91–149.

[31] V. Lorenzo, J. M. Pereña, J. G. Fatou, J. A. Mendez-Morales, J. A. Aznarez, Delayed elastic recovery of hardness indentations in polyethylene, J Mater Sci 23 (1988) 3168–3172.

[32] C. A. Tweedie, K. J. Van Vliet, On the indentation recovery and fleeting hardness of polymers, Journal of Materials Research 21 (2006) 3029–3036.

[33] T. Chatel, H. Pelletier, V. Le Houérou, C. Gauthier, D. Favier, R. Schirrer, Original in situ observations of creep during indentation and recovery of the residual imprint on amorphous polymer, Journal of Materials Research 27 (2012) 12–19.

[34] P. A. Yuya, N. G. Patel, Analytical model for nanoscale viscoelastic properties characterization using dynamic nanoindentation, Philosophical Magazine 94 (2014) 2505–2519.

[35] G. Williams, D. C. Watts, Non-symmetrical dielectric relaxation behaviour arising from a simple empirical decay function, Trans. Faraday Soc. 66 (1970) 80–85.

[36] A. C. Fischer-Cripps, A simple phenomenological approach to nanoindentation creep, Materials Science and Engineering: A 385 (2004) 74–82.

[37] M. A. Monclus, N. M. Jennett, In search of validated measurements of the properties of viscoelastic materials by indentation with sharp indenters, Philosophical Magazine 91 (2011) 1308–1328.