

Polymer Bisphenol-A, the Incorporation of Silica Nanospheres into Epoxy–Amine Materials and Polymer Nanocomposites

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ABSTRACT

It is presented the three principal reactions involved in the curing of a diamine with a diepoxide, the modelling of functional groups for crosslinked polymers, the formation of a DGEBA monomer, the polyaddition of bisphenol-A to DGEBA forming a polyether product, the reaction of DGEBA monomer with curing agent Jeffamine D-230 and the start of the crosslinking process to form DGEBA–Jeffamine D-230 resin. Composites of silica (SiO_2) nanospheres, coated with cross-linked epoxy–amine, were synthesised and examined by²⁹ Si-magic-angle-spinning nuclear magnetic resonance spectroscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. The most representative fact is that epoxy-modified nanospheres lost less weight at high temperatures. At temperatures greater than 300°C the loss of weight for epoxy-modified nanospheres was lower than for unmodified nanospheres. This helped them to retain their structures as the loss of weight can have adverse effects on network defects, because of the loss of crosslinks by unit of volume. The mechanical properties of epoxy nanocomposites, strengthened with SiO_2 spherical nanoparticles unfunctionalized or functionalized with amine or epoxy, increase up to reinforcement percentages of 3–5%.

KEYWORDS: polycarbonate, bisphenol-A, polymer nanocomposites, silica nanospheres, epoxy–amine material.

RESUMEN

Se presentan las tres principales reacciones en el curado de una diamina con un diepóxido, el modelado de grupos funcionales para polímeros entrecruzados, la formación de un monómero de DGEBA, la poliadicción de bisfenol-A a DGEBA formando un producto poliéter, la reacción de monómero de DGEBA con el agente de curado Jeffamine D-230 y el inicio del proceso de entrecruzamiento para formar la resina DGEBA–Jeffamine D-230. Composites de nanoesferas de sílice (SiO_2), cubiertas con epoxi–amina entrecruzada, se sintetizaron y examinaron por espectroscopia de resonancia magnética nuclear de ángulo mágico, análisis termogravimétrico, espectroscopia infrarroja de transformada de Fourier y microscopia electrónica de barrido. El hecho más representativo es que las nanoesferas modificadas con epoxi pierden menos peso a altas temperaturas. A temperaturas mayores de 300 °C la pérdida de peso para nanoesferas modificadas con epoxi fue menor que para las nanoesferas no modificadas. Esto les ayudó a retener sus estructuras, ya que la pérdida de peso puede tener efectos adversos sobre los defectos de la red, por la pérdida de entrecruzamientos por unidad de volumen. Las propiedades mecánicas de los nanocomposites epoxi, reforzados con nanopartículas esféricas de SiO_2 no funcionalizadas o funcionalizadas con amina o epoxi aumentan hasta porcentajes de refuerzo de 3–5%.

PALABRAS CLAVE: policarbonato, bisfenol-A, nanocomposites de polímeros, nanoesferas de sílice, material epoxi–amina.

INTRODUCTION

Bisphenol-A (BPA) is a health risk although definitive proof in people is still not compelling; there is a lot of evidence [1]. It has oestrogenic activity and is a cell epigenetic modifier. Changes that BPA induces can be inherited and model is based on findings from diethylstilbestrol (DES), which is structurally similar to BPA. Both are biphenolic molecules originally synthesized as part of the same derivative series. The DES was used as a substitute for oestrogens in

women; one use was to administer DES to pregnant women who were thought to be close to a miscarriage. It was given to provide extra oestrogens to bolster and maintain pregnancy. It worked to uphold expectants, so it was used frequently in setting for the purpose of stabilizing a threatened miscarriage. However, 20–30 years later DES babies developed an increased risk for rare vaginal neoplasia, which one doctor recognized and went back and looked for common denominator. He found that the mothers of young women, who developed vaginal neoplasia, received DES during pregnancy, which



use was discontinued because of carcinogenic effects. Finding indicated that exposing mother to a molecule can affect offspring many years later and perhaps the next generation. Mother DES exposure affects offspring inheritance, increasing the risk of rare malignancy vaginal neoplasia, which is a big worry because DES and BPA are so similar that alike action possibility is strong. Research shows that BPA alters the epigenetic profile of exposed animals. Genetics is based on deoxyribonucleic acid (DNA) code and molecules do not change this, which is called epigenetics, which modifiers affect inheritance but they do not change DNA code, and there is concerning that BPA does that just like DES. However, one may not see BPA risks in diet for years. Exposure of pregnant women and young children to BPA may cause an increased risk of breast, vaginal, uterine or some oestrogen-driven neoplasia down line, which is only one potential risk.

The endocrine system is tightly regulated so that the mother, developing foetus or young child has not too much wrong hormones signalling at incorrect time [2]. When a girl goes via puberty oestrogens come out; they are not supposed to be there during development and infancy. If one puts something there that should not be present and that can cause changes, which should not be induced in the baby at that time, it is a risk factor. The risk of BPA accumulation, and combining with other endocrine disruptors to magnify its actions, is a possibility. However, DES and PBA are not just oestrogenic; both are structurally different from oestrogens and carry additional risks. There was no evidence that BPA increases neoplasia risk in people as DES, which did, but it was recognized in retrospect. It is not known if that is the case for BPA. However, enough parallels to DES does the principle of caution to ask for safe BPA alternatives.

Polymer diglycidyl ether of bisphenol-A (DGEBA), especially when crosslinked with a diamine, is a commercially important epoxy resin and a candidate for applications in nanocomposites. In earlier publications it was reported the treatment of poly(styrene-co-methacrylic acid)/poly(4-vinylpyridine) blends in solution under liquid-liquid phase-separation conditions, with a new method for phase-separation data attainment from viscosity measurements [3], the compatibility between polystyrene copolymers and polymers in solution via hydrogen bonding [4] and a study and comparison of interaction parameters and phase behaviour of epoxy/polystyrene and epoxies copolymer polystyrene-b-poly(methyl methacrylate) blends [5]. It was examined the modelling studies of the phase behaviour of monomer/polymer/disk composites [6], the experimental studies for modelling the phase behaviour of monomer/polymer/disc composites [7] and the modelling monomer/disc composites phase behaviour [8]. It was used DGEBA in polymer nanocomposites to carry out the study and comparison of the interaction parameters, and phase behaviour of epoxy/polystyrene and epoxies copolymer polystyrene-b-poly(methyl methacrylate) blends [9], the incorporation of silica (SiO₂) nanospherical particles into epoxy-amine cross-linked materials [10], the dynamic mechanical measurements of epoxy matrix-SiO₂ nanocomposites [11,12] and the incorporation of SiO₂ nanospheres into epoxy-amine materials forming polymer nanocomposites [13,14]. The goal of the present report is to analyze the principal reactions involved in the curing of a diamine with a diepoxide and further progress of the reaction mixture.

EXPERIMENTAL PROCEDURE

Epoxy Resin

The thermosetting matrix considered in this work was obtained via the polycondensation of an epoxy-amine system. The used diepoxide prepolymer was a DGEBA (diglycidyl ether of bisphenol-A, DER332 from Dow Chemicals, cf. Figure 1).

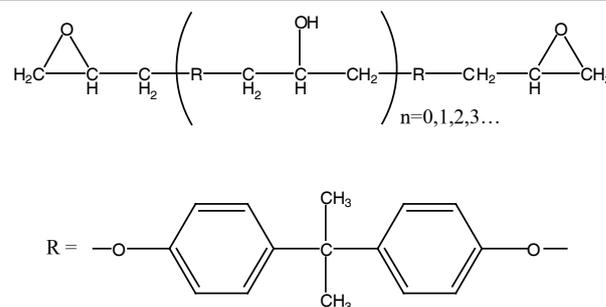


Figure 1. Diglycidyl ether of bisphenol-A (DGEBA).

The uniqueness of liquid epoxy resin, DER332, is reflected in its maximum epoxy equivalent weight of 176 grams-equivalent⁻¹ (the chemically pure DGEBA has an epoxy equivalent weight of 170 g-eq⁻¹, cf. Table 1). Because of its high purity and low polymer fractions content, epoxy resin DER332 assures uniform performance and exceptionally low viscosity coefficient, low chloride content and light colour. Under some cure conditions, this epoxy resin provides improved elevated-temperature properties over standard bisphenol-A-based epoxy resins, e.g., epoxy resin DER331. It is liquid at room temperature so that the fillers can be dispersed into this part of the reactive system. Its coefficient of viscosity is equal to ca. 5 Pa·s at 25°C.

Table 1. Technical characteristics of the DER332 epoxy resin.

Property	Value	Method
Epoxide equivalent weight (g-eq ⁻¹)	171–175	ASTM D-1652
Epoxide percentage (%)	24.6–25.1	ASTM D-1652
Epoxide group content (mmol·kg ⁻¹)	5710–5850	ASTM D-1652
Colour (platinum cobalt)	75 max.	ASTM D-1209
Viscosity coefficient at 25°C (mPa·s)	4000–6000	ASTM D-445
Hydrolyzable chloride content (ppm)	300 max.	ASTM D-1726
Water content (ppm)	700 max.	ASTM E-203
Density at 25°C (g·mL ⁻¹)	1.16	ASTM D-4052
Flash point (°C)	252	ASTM D-93
Epichlorohydrin content (ppm)	5 max.	DowM 101321
Shelf life (months)	24	–



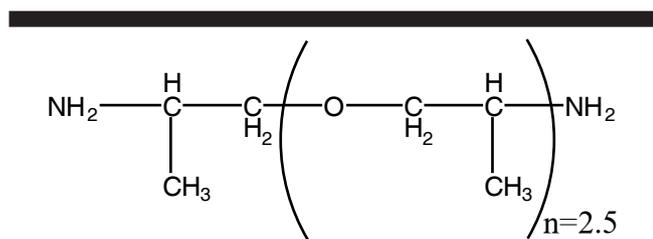


Figure 2. Curing agent (Jeffamine D-230).

Epoxy resin DER332 is used mainly in filament winding, electrical laminates and encapsulation applications. A wide variety of curing agents is available to cure this liquid epoxy resin at ambient conditions. Most frequently used curing agents are cycloaliphatic polyamines, polyamides, amidoamines and modified versions of these. Curing may also be done at an elevated temperature to improve selected properties, e.g., chemical resistance and glass transition temperature. Elevated-temperature cures are necessary and long post-cures are required to develop full-end properties, if anhydride or catalytic curing agents are employed. The product above is suitable for use in applications, e.g., adhesives, casting and tooling, composites, photocure industrial coatings, as well as potting and encapsulation. The molar mass and polydispersity of resin DER332 were experimentally determined in our laboratory, via gel permeation chromatography (GPC) using an equipment from Waters. The obtained values (taking as Cañente the polystyrene calibration equation) follow.

$$\begin{aligned}\overline{M}_w &= 316 \text{ g} \cdot \text{mol}^{-1} \\ \overline{M}_n &= 310 \text{ g} \cdot \text{mol}^{-1} \\ I &= \frac{\overline{M}_w}{\overline{M}_n} = 1.02\end{aligned}$$

Curing Agent

The curing agent used in the study, Jeffamine D-230 [O,O'-bis(2-aminopropyl) poly(propylene glycol) from Huntsman, cf. Figure 2], is a polyetheramine characterized by repeating oxypropylene units in the backbone. As shown by the representative structure, Jeffamine D-230 is an aliphatic primary diamine presenting long and flexible chains. Its molar mass is equal to 230 g·mol⁻¹. The primary amine groups are located on secondary carbon atoms at the end of the aliphatic polyether chain.

The applications of the product above are: epoxy curing agent, it reacts with carboxylic acids to form hot-melt adhesives, it reacts quickly with isocyanates and salts may be formed readily for surfactant use. The benefits of the product above are: low viscosity coefficient, colour and vapour pressure, completely miscible with a wide variety of solvents, including water, it provides tough, clear, impact-resistant coatings, castings and adhesives, as well as coatings are free of surface blush prevalent with many amine curing agents (cf. Table 2).

The epoxy networks were synthesized from the reaction between difunctional epoxy prepolymer DGEBA and tetrafunctional primary diamine comonomer Jeffamine D-230. Three principal reactions take place in the curing of a diamine with a diepoxide, where epoxy groups react with primary amine H atoms to form secondary amines, which can in turn react with epoxy groups. Therefore a polymer network

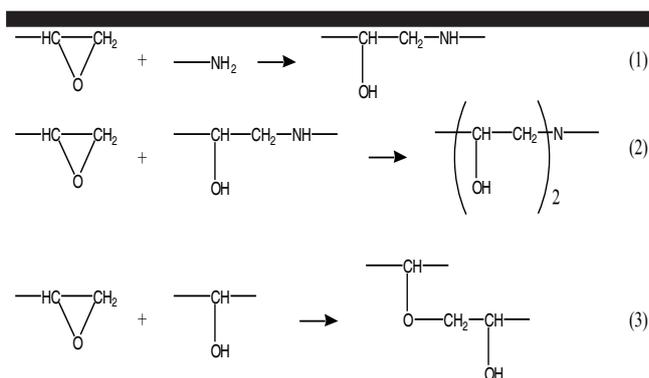


Figure 3. Three principal reactions involved in the curing of a diamine with a diepoxide.

emerges both chemically and physically. In high temperature or in the presence of catalysts homopolymerization of epoxy groups would also occur.

Table 2. Technical characteristics of the Jeffamine D-230 amine.

Property	Specifications	Test method
Appearance	Colourless to light yellow with slight haze	ST-30.1
Colour, Pt-Co	25 max.	ST-30.12
Primary amine, % of total amine	97 min.	ST-5.34
Total acetyltables, meq·g ⁻¹	8.3 min–9.1 max.	ST-31.39
Total amine, meq·g ⁻¹	8.1 min–8.7 max.	ST-5.35
Water, weight %	0.20 max.	ST-31.53, 6
Shelf life, months	36	–
Amine hydrogen equivalent weight (AHEW), g·eq ⁻¹	60	–
Viscosity coefficient at 25°C (77°F), cSt	9.5	–
Density at 25°C, g·mL ⁻¹ (pnd·gal ⁻¹)	0.948 (7.90)	–
pH, 5% aqueous solution	11.7	–

CALCULATION RESULTS AND DISCUSSION

Curing Reactions

The epoxy networks were synthesized from the reaction between difunctional epoxy prepolymer DGEBA and tetrafunctional primary diamine comonomer Jeffamine D-230. Three principal reactions taking place in the curing of a diamine with a diepoxide are illustrated in Figure 3, where epoxy groups react with primary amine H atoms to form secondary amines, which can in turn react with epoxy groups. Therefore a polymer network emerges both chemically and physically. In high temperature or in the presence of catalysts, homopolymerization of epoxy groups would also occur.



Molecular Structure in DGEBA–Jeffamine D-230

From the combination of DGEBA DER332 with Jeffamine D-230, a network having a low crosslink density is obtained and, at room temperature, this network is in the glassy state. The reactivity of aliphatic amines is generally higher than that of aromatic ones. However, because of its long chains and of the presence of methyl groups ($-\text{CH}_3$) close to the amine functions, the kinetics of the reaction between DER332 and Jeffamine is rather slow. The presence of O atoms in the chain must be pointed out, because it induces a high polarity that influences the interactions with SiO_2 . Original, active and reactive functional groups for crosslinked polymers are schemed in Figure 4.

Before analysing the strengthening material, it is instructive to consider how DGEBA and its Jeffamine D-230-cured polymeric forms are synthesized. Figure 5 shows the synthesis of a DGEBA monomer from bisphenol-A and an epoxide; the R-group in the latter is typically a Cl atom. The reactant bisphenol-A and the product DGEBA monomer may be in one of three different structural forms: ortho–ortho, para–para or para–ortho; only the para–para form is shown in Figure 5.

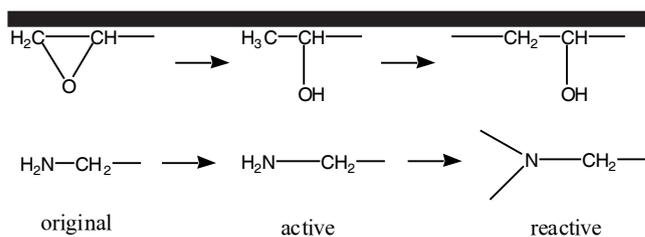


Figure 4. Modelling of functional groups for crosslinked polymers.

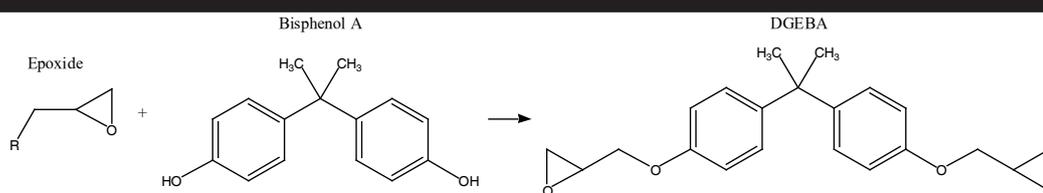


Figure 5. Formation of a DGEBA monomer.

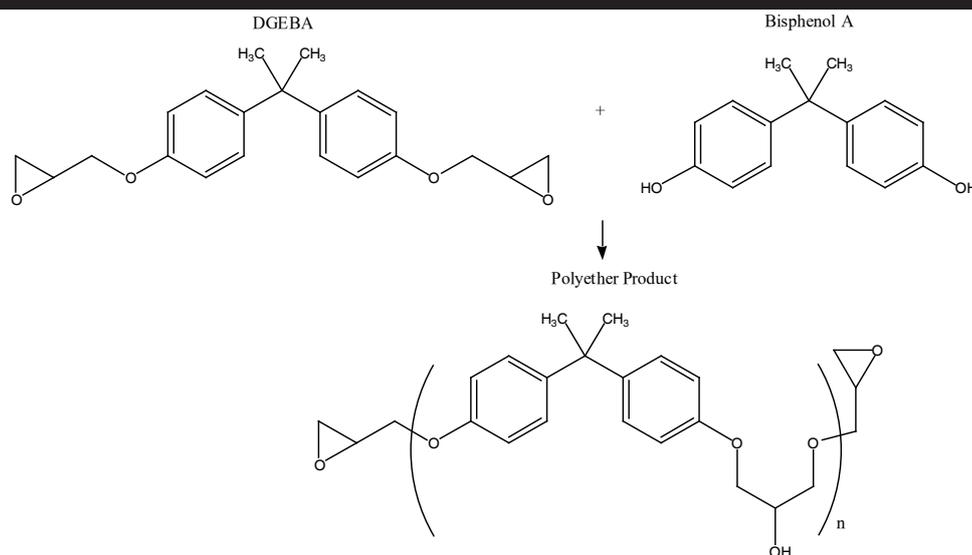


Figure 6. Polyaddition of bisphenol-A to DGEBA forming a polyether product.

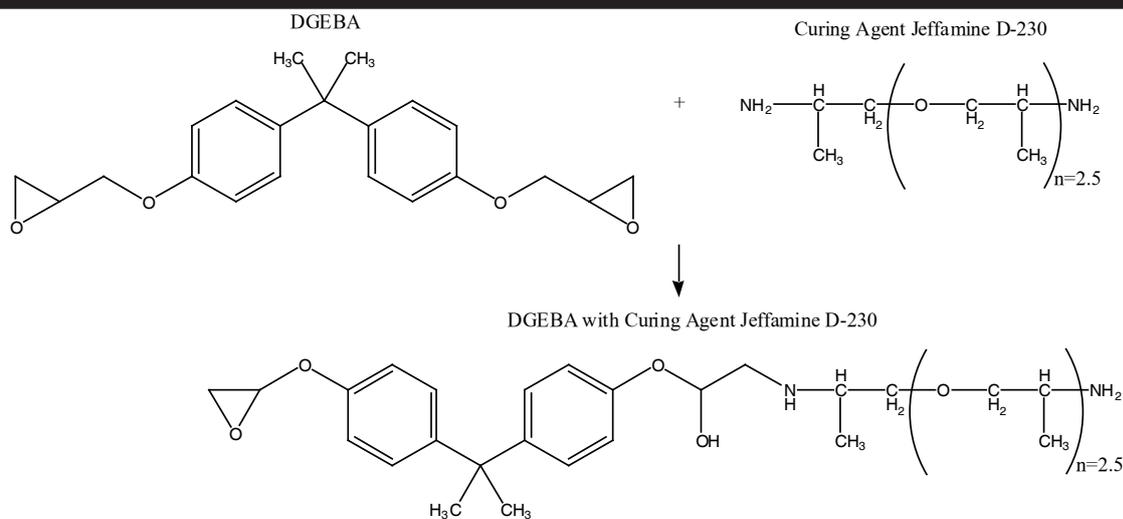


Figure 7. Reaction of DGEBA monomer with curing agent Jeffamine D-230.

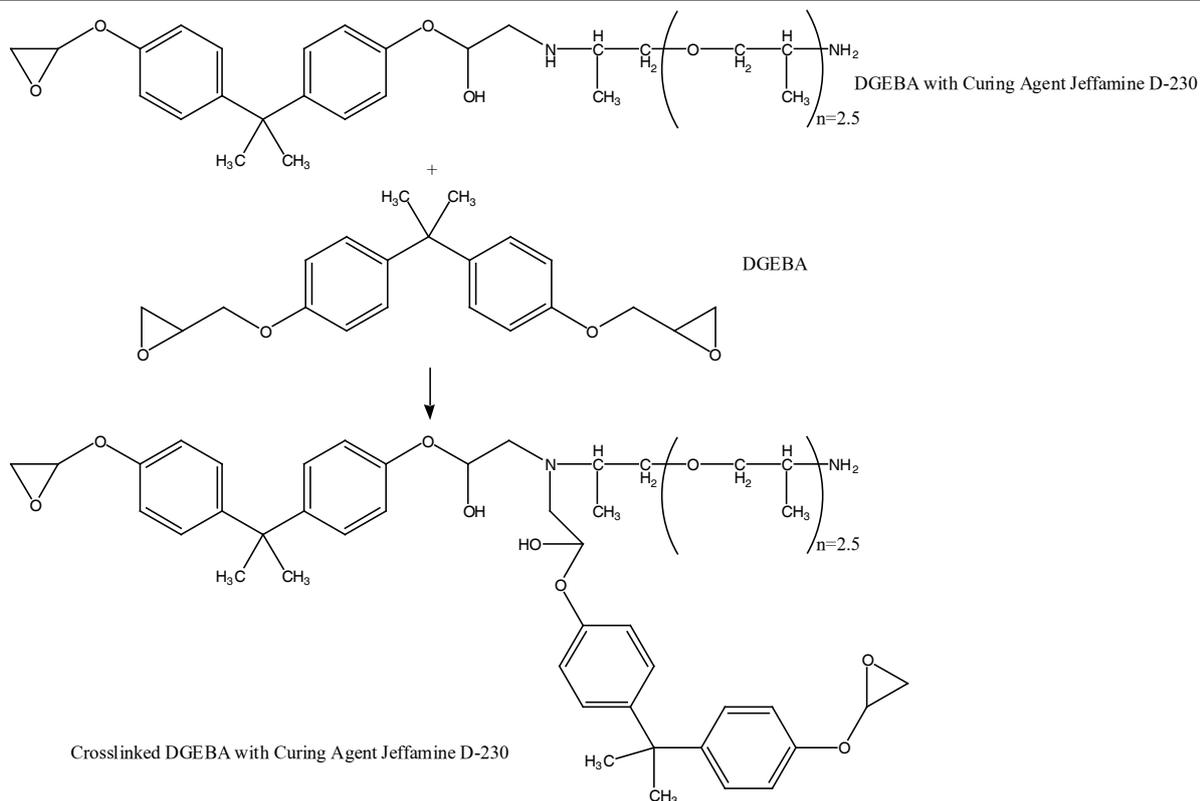


Figure 8. Start of the crosslinking process to form DGEBA–Jeffamine D-230 resin.

During the synthesis, a newly formed DGEBA monomer can also undergo a polyaddition reaction with bisphenol-A as seen in Figure 6, to form a polyether product; the reaction can be enhanced by temperature and an appropriate catalyst.

Next, it is considered the crosslinking of DGEBA monomer (or its extended polyether form) with Jeffamine D-230. Figure 7 shows the

reaction of an epoxide group at the end of the DGEBA monomer with an amine group on the Jeffamine D-230.

The resulting product may react with up to three more epoxide groups, since there are still three H atoms remaining between the two amine groups. Figure 8 shows the start of such further crosslinking, which ultimately leads to the formation of a networked polymer. When



examining the molecular structure of crosslinked DGEBA–Jeffamine D-230, there are considerations to be made regarding: 1) ortho/para structural conformation of DGEBA monomers, 2) fraction of polyether species present (Figure 6) and 3) degree of crosslinking and molecular topology. However, for high degrees of cure the molecular topology has remarkably little effect on properties, e.g., density.

SUMMARY

It was presented the molecular structures of diglycidyl ether of bisphenol-A (DGEBA) and curing agent (Jeffamine D-230), three principal reactions involved in the curing of a diamine with a diepoxide, the modelling of functional groups for crosslinked polymers, the formation of a DGEBA monomer, the polyaddition of bisphenol-A to DGEBA forming a polyether product, the reaction of DGEBA monomer with curing agent Jeffamine D-230 and the start of the crosslinking process to form DGEBA–Jeffamine D-230 resin.

CONCLUSIONS

From the present results and discussion the following conclusions can be drawn.

1. Composites consisting of epoxy cross-linked with SiO₂ nanospheres were synthesised, which show better thermal and may be expected to show better high temperature mechanical properties than the product cured in the absence of nanospheres.

2. As expected, the epoxy resin is chemically connected to the surface of nano-SiO₂. As a result, the following effects can be inferred. (a) Hydrophobicity of the nanoparticles is increased, facilitating the filler/matrix compatibility. (b) Filler/matrix interaction is enhanced via the entanglement between the grafting polymer and the polymer matrix. (c) The nanoparticle agglomerates become stronger because they are now turned into a kind of nanocomposite microstructure consisting of nanoparticles and grafted polymer. (d) The interfacial characteristics between the grafted nanoparticles and matrix polymer can be tailored by changing the species of the grafting polymer and grafting conditions. Collectively, all these inferred effects facilitate a uniform dispersion of nanoparticles in the matrix, which might otherwise pose a critical problem.

3. The mechanical properties of the epoxy nanocomposites, strengthened with SiO₂ spherical nanoparticles unfunctionalized (SiO₂), with SiO₂ nanospheres functionalized with amine groups (SiO₂-amine), with SiO₂ nanoballs functionalized with epoxy groups (SiO₂-epoxy), or with both SiO₂ nanoparticles functionalized with epoxy groups and SiO₂ nanospheres functionalized with amine groups (SiO₂-epoxy + SiO₂-amine), increase up to reinforcement percentages of 3–5 wt.%, as reflected in the study of the storage modulus in shear carried out in dynamic mechanical analysis. The improvement is observed in both glassy and rubbery states, without affecting in an appreciable way the glass transition temperature of the material. From these strengthening percentages the mechanical properties begin to decrease but keeping, in all the studied reinforcement percentages (up to 10 wt.%), a mechanical behaviour (greater storage modulus in shear) higher than the one of the pristine epoxy resin.

4. On the other hand, a slightly erratic behaviour of the storage modulus in shear is observed when, for a given strengthening percentage, the samples with spherical nanoparticles functionalized and unfunctionalized are compared. However, in this behaviour more or less erratic two trends can be discerned: first it is observed that for low strengthening percentages (3 wt.%) the samples, reinforced with both

nanospheres functionalized with amine and nanoballs functionalized with epoxy, show a clearly higher mechanical behaviour; second as the strengthening percentage increases in the nanocomposite, the materials reinforced with SiO₂ nanoparticles functionalized with epoxy groups show a mechanical behaviour higher than the ones of the rest. We think that to improve the mechanical properties in this type of systems, it is important to arrive to a compromise between the percentage of added strengthening (not much higher than 3–5 wt.%), as a function of the precise type of reinforcement.

5. The strong effect of SiO₂ on the storage moduli in shear and loss factor is related to a reduction in the molecular mobility of the macromolecular chains around the filler, because of strong van der Waals interaction established between the SiO₂ surface and the epoxy matrix, e.g., dispersion, and dipolar interaction and hydrogen bonds to SiO₂ silanols. Additionally, these properties no longer increase when the SiO₂ content is increased up to 3–5 wt.%. The corresponding interpretation is that an increase in SiO₂ proportion causes an increase in viscosity, which produces a poorer dispersion.

6. The variation of the flow stress with temperature leads to the following additional conclusions: (a) The main physical parameter determining the flow stress of polymers is the cohesion of the solid state, resulting from intermolecular interactions. The storage modulus in shear gives a good representation of this cohesion, which depends on the chemical nature of the nanoparticles in the composite. (b) The loss of this cohesion, as the temperature increases, corresponds to the main mechanical relaxation associated with the glass transition, which depends on the chemical nature of the nanoparticles in the composite. Actually, some slight differences because of different strain-rate sensitivities are expected to be related to the secondary mechanical relaxation (conformational change-β at the level of hydroxy ether groups) or, even, the third relaxation [conformational change-α at the level of methylene (-CH₂-) units]. In our case such differences are also observed, but they are not as important as the ones detected near the glass transition temperature, in the measured range of temperatures.

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