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THE EFFECT OF EPOXY FUNCTIONALIZED POLYDIMETHYLSILOXANE ON EPOXY RESINS THERMOMECHANICAL AND MORPHOLOGICAL PROPERTIES

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In this study, different hybrid materials based on epoxy resin and epoxy functionalized poly(dimethylsiloxane) used in different weight ratios (95:5wt%, 93:7wt.% and 90:10wt.%) were prepared by in situ polymerization. The effect of poly(dimethylsiloxane) concentration on the features of the obtained networks was investigated through AFM, contact angle measurements, DMA and TGA. The hybrid network with 5wt.% poly(dimethilsiloxane) shows good thermal stability, a well-defined glass transition temperature and a morphology without phase segregation. When 7wt.% or 10wt.% of poly(dimethylsiloxane) was used, the obtained networks exhibit heterogeneous morphologies with phase segregation and lower thermal properties.

Keywords: epoxy resins, diglycidylether terminated poly(dimethylsiloxane), hybrid materials, thermomechanical properties, morphology

1. Introduction

During the recent years, the worldwide interest in the use of high-performance polymer based materials in engineering applications has increased significantly because of their promising technological applications. [1].

Most polymer based materials are prepared by using as polymer matrix a thermosetting resin. Among these thermosets, epoxy resins have been extensively

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used in a wide range of industrial applications as structural adhesives, surface coatings and matrices for (nano)composites due to their advanced chemistry which gives unique combination of properties unattainable by using other thermosetting resins. In general, epoxides exhibit good mechanical and thermal properties, low shrinkage upon cure, excellent adhesion to various substrates, high chemical and corrosion resistance [2-3]. Unfortunately, as a consequence of their highly crosslinked structure, epoxy networks exhibit a brittle behavior, poor crack resistance, and low fracture toughness which decrease the durability of these networks reducing their utility for a large number of high-performance applications [4].

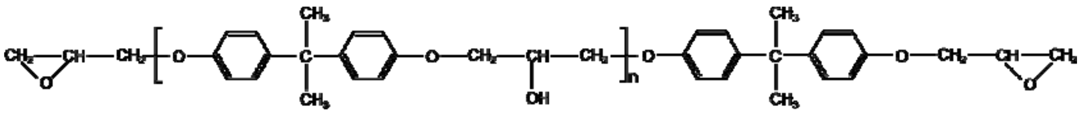
Therefore, according to a detailed literature survey regarding this subject, great efforts have been focused on the modification of epoxy resins for further improvement of multifunctional properties. An entirely different route to extend the range of epoxy polymer products properties consists in blending of epoxy resin with flexible elastomers as polysiloxanes. These kinds of polymer combinations lead to materials with better mechanical and thermal properties. Among flexible elastomers, polydimethylsiloxane (PDMS) was generally selected as modifier to improve the thermal and chemical stability, hydrophobicity, and flexibility at low temperatures of epoxy resins because of its high thermostability and industrial versatility that allows the formation of siloxane hybrids with a large range of organic polymers due to the presence of certain organic groups attached to the Si atoms [5-9].

Based on our previous experience [10-15] in this study we intend to design different hybrid materials by *in situ* polymerization of diglycidylether of bisphenol A (DGEBA) with diglycidylether terminated poly(dimethylsiloxane) (DG-PDMS) used in different weight ratios (95:5wt%, 93:7wt.% and 90:10wt.%). To evaluate the effect of DG-PDMS concentration on the properties of epoxy network, the thermal properties and morphology of the obtained DGEBA:DG-PDMS hybrids were evaluated by using DMA, TGA, AFM and contact angle measurements.

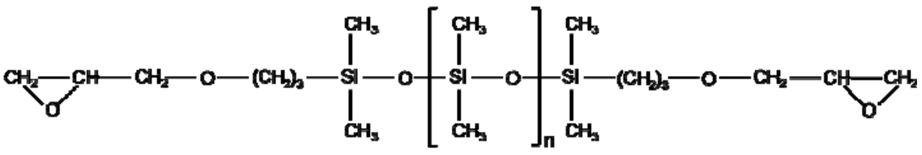
2. Materials and methods

2.1 Materials

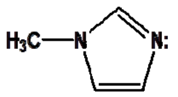
Experimental formulations were prepared by using diglycidylether of bisphenol A (DGEBA) with an epoxy equivalent weight of 171–175g/eq and diglycidylether terminated poly(dimethylsiloxane) (DG-PDMS) having an epoxy equivalent weight of 470g/eq and M_n of 800g/mol. The polymerization reactions were performed in the presence of 1 methyl imidazole (1-MeI). All chemicals were purchased from Sigma-Aldrich Chemicals and used as received, without further purification. The structures of these materials are further displayed in Fig. 1.



Diglycidyl ether of bisphenol A ***(DGEBA)***



Diglycidylether terminated poly(dimethylsiloxane) ***(DG-PDMS)***



1 methyl imidazole ***(1MeI)***

Fig. 1. The chemical structure of raw materials

2.2 Sample preparation

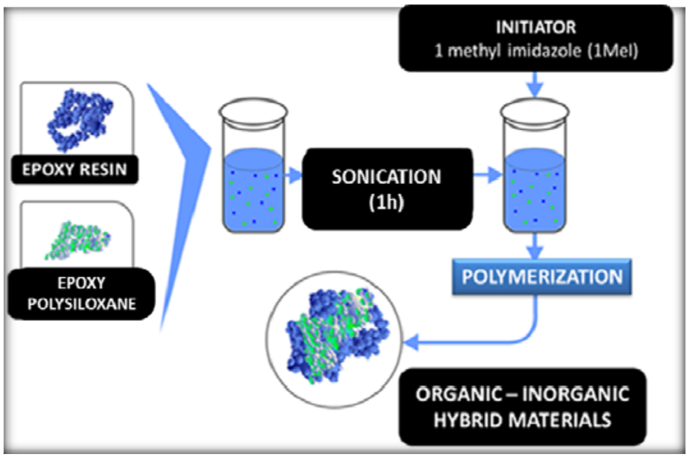
As represented in Table 1, several types of organic–inorganic DGEBA:DG-PDMS networks were synthesized by replacing DGEBA epoxy resin with different DG-PDMS concentrations (5wt.%, 7wt.% and 10wt.%).

Table 1

Compositions of DGEBA:DG-PDMS hybrids

Sample code	DGEBA (wt.%)	DG-PDMS (wt.%)
D0	100	0
D5	95	5
D7	93	7
D10	90	10

The hybrid systems were prepared by *in situ* polymerization in the presence of 1MeI. The curing process was followed 2h at 120°C and 3h at 160°C. To ensure a good homogeneity of DGEBA:DG-PDMS hybrids, the obtained blends undergoes a sonication process for 1h on ice. In Scheme 1 are illustrated the main steps for synthesis of DGEBA:DG-PDMS hybrids.



Scheme 1. Preparation of DGEBA:DG-PDMS hybrids

2.3 Sample characterization

Surface topography was examined by using MultiMode NanoScope IIID Controller Atomic Force Microscope (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA) working in the so-called tapping mode. Images were achieved using a TESP (0.01-0.025 Ohm-cm Antimony (n) doped Si) tip at 1 Hz scan rate. All the measurements were performed in ambient environment. Images were flattened using first order fitting to remove any background tilt. All images were achieved at 10µm size scale. The *roughness measurements* were performed by analyzing a 10x10μm^2 surface area. A minimum of five specimens were tested for each sample and the average values are reported.

Contact angle measurements. The surface wettability was determined using KSV Instruments's CAM 100 by measuring the contact angle on the surface of the films with small water droplets. The contact angles reported represent the mean of three tests.

The *dynamic mechanical analysis (DMA)* tests were run on a Tritec 2000 (Triton Technology) instrument in a single cantilever bending mode from -130 to 200°C using 5°C/min heating rate at a frequency of 1 Hz. The experiment was performed in triplicate.

The *thermogravimetric analysis (TGA)* curves were recorded on a Q500 TA Instrument at 10°C/min heating rate, from 20°C to 650°C, under a constant nitrogen flow rate (balance flow 10mL/min, oven flow 90mL/min). Three different experiments were run for each sample.

3. Results and discussion

3.1 Morphological structure of DGEBA:DG-PDMS hybrid networks

As reported in the literature, polydimethylsiloxane exhibits lower compatibility with epoxy resins even it is functionalized with epoxy groups. To establish the compatibility degree of the selected epoxy functionalized polydimethylsiloxane (DG-PDMS) with DGEBA resin, the morphology of the obtained DGEBA:DG-PDMS networks was investigated through AFM analysis. Using this technique both the surface morphology and the surface roughness (Ra) of the synthesized materials were determined and the obtained 2D, 3D images and Ra values are shown in Fig. 2. Roughness parameter (Ra) represents the arithmetic average of the deviations from the center plane and was measured over the entire image using the roughness analysis option of the 531r1 NanoScope AFM software.

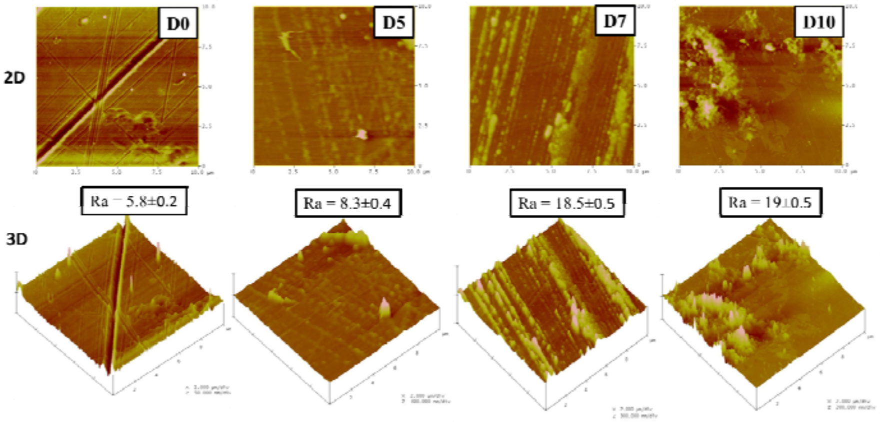
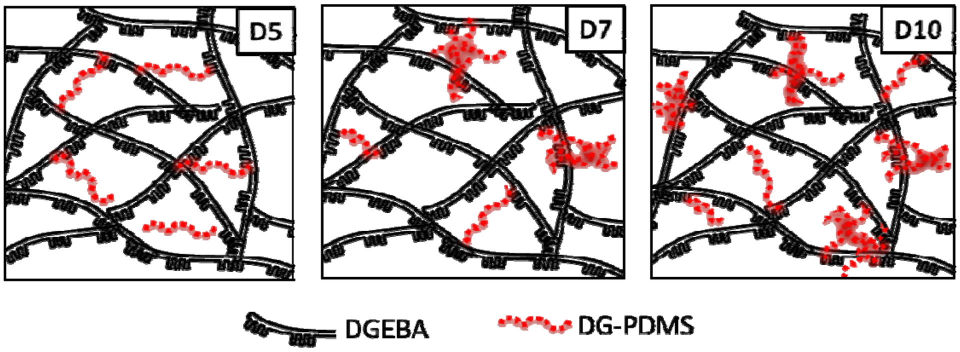


Fig. 2. 2D and 3D AFM images of all the studied samples

Analyzing the 2D and 3D AFM topography images (Fig. 2) obtained for all the studied materials, it may be observed that DG-PDMS is well dispersed within the epoxy matrix when is added in a low concentration (5wt.%). In this case, although the hybrid network consist a mixture of heterogeneous polymers, the obtained material exhibits a relatively smooth surface and it looks like homogeneous.

For D7 and D10 hybrid materials with higher amount of DG-PDMS, two-phase morphology was easily observed. As shown in Fig. 2, the self-assembly tendency of DG-PDMS increase with increasing of DG-PDMS concentration. The topography results were also sustained by the surface roughness (Ra) measurements. The calculated Ra values exhibit an increasing tendency with increasing of DG-PDMS content [8, 16]

For a better understanding of AFM results and to underline the influence of DG-PDMS concentration on the morphology features of the obtained networks a schematic illustration of hybrid materials microstructure is displayed in scheme 2.



Scheme 2. The microstructure of DGEBA:DG-PDMS hybrid materials

Supplementary, another useful method to characterize the surfaces of the obtained networks and to determine the influence of DG-PDMS concentration on the "wettability" of the obtained materials is contact angle measurements.

In Fig. 3 are shown the water contact angles measured for the specimens with different amount of DG-PDMS.

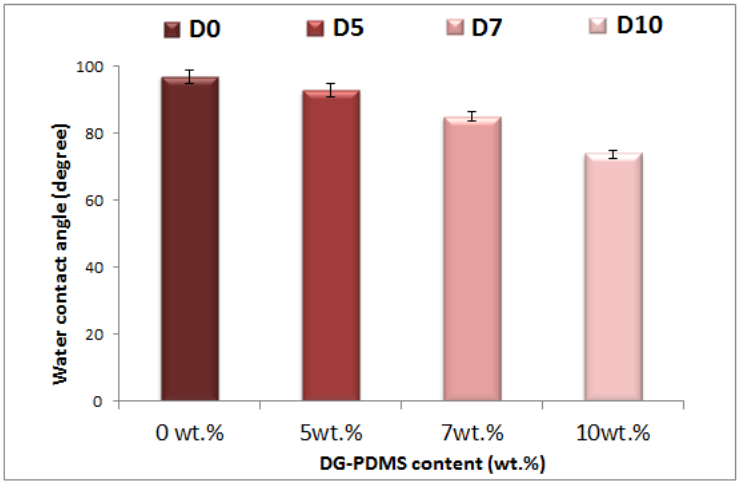


Fig. 3. The influence of DG-PDMS concentration on the hybrid materials wettability

From Fig. 3 it can be observed that the surface hydrophobicity of the resulted materials decreases with increasing of DG-PDMS content. This behavior is probably caused by the numerous hydrophilic OH groups that were formed during the polymerization reaction of epoxy groups.

3.2 The influence of DG-PDMS concentration on the glass transition temperature (T_g) and storage modulus (E') of the obtained hybrids

To study the influence of DG-PDMS concentration on both T_g and E' of the cured DGEBA/DG-PDMS networks, DMA tests were performed (Figs 4-5, Table 2).

As illustrated in Fig. 4 and Table 2, the addition of DG-PDMS in different weight ratios within DGEBA resin results in a decrease of T_g of DGEBA:DG-PDMS hybrids with respect to DGEBA homopolymer (D0).

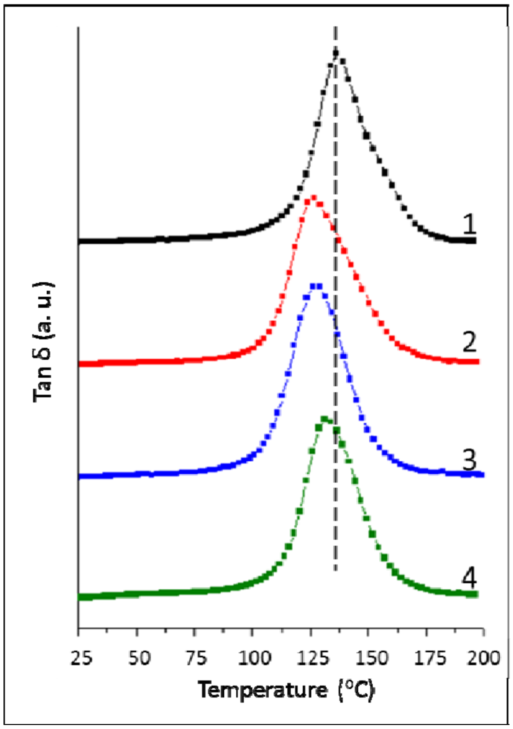


Fig. 4. Tan δ curves against temperature of: 1) D0, 2) D5, 3) D7, 4) D10

Table 2

Thermal features of all DGEBA/DG-PDMS materials

Sample	**DMA**	**TGA**		
	[a]T_g, (°C)	**[b]$T_{d5\%}$, (°C)**	**[c]T_{max}, (°C)**	**[d]Weight loss, (%)**
D0	137	383	440	87
D5	**126**	**397**	**440**	**88**
D7	129	378	440	87
D10	131	372	439	88

[a] T_g = glass transition temperature (maximum of $\tan \delta$);

[b] $T_{d5\%}$ loss = the temperature at which the weight loss is 5%;

[c] T_{max} = the temperature corresponding to the maximum weight loss rate;

[d] the percentage of the weight loss at 600°C.

When 5wt.% of DG-PDMS is introduced within DGEBA resin, T_g of D5 is shifted with 11°C towards lower temperatures (126°C) compared with T_g of D0 (137°C). For D7 and D10 hybrids with 7wt.% or 10wt.% DG-PDMS, the obtained T_g values are also lower than for the corresponding polymer matrix (D0) but are slightly higher than for T_g obtained for D5.

The effect of decreasing T_g is caused mainly by the introduction of DG-PDMS flexible linkages within the epoxy structure which subsequently lead to a lower crosslinking density [17-19]. From Fig 4 and Table 2 it can be observed that the T_g values increase with DG-PDMS content and are shifted towards the T_g obtained for D0. These results are also in concordance with the AFM results indicating that the higher the dispersion degree of DG-PDMS the lower the T_g values.

From Fig. 5 it may be observed that the inclusion of DG-PDMS flexible chains within DGEBA resin reduces also the *E'* of the obtained hybrid networks in both the glassy and rubbery regions [18].

Among all DGEBA:DG-PDMS networks, a noticeable reduction of *E'* was observed for D5. In this case DG-PDMS being well dispersed within DGEBA resin leads to a lower crosslinking density. When higher amounts of DG-PDMS were used, the corresponding hybrid networks, D7and D10, exhibit higher *E'* than D5. For these hybrids a heterogeneous morphology was obtained which means that only a small part of DG-PDMS is dispersed within DGEBA resin. Increasing the DG-PDMS content the *E'* curves are shifted towards the *E'* registered for D0.

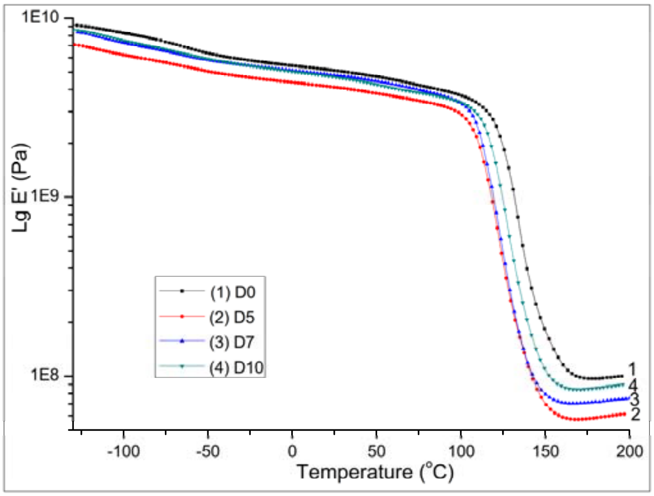


Fig. 5. Storage modulus (E') plots versus temperature of all the studied materials

3.3 The influence of DG-PDMS concentration on the thermostability of DGEBA:DG-PDMS hybrids

To investigate the effect of DG-PDMS concentration on the DGEBA:DG-PDMS hybrids thermostability, TGA / DTG measurements were performed and the obtained results are reported in Fig. 6 and Table 2.

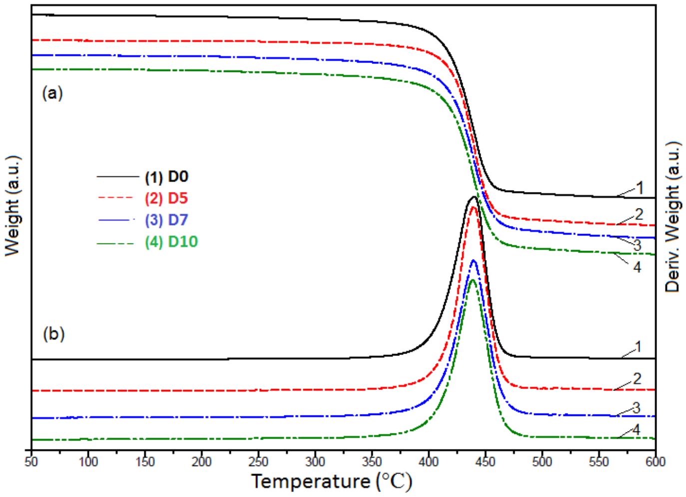


Fig. 6. TGA (a) and DTG (b) curves of all the studied materials

From Fig. 6 it may be observed that the thermal degradation of the studied hybrids occurs in one stage as DGEBA homopolymer (D0). This behavior suggests that the incorporation of different concentrations of DG-PDMS within DGEBA matrix exhibits no influence on the thermodegradation mechanism of epoxy network.

From Table 2 it can be observed that all the obtained hybrid networks are thermally stable up to 370°C. Among all DGEBA:DG-PDMS hybrids the highest thermostability was obtained for D5. In this case the obtained $T_{d5\%}$ value is with 14°C higher compared with the $T_{d5\%}$ registered for DGEBA homopolymer.

When 7wt.% or 10wt.% of poly(dimethylsiloxane) was used the obtained D7 and D10 networks exhibits lower thermal properties in comparison with D0 and with D5 system. As one may see from AFM images (Fig. 2) this behavior is probably a consequence of the heterogeneous structure of the obtained networks in which DG-PDMS forms large aggregates.

4. Conclusions

Hybrid networks containing diglycidylether of bisphenol A (DGEBA) and diglycidylether terminated poly(dimethylsiloxane) (DG-PDMS) in different weight ratios (95:5wt%, 93:7wt.%, 90:10wt) were prepared by in situ polymerization.

The morphological properties of DGEBA:DG-PDMS hybrids were investigated through AFM and contact angle measurements. The obtained results reveal that the hybrid network with 5wt.% poly(dimethylsiloxane) shows a morphology without phase segregation while the hybrids with higher amounts (7wt.% and 10wt.%) of DG-PDMS exhibit heterogeneous structures.

These results are also in good agreement with DMA and TGA tests indicating that a good dispersion degree of DG-PDMS within DGEBA leads to hybrid materials (D5) with lower T_g values and storage modulus (E') and with improved thermostability. The obtained TGA results indicate that for D5 the obtained $T_{d5\%}$ value is with 14°C higher than $T_{d5\%}$ registered for DGEBA homopolymer.

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