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# Morphology, flexural, and thermal properties of sepiolite modified epoxy resins with different curing agents

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## Abstract

A bisphenol A-based epoxy resin was modified with 5 wt% organically modified sepiolite (Pangel B40) and thermally cured using two different curing agents: an aliphatic diamine (Jeffamine D230, D230) and a cycloaliphatic diamine (3DCM). The morphology of the cured materials was established by scanning and transmission electron microscopy analysis. The thermal stability, thermo-mechanical properties, and flexural behaviour of the sepiolite-modified matrices were evaluated and compared with the corresponding neat matrix. The initial thermal decomposition temperature did not change with the addition of sepiolite. The flexural modulus of the epoxy matrix slightly increases by the incorporation of the organophilic sepiolite. The flexural strength of the sepiolite modified resin cured with D230 increased by a 10% while the sepiolite modified resin cured with 3DCM resulted in a lower flexural strength compared with the unmodified resin. The reduced flexural strength was attributed to the stress concentrations caused by the sepiolite modifier, which rendered the resins more brittle.

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## 1. Introduction

The demand for advanced materials with better properties to meet new requirements or to replace existing materials is incessantly increasing. Among them, epoxy resins are one of the most important

classes of thermosetting polymers. These networks have many desirable properties, which include high modulus, excellent chemical and corrosion resistance, good dimensional stability and high working temperature. They are extensively used in many applications such as coatings, adhesives, laminates and matrices for composite materials and structural components. Unfortunately, these highly crosslinked networks are inherently brittle and consequently have limited utility in applications requiring high

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fracture strength. Moreover, being organic materials they degrade to give volatile combustible products when they are heated above critical temperatures or involved in fires. Among the different curing paths, amine-cured epoxies are one of the most commonly used matrix materials in engineering applications of reinforced polymeric matrix composites, in part due to their excellent engineering performance and ease of processing prior to cure. Depending on the chemical structure of the curing agent, it is possible to vary the mechanical properties ranging from extreme flexibility to high strength and hardness, and the physical properties such as adhesive strength, chemical resistance, heat resistance and electrical resistance. Different chemical compositions permit to process over a wide range of temperatures and control the degree of crosslinking [1–4].

In order to improve toughness and thermal resistance, the addition of filler particles of micro-/nano size is being a common practice, because it improves not only the mechanical properties of the resulting polymer, but also reduces significantly the processing cost [5–9]. This improvement depends strongly on the particle content, particle shape and size, surface characteristics and degree of dispersion [8–17]. It has been reported that the mechanical and thermomechanical properties of composites filled with micron-sized filler particles are inferior to those filled with nanoparticles of the same filler [12]. Pioneering work by Toyota researchers led to the discovery of nanoscale polymer–clay hybrid composites for lightweight material applications, even at very low clay content [18,19]. In addition, the improved physical properties, such as surface smoothness and barrier properties, cannot be achieved by using conventional micron-sized particles. Therefore, in recent years, nanoparticle based composites have drawn considerable attention [5–25]. The improvements of these nanoparticle-modified polymers, such as clay nanocomposites, are achieved through conventional processing techniques and without affecting substantially the density of the matrix. These nanocomposites are now being considered for a wide range of applications including packaging, coating, electronic, automotive and aerospace industries. It is generally believed that the improvement of properties of clay nanocomposites is directly related to the homogenous dispersion of silicate layers in the polymer matrix (known as exfoliation). However, a processing technique that produces complete dispersion is still

a technical challenge, probably due to the high viscosity of the polymer matrix and the strong tendency of clay nanoparticles to agglomerate. In this sense, thermoplastic polymer nanocomposites have been studied extensively while thermoset polymer nanocomposites are beginning to receive attention [14–17,22,25–27]. It has been reported that the degree of silicate exfoliation attained in thermoset composites depends on the structure and percentage of the clay, the curing temperature and the curing agent [14–17,20,27]. However, it is interesting to note that the precise mechanism by which the properties enhancements are achieved remains a matter of ongoing debate.

The objective of the present work was to study the influence of the addition of sepiolite upon some selected properties of an epoxy resin. Composite materials containing 5 wt% organically modified sepiolite (Pangel B40) were fabricated and the mechanical, thermal and viscoelastic properties of the resultant composites were evaluated.

In this work, we use sepiolite as inorganic filler, that is, a microcrystalline-hydrated magnesium silicate with  $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH},\text{F})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$  as the unit cell formula [28] that exhibits a micro fibrous morphology with a particle length of 2–10  $\mu\text{m}$ . Structurally it is formed by an alternation of blocks and cavities (tunnels) that grow up in the fibre direction. The unique structure of sepiolite [28–30] induces sorptive, colloidal/rheological and catalytic properties, which find a variety of diverse applications. Since it is demonstrated that the curing agent and curing conditions, among other conditions, play a determinant role in the dispersion extent of the inorganic filler in the polymer matrix [16,27], two different amine curing agents (aliphatic and cycloaliphatic) were used in combination with a diglycidyl ether bisphenol A epoxy resin. The morphology development of the clay in the nanocomposites is characterised by scanning (SEM) and transmission electron microscopy (TEM). The flexural strength of the unmodified and modified epoxy resins were determined by flexural tests.

## 2. Experimental

### 2.1. Materials

The epoxy resin used was a commercial diglycidyl ether of bisphenol-A (DGEBA), Araldit GY 250 kindly provided by Vantico Spain. The epoxy content was 5.34 eq/kg, as determined by acid titration

[31], weight per equivalent of 187.3 g/eq and hydroxyl/epoxy ratio of 0.122. The curing agent were a diamine terminated polypropylene oxide Jeffamine D230 (D230) kindly supplied by Huntsman Corporation (equivalent [H] weight: 57.5) and a cycloaliphatic diamine 3,3'-dimethylmethylenedi(cyclohexylamine) (3DCM) from BASF. Stoichiometric ratio epoxy/amine,  $[E]/[H]=1$ , was used for this study. The clay modifier was sepiolite Pangel B40 kindly supplied by Tolsa (Spain). It is an organophilic sepiolite, obtained from pristine sepiolite by means of specific physico-chemical purification, micronization and chemical modification processes developed and patented by Tolsa. The micronization leads essentially to a disagglomeration of the bundles of microfibrils thus favouring interactions between sepiolite particles and polymer chains. On the other hand, the hydrophilic surface of sepiolite was modified with benzylbis(hydrogenated tallow alkyl) methyl chloride in order to make it more compatible with low polarity polymers. Fig. 1 depicts the chemical structures of the different reagents.

## 2.2. Sample preparation

The unmodified epoxy resin (UER) was prepared by mixing the epoxy prepolymer (GY 250) with the stoichiometric amount of the curing agent at 75 °C, outgassing the liquid mixture under vacuum and

pouring immediately the mixture into moulds. To prepare the sepiolite modified epoxy resin (MER), the dried sepiolite (5% of sepiolite over the total weight) was slowly added to the required amount of epoxy prepolymer while stirring the mixture under high shear at 75 °C for 1 h. The mixture was completely degassed under vacuum at 75 °C, then the curing agent was slowly added and the mixture was poured into the mould.

Plates were obtained by casting the mixtures into moulds consisting of two rectangular glass plaques covered with Freetoke release agent spaced by a 5 mm Teflon frame and held together with clamps. The cure schedule was 3 h at 75 °C and 12 h at 110 °C with Jeffamine D230, and 4 h at 75 °C and 3 h at 160 °C with 3DCM. The cured plaques were allowed to cool slowly to room temperature, removed from the mould and cut to produce bars for mechanical testing. Dynamic differential scanning calorimetry (DSC) scans of all samples confirm that they were fully cured since no residual heat was detected after a dynamic temperature scan.

## 2.3. Dynamic mechanical properties

Dynamic mechanical analysis (DMA) of both unmodified and modified resins were performed on a 2980 Dynamic Mechanic Analyzer (TA instruments) in the three point bending mode. The experiments were carried out on prismatic samples of

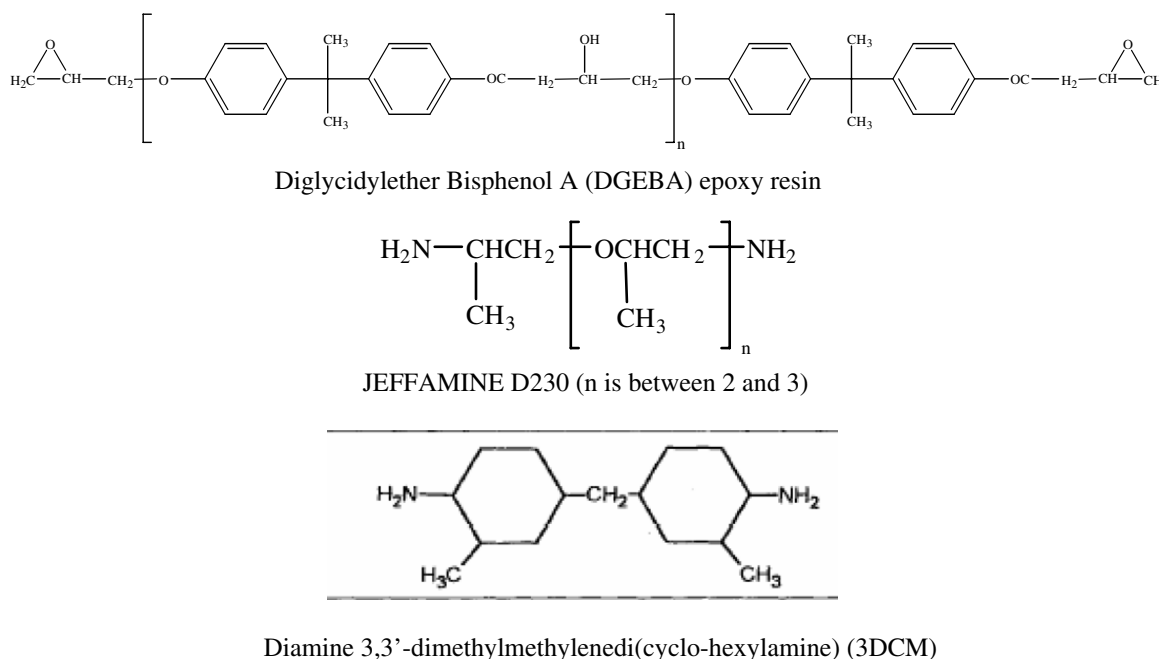


Fig. 1. Chemical structures of epoxy resin GY250, Jeffamine D230 and 3DCM.

dimensions 50 mm × 12 mm × 5 mm. Experimental conditions employed were frequency of 1 Hz and amplitude of 30 μm with a temperature ramp of 3 °C/min and a scanning temperature range from 35 to 175 °C. These experiments yield the storage modulus,  $E'$ , the loss modulus,  $E''$ , and the damping factor  $\tan \delta$  ( $=E''/E'$ ). The glass transition temperature,  $T_g$ , was determined from the peak of the  $\tan \delta$  curve. At least three tests were carried out for each case.

#### 2.4. Scanning and transmission electron microscopy

The morphology of the composites was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Sepiolite modified epoxy samples were fractured at ambient temperature. The morphology of the fractured surface by SEM was analyzed by using a Hitachi S-4100 with an acceleration of 10 kV and a distance between 12 and 14 mm. The TEM specimen was cut from a composite block using an ultramicrotome, Reichert–Jung Ultracut-*E*, equipped with a diamond knife. A thin specimen (80 nm) was cut from a sample of about 1 × 1 mm<sup>2</sup>. It was collected in a trough filled with water and placed on a 200 mesh copper grid. The composite structure was observed using a Jeol TEM at an acceleration voltage of 100 kV.

#### 2.5. Thermo-gravimetric analysis (TGA)

The thermal stability of the composites was investigated using a TGA Perkin Elmer 7. The TGA scans were recorded at a temperature ramp of 5 °C/min under constant argon flow of 100 ml/min from room temperature to 1000 °C.

#### 2.6. Flexural properties

The unmodified and 5 wt% sepiolite modified epoxy resins were tested under flexure using the three-point bending experiment according to ASTM D790 protocol [32] on an Instron 5582 Universal Tester at (23 ± 2) °C and crosshead displacement rate of 5 mm/min. The specimen dimensions were equal to (5 ± 0.1) mm × (10 ± 0.2) mm cross-section and (100 ± 5) mm in length. The length between supports was 80 mm as recommended by the protocol.

The flexural strength ( $\sigma_f$ ), the maximum strain in the outer fibre ( $\varepsilon$ ) and the flexural modulus ( $E$ ) were

calculated from the following expressions by loading the bars to failure:

$$\sigma_f = \frac{3FL}{2bd^2} \quad (1)$$

$$\varepsilon = \frac{6\delta d}{L^2} \quad (2)$$

$$E = \frac{L^3 s}{4bd^3} \quad (3)$$

where  $F$  is the load at break,  $b$  and  $d$  are the width and the thickness of the specimen respectively,  $L$  is the length between supports,  $\delta$  is the maximum deflection of the centre of the beam and  $s$  is the slope of the tangent to the initial straight-line portion of the load-deflection curve.

According to the protocol, Eq. (1) is valid if the maximum outer-fibre strain,  $\sigma_f$ , is lower than 5%. If strains exceed 5% before fracture, the following expression is recommended [33]:

$$\sigma_f = \frac{3FL}{2bd^2} \left[ 1 + 6 \left( \frac{\delta}{L} \right)^2 - 4 \left( \frac{\delta d}{L^2} \right) \right] \quad (4)$$

### 3. Results and discussion

#### 3.1. Characterization

The morphology of the cured epoxy/sepiolite resins was determined by means of scanning and transmission electron microscopy. The pure epoxy matrix is transparent but the addition of sepiolite made the composite opaque. Figs. 2 and 3 show typical SEM and TEM images of the composites, as an example.

Scanning electron microscopy has the advantage to give a broad overview of the microscale dispersion of the silicate in these materials. For pure epoxy, the fracture surface was smooth, typical of a glassy material. In contrast, as can be seen in Fig. 2, the specimens containing sepiolite showed a considerable fracture surface roughness. The presence of the reinforcement would force the crack to progress along a more tortuous path, increasing the fracture surface area. The individual silicate fibres are extremely strong and are unlikely to break during crack growth. The lower magnification picture shows bright spots corresponding to small bundles of sepiolite fibres. The SEM images show a combination of shear cups and coarse features with debonding between matrix and sepiolite at different locations. It can be assumed that the sepiolite is debonded from the epoxy matrix under loading and

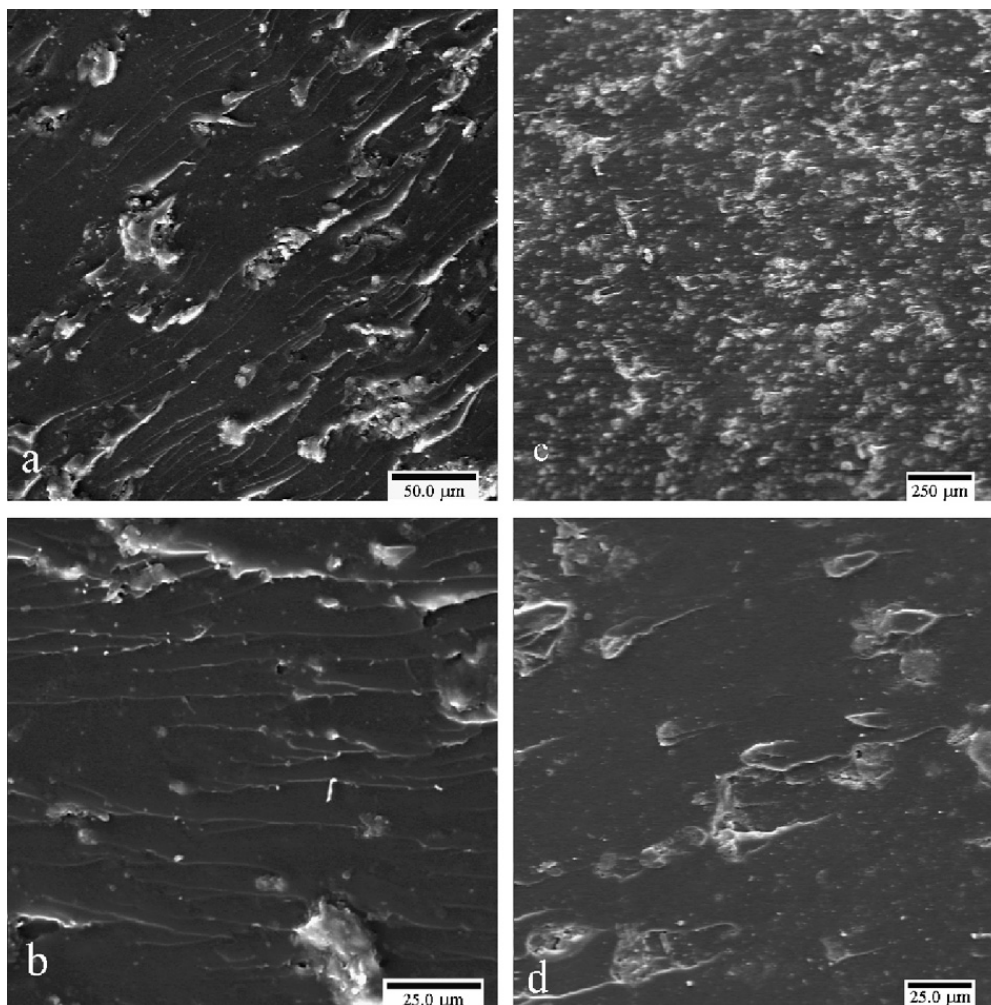


Fig. 2. SEM images of epoxy/sepiolite samples cured with 3DCM (a, b) and with Jeffamine D230 (c, d).

generate microcracks which upon further loading join to form a single dominant crack. These pictures show small aggregates of sepiolite, indicating that the individual fibres are not fully dispersed in the epoxy matrix.

The structure of the cured samples was further studied by transmission electron microscopy. We cannot use X-ray diffraction (XRD) as usual in layered silicate nanocomposites since for sepiolite the RX signal refers to the sepiolite tunnels and not to the separation between fibres. Fig. 3 shows the transmission electron images of the 5% sepiolite modified epoxy resin cured with 3DCM (a, b) and cured with Jeffamine D230 (c, d). The pictures display signs of the original ordering of the silicate layers (dark lines). The clay fibres are not uniformly distributed, and large regions of pure epoxy are observed. A closer observation of the photograph at higher magnification reveals that each dark line often corresponds to several sepiolite fibres which

stick together to build up bundles of fibres which can themselves form agglomerated structures. The presence of those structures was also observed in other systems [15,34]. TEM analysis reveals that the epoxy resin and hardener cannot be effectively well diffused between the fibres and so, they are not individually separated upon polymerization, the fibres remain agglomerated. As reported by Kornamnn [16], the epoxy system based on the 3,3'-dimethyl substituted curing agent (3DCM) shows higher reactivity than the system cured with Jeffamine D230. (the lower the reactivity, the better the dispersion, the higher the degree of exfoliation for epoxy/layered silicate systems). By comparing different curing agents, the authors concluded that the reactivity of the epoxy system is not the only factor controlling the dispersion of the clay. Both the polymerisation rate of the system and the rate of intercalation of the curing agent and epoxy in the clay galleries or between the filler particles influence

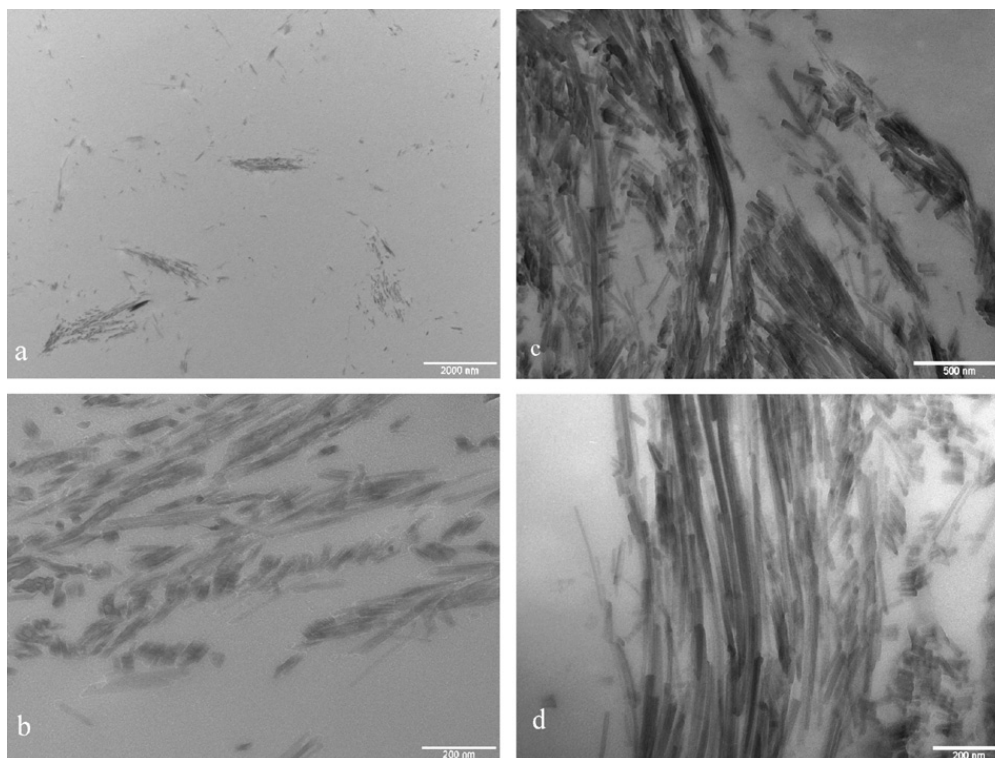


Fig. 3. TEM images of the sepiolite modified resin cured with 3DCM (a, b) and with Jeffamine D230 (c, d).

the dispersion of the clay in the epoxy matrix. Similarly, it appears that in order to obtain a more homogenous dispersion of the sepiolite fibres we should improve, as well, the interaction epoxy/sepiolite surface.

### 3.2. Viscoelastic properties

We use dynamic mechanical analysis (DMA) to study how different morphologies influence the mobility of the polymer. DMA plots are depicted in Fig. 4 as the variation of storage modulus and loss tangent with temperature for the modified and unmodified epoxy cured with 3DCM (Fig. 4a) and with D230 (Fig. 4b). In all cases, as the temperature increases, both pure and modified epoxy show a gradual drop in storage modulus followed by a sudden drop at the glass transition temperature ( $T_g$ ).

The glass transition of the modified 3DCM cured matrix is similar to that of the unmodified system (170 °C) while the storage modulus in the glassy state is increased in about 15% because of incorporation of 5% sepiolite into the epoxy matrix. The system cured with Jeffamine D230 shows a storage modulus in the glassy state about 19% higher than that of the unmodified one. The glass transition temperature is higher for 3DCM cured epoxy

because the cycloaliphatic groups of the curing agent bring some stiffness to the network as compared with the polyoxyalkylene chain of Jeffamine D230. Whilst increased glass transition temperatures were reported in some cases of nanocomposite systems, others have found a constant or slightly decreased  $T_g$  [16,25,35–37]. A decrease indicates that it is not an “adsorbed silicate” effect as this usually increases the glass transition temperature due to chains being tied down by the silicate’s surface. The presence of sepiolite has little effect on the temperature location of the glass transition temperature whereas the increase in modulus is more significant.

### 3.3. Thermal stability

The thermal stability of composites was determined using a thermo-gravimetric analyzer. Fig. 5 shows the TGA curves of the unmodified and sepiolite modified epoxy cured using the two different curing agents 3DCM and Jeffamine D230. All systems exhibit thermal degradation and significant weight loss with temperature. In addition, the thermal degradation always occurs in one-step. The peak degradation temperature was determined from the first derivative of the TGA curve: 321 °C and

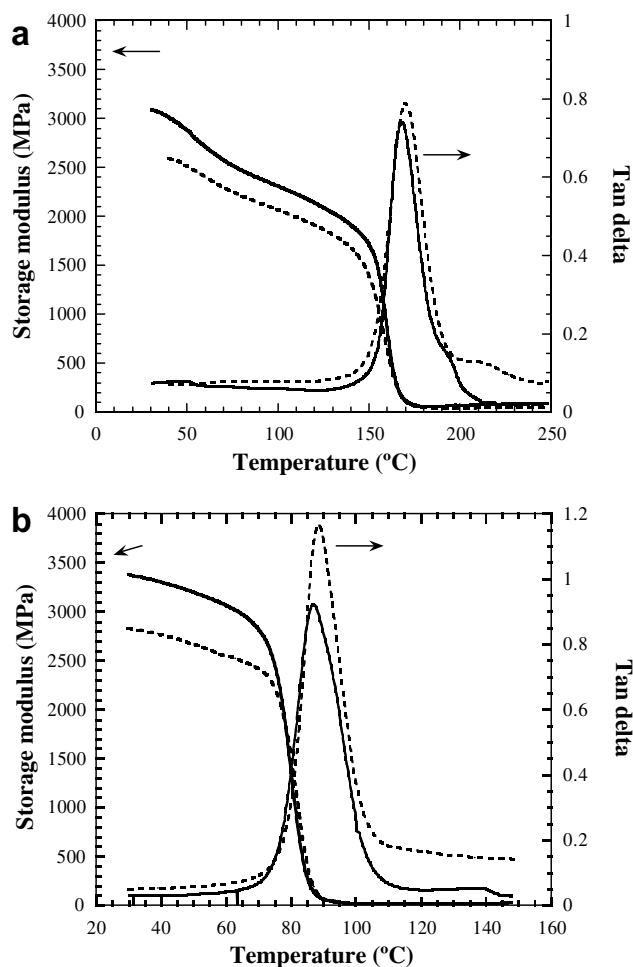


Fig. 4. Dynamic mechanical properties of the unmodified (dashed line) and 5% sepiolite modified epoxy resin (continuous line) cured with 3DCM (a) and with Jeffamine D230 (b).

327 °C for 3DCM and Jeffamine D230, respectively. The onset and the end set of thermal degradation temperature were determined from the intersection of two tangents. Table 1 lists these values together with the degradation temperatures at 5%, 10%, 50% and 80% weight loss as well as the non-volatile part or char content. The initial thermal decomposition temperature did not change with the addition of sepiolite and was very similar for the two cured systems. However, the interval of weight loss was the opposite in 3DCM systems than for those cured using Jeffamine D230. Jeffamine D230 as curing

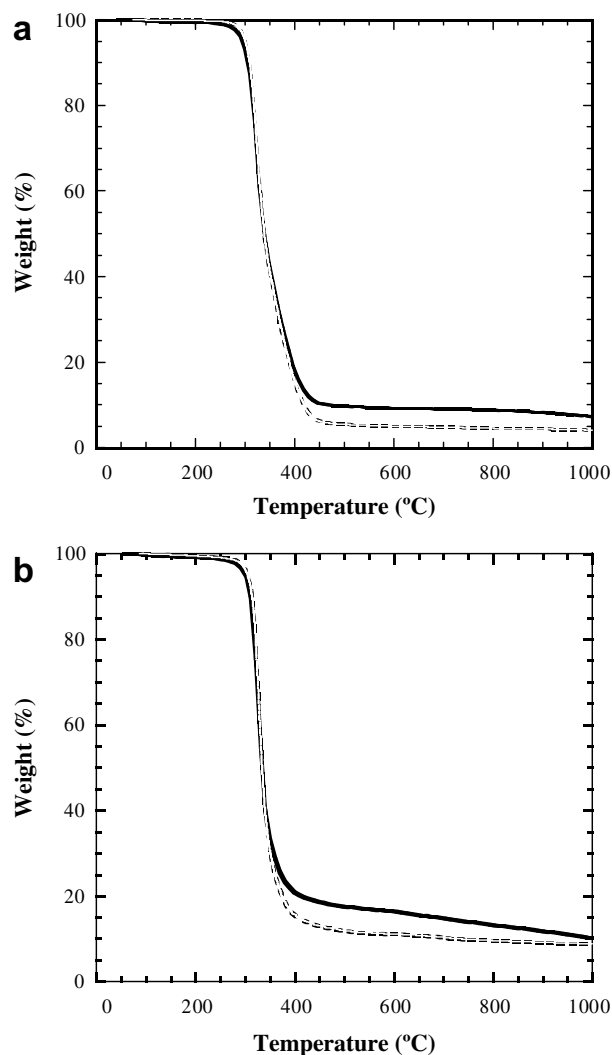


Fig. 5. Thermo-gravimetric analysis of the unmodified (dashed line) and sepiolite modified epoxy resin (continuous line) cured with 3DCM (part a) and with Jeffamine D230 (part b).

agent reduces the endset 11°, whereas using 3DCM it was increased by 11°.

The thermograms obtained during TGA scans were analyzed to give the percentage weight loss as a function of temperature (Table 1).  $T_5$ ,  $T_{10}$  and  $T_{50}$  (temperature of 5%, 10% and 50% weight loss, respectively) are the main criteria to indicate the thermal stability of the composites. The higher the values are, the higher is the thermal stability. It can

Table 1

Thermal analysis data for pure epoxy and 5 wt% Pangel B40 sepiolite modified epoxy cured with 3DCM and Jeffamine D230

System	Onset (°C)	Endset (°C)	$T_5$ (°C)	$T_{10}$ (°C)	$T_{50}$ (°C)	$T_{80}$ (°C)	Char (%)
3DCM	306	397	300	308	338	389	4
3DCM/B40	306	408	295	306	339	395	8
D230	308	353	304	313	334	374	9
D230/B40	308	342	301	311	333	415	10



be seen that  $T_5$ ,  $T_{10}$  and  $T_{50}$  are practically identical for both the modified and the unmodified resin. To observe a difference between them, it is necessary to overcome the 50% or 60% of weight loss in 3DCM or Jeffamine D230 systems, respectively.

3DCM pure epoxy shows a char content of 4%, the modified one shows about 8%, whereas Jeffamine D230 pure epoxy shows a char content of 9%, the modified one shows about 10%. These degradation data show no significant difference when the sepiolite is incorporated, which would be consistent with a poor dispersion of the clay and poor diffusion of the resin between fibres, as said before.

### 3.4. Flexural test

Flexural tests were performed to evaluate the stiffness and strength of unmodified and sepiolite modified epoxy systems. Fig. 6 shows typical stress–strain curves obtained during the tests for

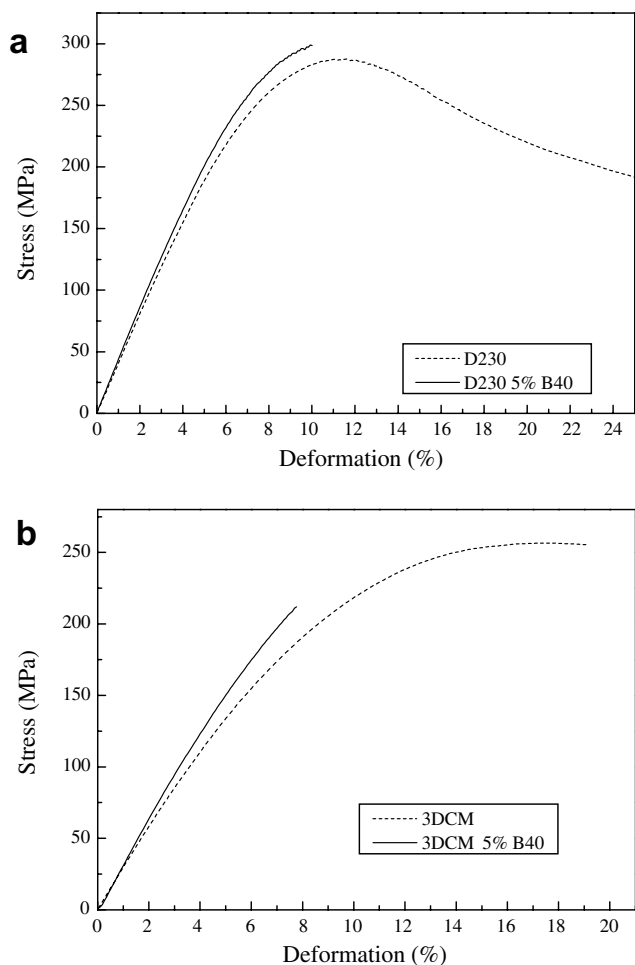


Fig. 6. Typical stress–strain plots for the unmodified and sepiolite modified epoxy resin cured with: (a) Jeffamine D230 and (b) 3DCM.

Table 2

Flexural strength ( $\sigma_f$ ), deformation at break ( $\varepsilon$ ) and flexural modulus ( $E$ ) for the unmodified epoxy resin (UER) and the 5 wt% sepiolite modified epoxy resin (MER) using the two curing agents

Curing agent	System	$\sigma_f$ (MPa)	$\varepsilon$ (%)	$E$ (GPa)
3DCM	UER	133.99 (11.6)	7.39 (1.32)	2.56 (0.02)
3DCM	MER	105.07 (16.6)	4.67 (0.96)	2.65 (0.06)
D230	UER	112.67 (5.4)	12.3 (1.6)	3.08 (0.04)
D230	MER	121.82 (2.6)	7.77 (1.10)	3.31 (0.02)

Standard deviation is given in parenthesis.

the 3DCM (part a) and Jeffamine D230 (part b) cured epoxy resin, respectively. The stress–strain curves reveal that the addition of sepiolite resulted in a considerable less plasticity compared with the unmodified systems. Except for the sepiolite modified resin cured with 3DCM, all samples displayed a strain at fracture value higher than 5%; so, in that cases the flexural strength was calculated from Eq. (4). Table 2 compiles the average properties obtained from 25 of these tests. As can be seen, irrespective of the curing agent used, the flexural modulus of the resin slightly increases by the incorporation of the organophillic sepiolite. About 8–10% improvement of the flexural strength and modulus has been obtained in the sepiolite modified Jeffamine cured system. Improving the dispersion of sepiolite into the epoxy matrix will probably improve the flexural properties. When the composites are under load, the fibres in the clusters may produce a high stress concentration and cause premature failure [23,24]. According with the results shown in Fig. 6, the reduced plasticity of the modified resins is attributed to the stress concentrations caused by the sepiolite modifier. The variation of flexural properties is similar to that found in other systems, such as graphite platelet epoxy resins [36].

## 4. Conclusions

Morphological, flexural and thermal properties of a bisphenol A-based epoxy resin modified with organophillic sepiolite PangelB40 and cured using an aliphatic and a cycloaliphatic diamines were determined experimentally. The morphology of the cured samples, as seen by SEM and TEM, shows that a complete separation of the sepiolite fibres was not attained, small bundles of fibres are seen. DMA data revealed slightly influence of the sepiolite on the glass transition temperature, while the modulus in the glassy state increases compared with

the unmodified resins. All systems exhibit thermal degradation and significant weight loss with temperature in one step, that is not significantly altered by the presence of 5% of sepiolite. The flexural modulus of the epoxy resin slightly increases by the incorporation of the organophillic sepiolite. The flexural strength show about a 10% increase for the modified resin cured with D230.

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