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Polymer 40 (1999) 935–943

polymer

Effects of thermal treatments on the viscoelastic behavior of the interphase relaxation in a compatibilized thermoset/thermoplastic blend

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Received 18 February 1997; revised 23 February 1998; accepted 26 March 1998

Abstract

Morphology and viscoelastic properties of a compatibilized epoxy/thermoplastic polymer blend were investigated. Transmission electron microscopy (TEM) showed that the introduction of the compatibilizer significantly reduces the size of the thermoplastic dispersed phase. Dynamic mechanical spectrometry (DMS) revealed an additional loss peak at about 333 K at 1 Hz in the compatibilized ternary blend spectrum which is detailed as the first unequivocal observation of a 'micromechanical transition' in a compatibilized thermoset/thermoplastic blend. In addition, the influence of thermal treatments (which were established according to structural recovery considerations, i.e. accelerated physical aging at $T_g - 20$ K and 'refreshing' process at $T_g + 20$ K) on the viscoelastic behavior (amplitude and temperature position) of the additional loss peak was studied. These investigations revealed that the occurrence of the 'micromechanical transition' on DMS spectra depends significantly on the thermal history of the sample and leads to the assumption that the viscoelastic behavior of the interphase relaxation is associated with the conditions of confinement of the components in the interphase zone. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Thermoset-thermoplastic blend; Micromechanical transition; Physical ageing

1. Introduction

In general, two or more polymers may be blended to form a wide variety of random or structured morphologies in order to obtain materials which can combine the characteristics of both components. This is an important technical advantage since polymer blends allow production of new materials by using pre-existing materials, thus reducing development costs. However, it may be difficult or impossible in practice to achieve these potential combinations through simple blending since most polymers are thermodynamically immiscible and form multiphase systems with weak physical and chemical interactions between phases.

It is well known that the presence of polymeric species, such as selected block or graft copolymers can avoid a macrophase separation or large particle sizes of the dispersed phase [1–5]. The effect of compatibilizers or emulsifiers on the structure of immiscible polymer blends has been investigated for many years. Earlier investigations focused mainly on immiscible binary blends of A and B homopolymers to which A–B block- or graft-copolymers were added [6–8]. Later on, studies were made of blends with compatibilizers consisting of components where one was identical to one of the homopolymers and the other was chemically different but completely miscible with the other homopolymer (A–C copolymer) [9]. Another way is to study polymer blends based on two immiscible homopolymers with C–D block- or graft-copolymers, where A and B were miscible with the C and D blocks [10,11], respectively. An efficient compatibilizer should:

1. reduce the interfacial energy between phases leading to a finer dispersion,
2. provide a notable stability against large-scale segregation, and
3. result in an improved interfacial adhesion.

It is well known that mechanical and viscoelastic properties of multiphase polymeric materials depend on the molecular relaxation processes. These can be associated with each constituent and their appearance depends also on the interactions between the phases. A zero thickness interface cannot be considered a realistic description of the continuity between phases even for immiscible polymers: at the molecular scale, one of the reasons is the

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PII S0032-3861(98)00303-6

ability for the macromolecules to be intermingled with each other because of their reptation movements, which can be evidenced by molecular dynamics simulation [12,13] or reflectivity techniques [14]. Generally, authors consider an interphase which could be defined as a region having a finite distance neighboring the dispersed phase. The properties of this interfacial region can differ from those of the pure components. The study of the interphases in multiphase materials (polymer blends and composites) remains an important subject of research since the interphase properties strongly affect the properties of these materials. Indeed, the lack of strong interphases in a majority of blends (due to the thermodynamic immiscibility of most polymer pairs) limits the stress transfer across the phase boundaries. Although the concept of the interphase is rapidly gaining acceptance, its in-situ detection and characterization remain a problem.

Dynamic mechanical spectrometry was shown to be an excellent way [15–23] for such a purpose. In fact, mechanical spectrometry allows a complete exploration of relaxational mechanisms in viscoelastic materials. In certain cases, a specific interphase can be previously introduced [15]. For example, by coating fibers or fillers with a thin layer of polymer, such as rubber, before inclusion in the composite, an interphase was located at the filler or fiber surface. However, in most cases, an interphase may be created in-situ. Different hypotheses were reported to justify the presence of an interphase in multiphase materials:

1. a polymer layer having a higher stiffness than the bulk polymer in the vicinity of the dispersed phase surface is created from a restricted molecular mobility due to interactions between phases [16–22],
2. a region close to the surface having a composition varying from the inclusion surface to the bulk matrix because of preferential adsorption of one of the components [23],
3. a region close to the surface having a different composition because of the incomplete dissolution of the fiber surface sizing in the reactive mixture of the matrix [24],
4. a layer close to the surface with different mechanical properties resulting from the residual thermal stresses, the adsorbed water, or the presence of voids [25,26].

Thus, an additional peak on the loss curve modulus can reveal an interphase region in the case of multiphase systems where viscoelastic properties are different from those in other regions in the material.

On the other hand, an additional peak cannot correspond to that of an interphase. Numerous examples were reported in the literature [27–29] concerning the appearance of an additional loss peak above the main relaxation peak, T_α, associated with the glass transition of the matrix. This can be associated for example, with an incomplete cure of the matrix, which then undergoes further curing as the temperature of testing exceeds T_g [27,28] or a drying of the sample during heating [29].

In addition, as reported by Thomason [30], an additional peak in fiber-reinforced polymer composites could be evidenced as an interphase relaxation. However, these investigations showed that it was an experimental artifact due to a complex interaction of the instrument, the thermal conductivity of the samples, the heating rate during experiment and the sample modulus above T_g.

Eklind et al. [31] recently studied the viscoelastic properties of compatibilized poly(2,6-dimethyl-*p*-phenylene ether) and poly(methyl methacrylate) (PPE/PMMA) blends by dynamic mechanical spectrometry. An interphase created by a poly(styrene-*graft*-ethylene oxide) (P(S-g-EO)) copolymer was found to significantly change the dynamic mechanical behavior of these ternary blends of thermoplastic polymers, and it was shown that the addition of the copolymer results in a new loss peak on the DMS spectra of the blends. Experimental data were compared to simulation by using a mechanical model: the new ‘transition’ was theoretically shown to be a ‘micromechanical transition’. It was explained by the change in the relative moduli values of the components in the matrix-interphase-particle structure of the blends, and not to originate from a molecular transition in any of the constituents. The ‘micromechanical transition’ temperature was predicted to depend on the Poisson ratio and on the volume fraction of the interphase.

In this paper, a compatibilized epoxy/thermoplastic polymer blend has been considered. The aim of the present work is to point out that the observation of a ‘micromechanical transition’ is not a peculiarity of ternary blends of thermoplastic polymers. In addition, the influence of thermal treatments on the viscoelastic behavior of what appears as an interphase relaxation has been investigated.

2. Experimental

2.1. Materials and sample preparation

An epoxy prepolymer, the diglycidyl ether of Bisphenol A (DGEBA from Dow Chemical DER332, $M_n = 348.5$ g/mol) with a low polydispersity index ($n = 0.03$) was used. The 4,4′-methylene bis[3-chloro-2,6-diethylaniline] (MCDEA from Lonza, $M_n = 380$ g/mol) was used as hardener (stoichiometric ratio amino-hydrogen-to-epoxy equal to 1). The cure schedule was 7 h at 408 K followed by post-curing at 458 K for 2 h. The synthesis of the epoxy network, i.e. the reaction kinetics and further characterization, was detailed in a previous paper [32].

The high-T_g thermoplastic used was poly(phenylene ether) (PPE from General Electric, $M_n = 12$ kg/mol, $M_w/M_n = 2$).

The compatibilizer used in this study was based on a grafted maleic anhydride (MA) triblock copolymer poly(styrene-b-ethylene-co-butene-b-styrene) (P(S-b-EB-b-S)). P(S-b-EB-b-S) was a commercial triblock copolymer from Shell (designated as Kraton FG, $M_n = 52.5$ kg/mol [PS: 7.5 kg/mol, PEB: 37.5 kg/mol], f_n(MA) = 10.4, wt.%(MA) = 1.94). Maleic anhydride functions were reacted with the diamine, MCDEA, in order to link the block copolymer to the epoxy network by means of the central block, whereas the PS blocks are miscible to PPE. Through this paper, the compatibilizer will be noted MCDEA-g-K or simply, compatibilizer.

MCDEA-g-K was prepared in a two-stage process. First, P(S-b-EB-b-S) and MCDEA were dissolved separately in toluene and then mixed. In order to avoid crosslinking, the grafting reaction was accomplished in a large excess of MCDEA (the unreacted amine functions will be taken into account further with the comonomers of the epoxy matrix). After solvent extraction under vacuum, the mixture was cured at 413 K for 4 h followed by a post-curing at 423 K for 2 h.

The compatibilized epoxy/thermoplastic polymer blend was prepared in a four-stage process. PPE and MCDEA-g-K were first dissolved in toluene, then DGEBA was added. The curing of the thermoplastic/epoxy mixture was performed at 433 K for 4 h followed by 2 h at 458 K. The resulting polymer blend contained 1.5 wt.% of MCDEA-g-K in a DGEBA/MCDEA network which contains 10 wt.% of PPE. Throughout this paper, this blend is denoted as M10PPE1.5MCDEA-g-K or simply, blend. The processing of the compatibilized epoxy/thermoplastic polymer blend was defined by Girard-Reydet et al. [32]. The morphology of the blend was controlled by knowledge of the competition between reaction kinetics and phase separation thermodynamics in epoxy/thermoplastic mixture, and of the modifications of the interfacial tension between the phases which follow the addition of the compatibilizer.

2.2. Samples characterization

Differential Scanning Calorimetry (DSC) thermograms were recorded using a DSC 7 Perkin Elmer device with a heating rate of 10 K/min under a nitrogen atmosphere.

For the dynamic mechanical properties, the dynamic analyzer Rheometric Scientific DMTA MK III was used operating in a double cantilever mode under isochronal conditions at frequencies of 0.3, 1, 3, and 10 Hz to measure the temperature dependence of the viscoelastic properties E^* (storage, E', and loss, E'', moduli) from 143 to 423 K with a heating rate of 1 K/min. The samples were approximately 27 mm long, 6 mm wide, and 1 mm thick.

2.3. Thermal treatment

The different temperatures concerning the thermal treatment of M10PPE1.5MCDEA-g-K samples were defined from differential scanning calorimetry experiments. The DSC trace displays the glass transition temperature, T_g, of the epoxy in M10PPE1.5kg MCDEA at 438 K (onset). No exothermal peak (during the first heating) and no increase of T_g (during a second heating) were observed. As a consequence, the epoxy network can be considered as fully reacted, *i.e.* 438 K is the maximum glass transition temperature and the following treatments cannot induce any chemical changes. The temperatures which were considered for further thermal treatments, are the following:

1. 458 K ($T_g + 20$ K) as the temperature for which the samples were refreshed.
2. 418 K ($T_g - 20$ K) as a temperature which leads to classical structural recovery (physical ageing).

As a consequence, in this paper, the samples were denoted as:

1. *'as received'* for samples without any thermal treatment after curing. Nevertheless, the samples have been left at least for 18 months, in classical laboratory conditions, before our first experiments.
2. *'refreshed'* for *'as received'* samples treated for 30 min at $T_g + 20$ K in the furnace of the DMTA, and then cooled down to room temperature with a cooling rate of 15 K/min.
3. *'aged'* for *'refreshed'* samples treated for 45 h at $T_g - 20$ K and then cooled slowly to room temperature at about 1 K/min.

3. Results and discussion

3.1. Evidence of an interphase in the blend M10PPE1.5MCDEA-g-K

The compatibilizer MCDEA-g-K is based on PS blocks which are miscible with the PPE chain, a central EB block totally immiscible with both epoxy and PPE, and the side-grafted MCDEA which can react in-situ with epoxy functions from DGEBA during curing of the PPE/reactive epoxy mixture. TEM analysis [32] demonstrated (Fig. 1) that the introduction of the compatibilizer significantly reduces the interfacial tension, thus leads to a decrease of particle size of the dispersed phase in the blend. Moreover, micrographs revealed the absence of a clear interface between the epoxy matrix and the thermoplastic dispersed phase. Thus, we can consider that the addition of an emulsifier leads to the creation of an interphase.

3.2. Viscoelastic characteristics of the pure components of the blend (epoxy matrix, PPE, and grafted-compatibilizer)

The experimental dynamic mechanical values of the storage modulus (E') and the loss factor (tan δ) at 1 Hz for the pure components (PPE and DGEBA-MCDEA matrix) are given in Fig. 2. It can be shown that the α-relaxation modes of both DGEBA-MCDEA and PPE appear at 467 K and 503 K, respectively. The β-relaxation mode of DGEBA-MCDEA—associated [15] with motions of small units of the macromolecular chains (hydroxyether groups and diphenylpropane units)—can be seen about 203 K. The slight relaxational process evidenced between

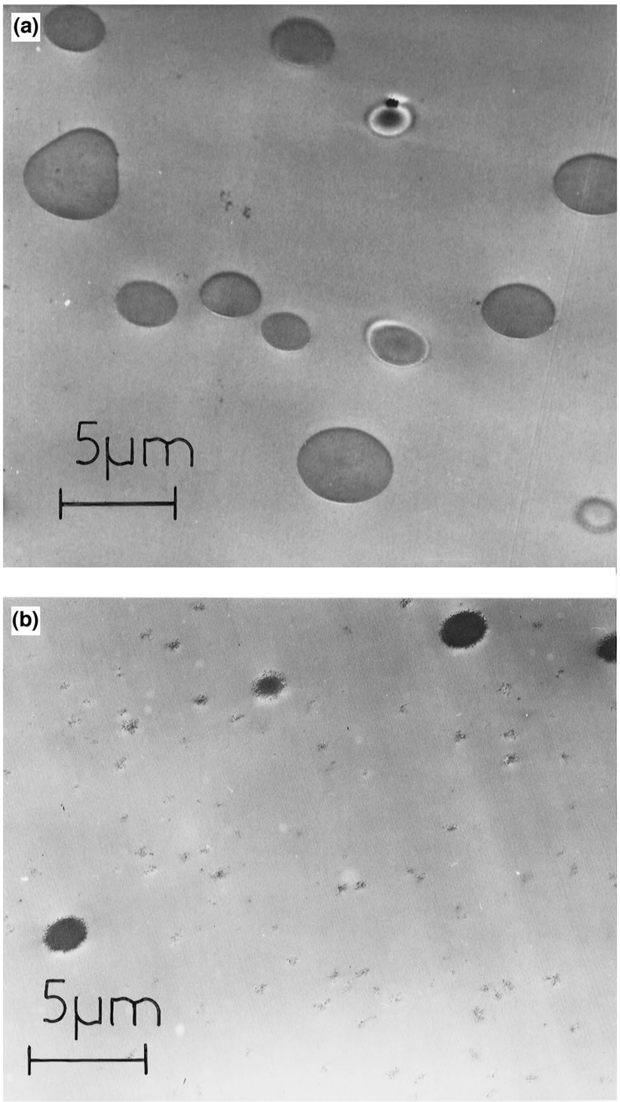

Fig. 1. Morphologies of blends observed by transmission electron microscopy (TEM) (a) M10PPE without compatibilizer; (b) MCDEA-g-K compatibilized DGEBA-MCDEA/PPE (10 wt.%).

the main (α) and secondary (β) relaxations of DGEBA-MCDEA network can be related to the classical ω-relaxation of epoxy materials. Numerous papers [35–43] concerning epoxy matrix composites reveal such as intermediate relaxation. In the past, Pogany [35] and Arridge and Speak [36] attributed it to the motions of less-crosslinked zones in the network, but now epoxy-amine networks are well-known to be homogeneous. Ochi and coworkers [37,38] associated ω with motions of the p-phenylene groups. Other authors [39–43] consider this additional relaxation as a probe of the structural or molecular rearrangements within the network resulting from the moisture sorption. Indeed, ω relaxation is extremely sensitive to moisture sorption: the amplitude of its corresponding peak on the viscoelastic spectra increases in the presence of water. In spite of all these results, the ω-relaxation assessment in terms of molecular mobility appears uncertain in literature.

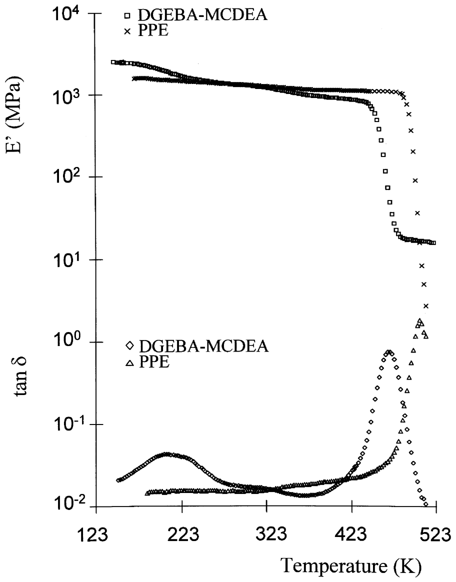

Fig. 2. Storage modulus, E', versus temperature at 1 Hz for: □ DGEBA-MCDEA network, × PPE. Loss factor, tan δ, versus temperature at 1 Hz for: ◇ DGEBA-MCDEA network, △ PPE.

The grafted MCDEA in the compatibilizer can react with the epoxy groups during the curing of the reactive mixture. Then, the definition of the constituent which would be the most representative of the effective component in the interphase region is questionable. It can be assumed that the viscoelastic properties of 'real' component should be intermediate between those of the pure Kraton FG and those of a crosslinked Kraton. This is synthesized from the reaction of Kraton FG and MCDEA in stoichiometric conditions (anhydride-to-amine equal to 1). The experimental dynamic mechanical values of the storage modulus and the loss factor

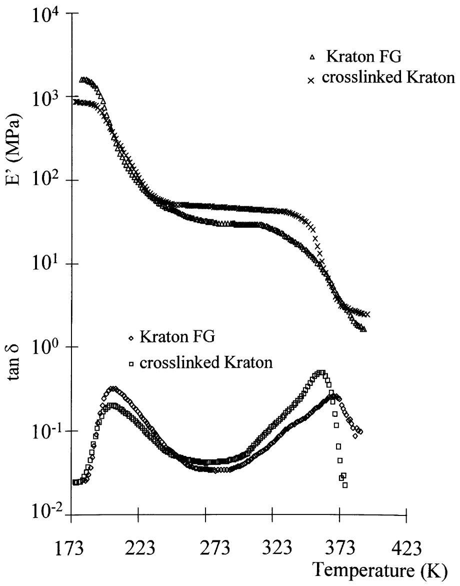

Fig. 3. Storage modulus, E', versus temperature at 1 Hz for: △ Kraton FG, × crosslinked Kraton. Loss factor, tan δ, versus temperature at 1 Hz for: ◇ Kraton FG, □ crosslinked Kraton.

for these model interphase components (Kraton FG and crosslinked Kraton) are given in Fig. 3. It can be shown that the loss factor spectra of both models of the interphase component reveal a first maximum at about 203 K and a second at about 363 K which correspond to the α-relaxation modes of the poly(ethylene-co-butene) elastomer and polystyrene blocks of the triblock copolymer, respectively. It can be noticed that T_α of the polystyrene blocks is slightly lower than that of a classical polystyrene because of the low molar mass of the polystyrene blocks in the Kraton FG. Moreover, the segregation of the polystyrene blocks seems to be affected by the crosslinking process. As can be shown in Fig. 3, the relaxation associated with the polystyrene blocks appears better defined on the DMS spectra of the crosslinked Kraton than on that of the Kraton FG.

Concerning the temperature evolution of moduli, Figs 2 and 3 show clearly a change in the relative modulus values in the temperature range between 123 and 423 K. Indeed, as the temperature increases, the decrease of the modulus is stronger for the model interphase components than for the two main constituents (thermoplastic PPE and DGEBA-MCDEA thermoset matrix) of the blend.

3.3. Viscoelastic characteristics of ‘as received’ blend

The experimental dynamic mechanical values of the storage modulus and the loss factor for ‘as received’ blend are given in Fig. 4. It can be seen that only 10 wt.% of a thermoplastic dispersed phase did not significantly affect the storage modulus of epoxy matrix. Indeed, no changes for storage modulus in the blend (compared to those of the two pure components) were induced by mixing PPE with epoxy in the presence of a grafted-compatibilizer. This is due to the low amount of rubbery component in the blend. The β-relaxation mode of thermoset continuous phase appears at a slightly higher temperature than the pure DGEBA-MCDEA network. The dynamic mechanical spectrum displays a maximum (at 484 K) and a weak shoulder (at 497 K) at high temperature corresponding to the α-relaxation modes of thermoset-rich and thermoplastic-rich phases, respectively. T_α of thermoset is higher than for the pure epoxy network whereas T_α of thermoplastic is lower than for the pure PPE. These modifications of the temperature position of T_α of thermoset and thermoplastic were already observed [32] in a binary blend of DGEBA-MCDEA and PPE. The effects of mechanical coupling could support these observations.

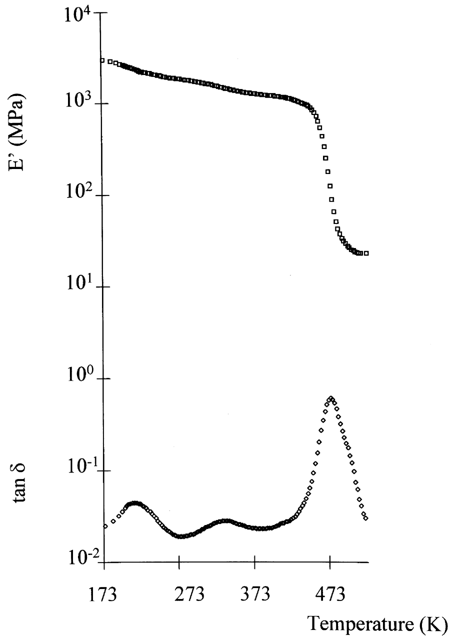

Fig. 4. Viscoelastic characteristics versus temperature at 1 Hz for MCDEA-g-K compatibilized DGEBA-MCDEA/PPE (10 wt.%). □ Storage modulus, E'. ◇ Loss factor.

In addition to the relaxations associated with the two main phases (dispersed, continuous), an additional loss peak can be seen at about 333 K in the compatibilized epoxy/thermoplastic polymer blend spectrum. This additional peak does not correspond to a secondary relaxation of one of the pure components (see Figs 2 and 3).

In fact, TEM analysis revealed the presence of an interphase. Moreover, the viscoelastic analysis (Figs 2 and 3) revealed the relative temperature-dependent moduli of the components of the blend (DGEBA-MCDEA, PPE, and models of the interphase component) at temperatures higher than 323 K. Thus, although grafted amine groups in the compatibilizer can react in-situ with the epoxy groups of the matrix and participate in the crosslinking process, the additional transition at about 333 K can be considered a ‘micromechanical transition’, as defined by Maurer and coworkers [31]. Such a ‘transition’ results from the combined influence of the microstructure of the blend including an interphase and the relative temperature-dependent moduli of the components of the blend. In order to support the assumption of a ‘micromechanical transition’, dynamic mechanical analyses were performed in a frequency range from 0.3 to 10 Hz. Considering an Arrhenius dependence of the relaxation process, the apparent activation energy of the additional ‘transition’ was calculated. Such apparent activation energy is about 135 kJ/mol. In previous work [34], Eklind and Maurer estimated at 170 kJ/mol the apparent activation energy of the ‘micromechanical transition’ in ternary thermoplastic blends. The two energy values are in the same order.

Thus, our results display the first complete description of a ‘micromechanical transition’ in a compatibilized thermoset/thermoplastic blend. Earlier, such a transition was only observed [31,33,34] in ternary thermoplastic blends.

3.4. Consequences of thermal treatments on the viscoelastic properties of the compatibilized blend

The influence of thermal treatment on the observed ‘micromechanical transition’ can be seen. The evolution with temperature of the experimental dynamic mechanical

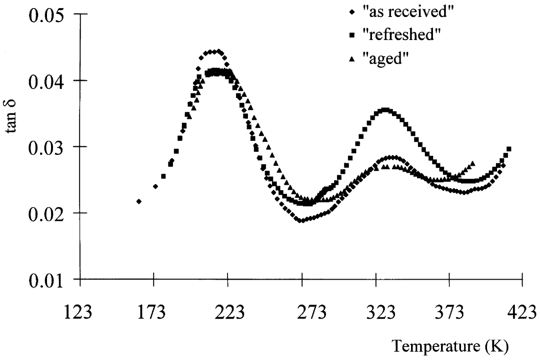

Fig. 5. Loss factor, tan δ, versus temperature at 1 Hz for the compatibilized DGEBA-MCDEA/PPE blend after different thermal treatments; ◆ 'as received'; ■ 'refreshed'; ▲ 'aged'.

values of the loss factor (tan δ at 1 Hz) is given in Fig. 5 for the various thermal treatments described previously (denoted 'as received', 'refreshed', and 'aged').

In order to quantify the relative intensity of each relaxation (β and 'micromechanical transition', mmt), the amplitude of relaxations, denoted h_β and h_{mmt} respectively, were measured in considering arbitrary the minimum value of the three tan δ curves at about 273 K. As the width of all relaxations does not change significantly with thermal treatment, the h_β/h_{mmt} ratio is chosen as a sensitive indicator of the relative importance of the two relaxations located between 123 K and 423 K (i.e. the relative importance of the 'micromechanical transition' compared to the β-relaxation mode increases at the same time as the h_β/h_{mmt} ratio decreases). The amplitudes h_β, h_{mmt}, and their ratio as well as the temperature position of each relaxation are listed in Table 1.

In this temperature region, a thermal effect on the viscoelastic spectra is observed. While the β-relaxation is not affected by 'refreshing' with or without an additional physical aging treatment, the amplitude and the temperature position of the 'micromechanical transition' are dependent on the thermal treatment. It can be seen in Table 1 that the relative amplitude of the 'micromechanical transition' increases significantly after 'refreshing' the sample and decreases after an additional physical aging. In fact, the value of the h_β/h_{mmt} ratio is higher for the 'aged' sample than for the 'as received' one. In addition to that, the temperature position of the 'micromechanical transition (T_{mmt}) decreases by 5 K when the 'as received' sample is 'refreshed'. After the accelerated physical aging, this temperature position appears to be identical to the initial one. On the other hand, no significant changes in the temperature position of the β-relaxation (T_β) can be noted.

Table 1
Characteristics of β-relaxation of the continuous epoxy phase and the 'micromechanical transition' (mmt) at 1 Hz

	'As received'	'Refreshed'	'Aged'
T_β (K)	214	214	215
T_{mmt} (K)	335	330	335
h_β ($\times 10^2$)	272	208	205
h_{mmt} ($\times 10^2$)	104	152	61
h_β/h_{mmt}	2.62	1.37	3.36

Experimental data obtained by Maurer and coworkers [31] were compared to a theoretical mechanical model. According to experimental and theoretical results concerning the ternary thermoplastic blends, the T_{mmt} value was predicted to depend on the Poisson ratio and the volume fraction of the interphase. In fact, while the volume fraction of the interphase increased, the temperature position of the 'micromechanical transition' decreased. In the different state of the compatibilized epoxy/thermoplastic polymer blend, the 'refreshing' treatment (458 K) increases the molecular mobility in the main amorphous components of the blend, as usual. This makes easier the reptation of their chains in the interphase, *i.e.* increases the interpenetrating of species in the interfacial area, and as a consequence, the volume fraction of the interphase in the blend.

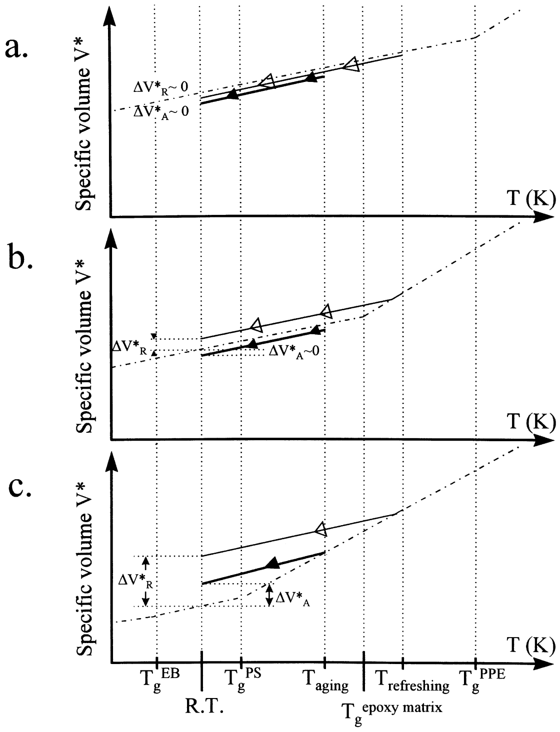

Fig. 6. Illustration of the plausible evolution of the specific volume V^* for the components of the blend (neat and in the blend) with different thermal treatments; (a) PPE-rich phase; (b) Epoxy-rich phase; (c) Kraton interphase; – · – classical evolution of specific volume V^* for the neat components; -◁- illustration, for each component in the blend, of the evolution of V^* immediately after the refreshing process and during cooling of the sample until room temperature; -◀- illustration, for each component in the blend, of the evolution of V^* immediately after the ageing process and during cooling of the sample until room temperature; ΔV^*_{R}, variation of V^* for each component in the blend after the refreshing process; ΔV^*_{A}, variation of V^* for each component in the blend after the ageing process; RT, room temperature; $T_{\mathrm{g}}^{\mathrm{EB}}$, $T_{\mathrm{g}}^{\mathrm{PS}}$ glass transition of the poly(ethylene-co-butene) elastomer (EB) and of the polystyrene blocks (PS) in Kraton interphase, respectively.

According to classical dilatometric variations and taking into consideration the mutual influence of the state of the neighboring component, an illustration of the plausible evolution of the specific volume V^* during cooling (to room temperature), which is applied to the samples immediately after the 'refreshing' and 'aging' processes, is given in Fig. 6 for each component (pure and blended) of the blend. After the 'refreshing' treatment, the blend is cooled from a temperature higher than T_g of the epoxy in the blend ($T_g + 20$ K). Although the viscoelastic experiments start at 123 K, the cooling was chosen to be illustrated only until room temperature to make an illustration as clear as possible. This choice seems to be justified because the effects of structural recovery on V^* are less and less the further from the glass transition temperature. It can also be considered an interesting choice while the occurrence of the 'micromechanical transition' on the DMS spectra is nearer (at about 333 K).

Although the 'refreshing' temperature is near the T_g of the thermoplastic-rich phase (PPE), this component is still in the glassy state all along the 'refreshing' time (Fig. 6a). As a consequence, a physical aging effect is generated when the 'refreshing' treatment is applied to PPE. Nevertheless, this effect can be considered negligible compared to the previous one during the 18 months in laboratory conditions. After 30 min at $T_g + 20$ K, the thermomechanical history of the epoxy-rich phase is erased. The following quenching increases classically its T_g until slightly less than $T_{\text{refreshing}}$. So, as indicated in Fig. 6b, the main component rapidly reaches the glassy state. In the same way, the Kraton interphase stays at the rubbery state all along the 'refreshing' time at 458 K. However it is important to note that, during the following quenching, the evolution of the specific volume of the interphase component (Fig. 6c) is imposed by one of the main components in the blend, which constitutes the continuous phase. As the thermal expansion coefficient of a rubber can rationally be considered as about ten times that of a polymeric glass, the shrinkage corresponding to the cooling of the Kraton interphase after 'refreshing' exceeds those of the other phases in the blend. Indeed, as mentioned above, the evolution of the specific volume of the interphase component is essentially conditioned by one of the epoxy matrix. Thus, the cooling after the 'refreshing' process results in an excess of volume for the interphase (in Fig. 6, see ΔV^*_R as an indicator). This phenomenon amplifies the molecular mobility in the interphase, and thus makes easier both above mentioned phenomena.

On the other hand, the 'ageing' treatment ($T_g - 20$ K) increases the density of the main amorphous components of the blend (black arrows in Fig. 6). This makes difficult the reptation of their chains in the interphase, i.e. decreases the interpenetrating of species in the interfacial area, and as a consequence, the volume fraction of the interphase in the blend.

As a partial conclusion, it can be assumed that the 'refreshing' treatment increases the effective volume fraction of the interphase in the blend. During the 'ageing' treatment, this could decrease. As a consequence of the change of the volume fraction of the interphase during the thermal treatments, the appearance of the 'micromechanical transition' on DMS spectra is modified.

3.5. Frequency dependence of the interphase relaxation

Dynamic mechanical thermal analyses were performed in a frequency range from 0.3 to 10 Hz. Fig. 7 gives the dynamic mechanical spectra obtained at various frequencies for the 'as received', 'refreshed', and 'aged' specimens. Considering an Arrhenius dependence of the relaxation processes, apparent activation energies of the β- and 'micromechanical' relaxations for the various samples were calculated (Table 2). In Table 2, apparent activation energies of the α-relaxation modes of pure DGEBA-MCDEA and epoxy-rich-phase in the compatibilized blend are listed as well as the apparent activation energy value of ω relaxation reported in the literature for epoxy networks. Table 2 shows that the activation energy of the 'micromechanical transition' is approximately constant (about 135 kJ/mol) for the three thermal treatments. This value appears to be lower than that of the ω relaxation process. Furthermore, the experimental activation energy of the 'micromechanical transition' is in between that of the β- (85 kJ/mol) and α- (550 kJ/mol) relaxations. This point is in a good agreement with a molecular mobility approach for the relaxation processes.

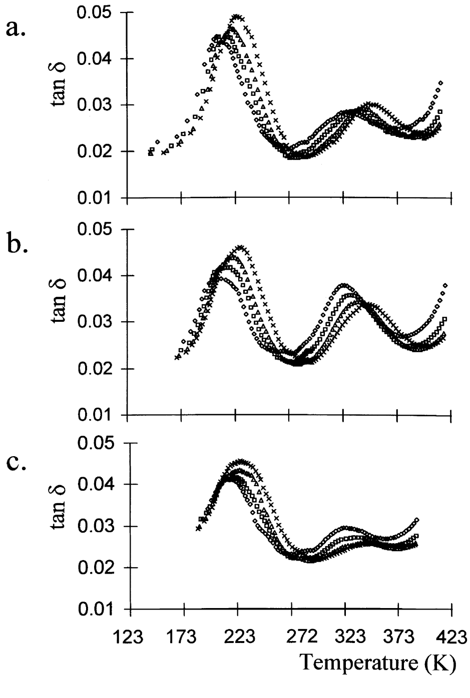

Fig. 7. Frequency dependence of the β-relaxation and the 'micromechanical transition' for MCDEA-g-K compatibilized DGEBA-MCDEA/PPE after different thermal treatments: (a) 'As received'; (b) 'Refreshed'; (c) 'Aged'; ◇ $f = 0.3$ Hz, □ $f = 1$ Hz, △ $f = 3$ Hz, × $f = 10$ Hz.

Table 2
Apparent activation energies of β-relaxation and 'micromechanical transition' (mmt) in MCDEA-g-K compatibilized DGEBA/PPE (10 wt.%) blends after thermal treatment. Apparent activation energies of the other relaxation processes, α and ω, of the epoxy network are reported

	'As received'	'Refreshed'	'Aged'
E_a^{β} (kJ/mol)	87 ± 14	82 ± 3	89 ± 7
E_a^{mmt} (kJ/mol)	146 ± 11	136 ± 1	125 ± 20
E_a^{α} of pure DGEBA-MCDEA (kJ/mol)		550 ± 50	
E_a^{α} of DGEBA-MCDEA in binary blend (kJ/mol)		520 ± 55	
D_a^{ω} in epoxies [35–43] (kJ/mol)		170–240	

Table 3
Characteristics of the different curves presented in Fig. 3

Frequency (Hz)	'As received'					'Refreshed'					'Aged'				
	T_β (K)	h_β ($\times 10^2$)	T_{mmt} (K)	h_{mmt} ($\times 10^2$)	h_β/h_{mmt}	T_β (K)	h_β ($\times 10^2$)	T_{mmt} (K)	h_{mmt} ($\times 10^2$)	h_β/h_{mmt}	T_β (K)	h_β ($\times 10^2$)	T_{mmt} (K)	h_{mmt} ($\times 10^2$)	h_β/h_{mmt}
0.3	210	264	329	100	2.64	210	186	323	173	1.08	208	195	326	83	2.35
1	214	272	335	104	2.62	214	208	330	152	1.37	215	205	335	61	3.36
3	220	280	342	112	2.5	220	230	337	134	1.72	219	214	342	45	4.76
10	226	308	350	124	2.48	226	253	347	128	1.98	221	243	350	42	5.79

Nevertheless, the frequency dependence of the interphase relaxation is slightly different for the 'as received' sample than for the other samples, which can be attributed to some parasitical effects. These could result from the presence of absorbed water, the occurrence of a physical ageing and/or the presence of the ω relaxation of the epoxy matrix. As the specimen is 'refreshed' at $T_g + 20$ K, all these effects disappear and the frequency dependence of the 'micromechanical transition' is not affected by an additional phenomena. Characteristics of the β and 'micromechanical transition' are listed in Table 3.

4. Conclusions

The first complete description of a 'micromechanical transition' in a compatibilized thermoset/thermoplastic blend was given in this paper. Such a 'transition' was previously studied only in ternary thermoplastic blends.

The modifications of the viscoelastic behavior of this interphase relaxation, which were induced by various thermal treatments (defined with an approach considering structural recovery of amorphous materials), revealed that the viscoelastic occurrence of the 'micromechanical transition' is controlled by the conditions of the confinement of components in the interphase area. Thus, the notion of 'effective volume fraction' of interphase seems to be of importance for understanding the viscoelastic observation of a 'micromechanical' relaxation, which could be defined as a relaxation resulting from specific stresses at the molecular scale together with limit conditions, at the boundary limit of the interphase.

These experimental observations will be investigated through an additional approach based on a viscoelastic modeling.

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