

## DYNAMIC MECHANICAL ANALYSIS ON MODIFIED BISMALEIMIDE RESINS

Mariana Cristea\*, C. Gaina, Daniela Gheorghiu Ionita and Viorica Gaina

'Petru Poni' Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A, 700487 Iasi, Romania

Polyaminobismaleimides (PAMBI) with diphenyl methane, diphenyl ether and hexamethylene segments were synthesized according to Michael type addition reaction. The modification of PAMBI with 2-glycidyl-phenyl-ether (GPE) was performed in order to ameliorate the toughness of the products. Dynamic mechanical analysis allowed the study of the processes that concur in the material through curing by tracking the storage modulus ( $E'$ ) and loss factor ( $\tan\delta$ ) changes. The small drop of  $E'$  with increasing temperature in the glass transition region argues for crosslinked structures. The viscoelastic behavior revealed complex processes, i.e., overlapping of glass transition temperature range with intra- and inter-crosslinking.

**Keywords:** dynamic mechanical analysis, polyaminobismaleimides, viscoelastic properties

### Introduction

The field of polymer chemistry is frequently associated with material science because polymer investigation outputs are often examined with a potential use in mind. An effective high-performance polymer should associate in a good balance performance properties, feasible processability and cost-effectiveness. From the vast array of high-performance materials, polybismaleimides represent a chief class of thermosetting polymers and have received a notable attention because they are used in applications where high service temperatures are claimed [1, 2].

It is important to emphasize that the majority of polyimides is preponderantly prepared through condensation polymerization that is predisposed to the formation of voids in the material [3, 4]. As opposed to this, polybismaleimides (PAMBI) are addition-type polyimides and represents products of thermal polymerization [5–9].

Therefore, the volatile products are not released during synthesis, which excludes the generation of voids in the crosslinked composition [10].

This fact designated an advantage over other polyimides because allows polybismaleimides to be processed with less difficulties than condensation-type polyimides. On the other hand, the outstanding thermal behavior comes from the attributes of the stable aromatic maleimide rings [11]. However the aromatic rings as well as the high crosslinking density confer to the polymer backbone rigidity that renders into brittleness. Fortunately, the incorporation of flexible units into the polymer chain would overcome

this drawback [12, 13]. The reactive double bonds of bismaleimides are prone to undergo Michael type nucleophilic addition reactions with numerous nucleophiles (amines, bistiols, bisphenols) [14–23]. If the selected nucleophilic entity is flexible or contains appropriate pendent groups, it lessens the stiffness of the bismaleimide resins [24]. Precautions are taken in choosing the modifying entity in order to maintain the high temperature capabilities of the resins. Among the means reported in literature for improving the toughness and processability of polybismaleimides can be recalled preparation of BMI monomers with flexible or long segments in the backbone and linear-chain extension using amines to diminish crosslinking density. These two ways can be approached simultaneously. In the foregoing papers we have reported the synthesis of bismaleimide resins containing urethane methylene links [25], pre-polymers of polyaminobismaleimides [26], bismaleimides that include ester groups and their polymers with diamine and bistiols [27]. This paper deals with polyaminobismaleimides derived from bismaleimide monomers with diphenyl methane, diphenyl ether and hexamethylene segments as flexible units and amines with variable nucleophilicity. A new strategy was adopted in the continuing search for ameliorating the toughness of the products, i.e., the modification of polyaminobismaleimide resin by the reaction of the secondary amine group with 2-glycidyl-phenyl-ether (GPE). There are reports on the N-grafting of polyaniline by using ring-opening graft copolymerization of GPE that confirm the decreasing of the glass transition temperature with increase in the degree of

\* Author for correspondence: mcristea@icmpp.ro

N-grafting [28]. The reaction was also applied to imines in the presence of water [29] and the thermal behavior of 4-maleimidophenyl glycidyl ether resins sustains that they are more stable than the state-of-the-art epoxy resins [30]. As we are aware there are no descriptions of the modification of PAMBI with GPE.

Dynamic mechanical analysis (DMA) method allows the examination of structure-property-performance correlation, that means in what manner changes in the chemistry, processing or composition of a material affect the performance. DMA will be used to follow the processes that concur in the material through heating by tracking the storage modulus ( $E'$ ) and the loss tangent factor ( $\tan\delta$ ) changes. It is generally accredited that this method is more sensitive to molecular motion than other thermal methods for assessing transitions and transformations in polymers [31–33].

## Experimental

### Materials

Maleic anhydride (briquette 99.6%), 1,6-hexamethylenediamine (98%) (A-1), 4,4'-methylenedianiline (97%) (A-2), 4,4'-oxydianiline (97%) (A-3), 4,4'-diaminodiphenylsulfone (97%) (A-4), triethylamine (99.5%), N-methyl-2-pyrrolidone (99%) (NMP) and 2-glycidylphenylether (99%) were purchased from Aldrich. 4,4'-bismaleimidodiphenylmethane (BMI-1), 4,4'-bismaleimidodiphenyloxide (BMI-2) and 1,1'-hexamethylene bismaleimide (BMI-3) were synthesized from aromatic diamines (1 mol) and maleic anhydride (2 moles) in dry acetone according to a two-step method as described in the literatures [15, 34].

### Synthesis

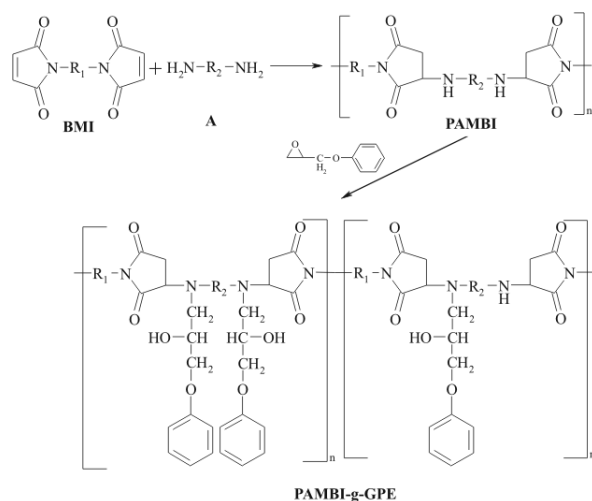
#### Polyaminobismaleimide polymers (PAMBI)

The polyaminobismaleimide polymers were prepared according to the method described in the literature [14], in virtue of Michael addition reaction of aromatic diamines to bismaleimides, in NMP at 95°C (Scheme 1). Into 50 mL three-necked flask fitted with mechanical stirrer, thermometer and nitrogen inlet were charged BMI (0.01 mol), diamine (0.01 mol), NMP (20 mL) and 0.5 mL of acetic acid. The reaction mixture was kept in a water bath at 95°C for 20 h. For viscosity and GPC measurements, the polymers were isolated by pouring of the mixture into methanol to give brown powder polymers. The polymers were filtered off, washed thoroughly and refluxed in methanol for 2 h, filtered and dried under vacuum for

2 h at 60°C. The inherent viscosities measured in DMF ranged between 0.27–0.55 dL g<sup>-1</sup>, the number-average molecular mass varied between 11400 and 15800 and the polydispersity was 1.260–1.346. All polymers exhibited high solubility in aprotic dipolar solvents. To prepare the polyaminobismaleimide films, a solution of polyaminobismaleimide (10 mL) in NMP was transferred to a glass plate placed in a preheated oven at 120°C. The solvent was evaporated in a convection oven at 120°C for 1 h and 150°C for 1 h. Then, the final reaction was accomplished at 200°C for 2 h and 240°C for 2 h. The film was removed from the glass plate by soaking it in cold water. After 12 h, the films were dried at 100°C in vacuum. All the films were similarly treated.

#### GPE grafted polyaminobismaleimide polymers (PAMBI-g-GPE)

To a solution of polyaminobismaleimide (10 mL) in NMP, 1,2-epoxy-3-phenoxypropane (1.5 mL) was added. The reaction mixture was stirred and heated at 150–160°C for 5 h and then was processed in a similar way to the unmodified polyaminobismaleimide films. The reaction is presented in Scheme 1.



**Scheme 1** The synthesis of PAMBI and PAMBI-g-GPE

### Methods

Dynamic mechanical experiments were made using a Diamond PerkinElmer instrument that applies a sinusoidal stress to the sample and measures the resulting strain. The force amplitude used was well within the linear viscoelastic range for all investigated samples. The thermo-mechanical properties were evaluated, starting from room temperature up to beyond the temperature corresponding to the glass transition, at a heating rate of 4°C min<sup>-1</sup> and a frequency of 1 Hz, under nitrogen atmosphere.

**Table 1** The structures of the synthesized polymers

PAMBI	R <sub>1</sub>	R <sub>2</sub>	PAMBI-g-GPE
1 (BMI-1/A-2)			yes
2 (BMI-1/A-3)			no
3 (BMI-2/A-2)			yes
4 (BMI-2/A-4)			yes
5 (BMI-3/A-3)	$-(CH_2)_6-$		yes
6 (BMI-3/A-1)	$-(CH_2)_6-$	$-(CH_2)_6-$	no

The size of films was of 10×10×0.5 mm for the tension attachment.

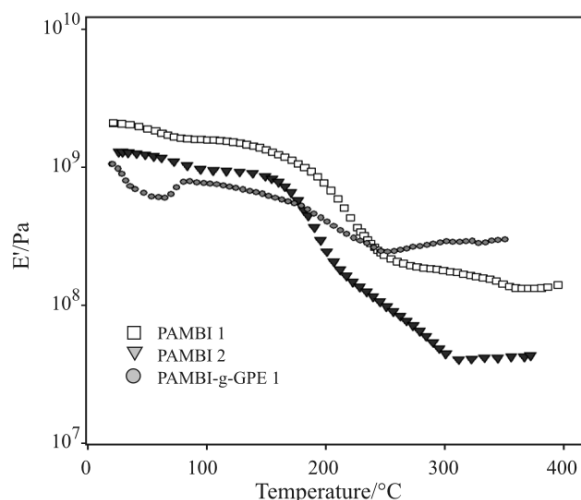
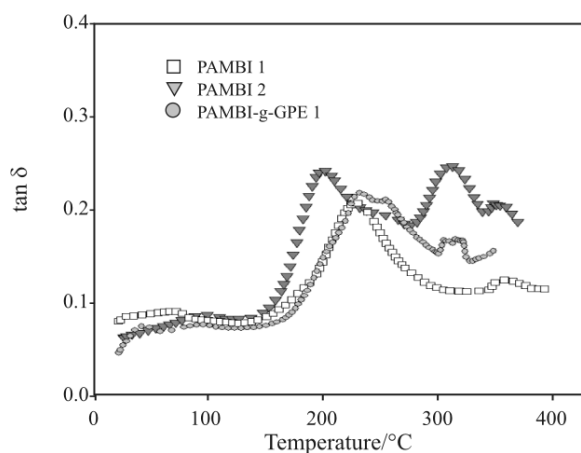
## Results and discussion

The structures of the PAMBI and PAMBI-g-GPE polymers are presented in Table 1.

For a given bismaleimide, the viscoelastic behavior of PAMBI depends on the nature of the diamine. For the sake of clarity, in order to analyse the thermo-mechanical behavior of the compounds they are divided on three categories; each category includes PAMBI and PAMBI-g-GPE containing the same BMI unit in the structure.

Figures 1 and 2 show the temperature dependence of the storage modulus ( $E'$ ) and loss tangent ( $\tan\delta$ ) for PAMBI 1, PAMBI-g-GPE 1 and PAMBI 2 polymers. The drops in  $E'$  curves and the peaks of  $\tan\delta$  plot report on the physical transitions in polymers. Usually, the transition temperatures are taken at the maximum rate of turndown of the storage modulus  $E'$  or at the maximum of  $\tan\delta$  peaks.

At room temperature all three polymers exhibited high tension  $E'$  modulus: PAMBI 1 (2.1 GPa) > PAMBI 2 (1.33 GPa) > PAMBI-g-GPE 1 (1 GPa). The  $E'-T$  curve offers a valuable insight into the stiffness of the sample as a function of temperature. A small drop in  $E'$  of PAMBI 1 is noticed between 50 and 100°C that may be associated with a  $\beta$  transition. The onset of glass transition region occurs around 150°C and spans till 240°C. The analogous mark on the  $\tan\delta$  curve is a broad peak centered at 230°C. During the glass transition process the elastic modulus  $E'$  abates till 0.2 GPa, that means one order of magnitude. Recall


**Fig. 1** Variation of the storage modulus with temperature for PAMBI 1, PAMBI-g-GPE 1 and PAMBI 2

**Fig. 2** Variation of the loss factor with temperature for PAMBI 1, PAMBI-g-GPE 1 and PAMBI 2

that for an amorphous linear polymer the decline of  $E'$  in the glass transition range amounts three orders of magnitude in a narrow temperature span. Consequently, we can infer that the compound contains crosslinkings that obstruct the large movement of ample chain segments and it acts as a rigid material.

The next question is about the origin of this crosslinkings. Some reactions are feasible during the curing of PAMBI resins. A concise review of them will be helpful in understanding the trend of all viscoelastic curves. First, the addition of primary amine group to maleimide group, according to Michael addition, takes place around 150°C. Second, further increasing in temperature up to 220°C initiates the addition of secondary amine groups, included in PAMBI macromolecular chains, to unreacted maleimide groups situated at the end of the chains. These reactions will determine simultaneously crosslinkings and extension in chain length that will amplify the rigidity and hence the glass transition temperature of the compound. Third, whether there are still unreacted maleimide groups over 230°C, they will homopolymerize causing additional crosslinking, i.e., extra-stiffness. If these processes are not completed during the thermal preparative stage, they may occur also in the DMA oven throughout the thermal scanning.

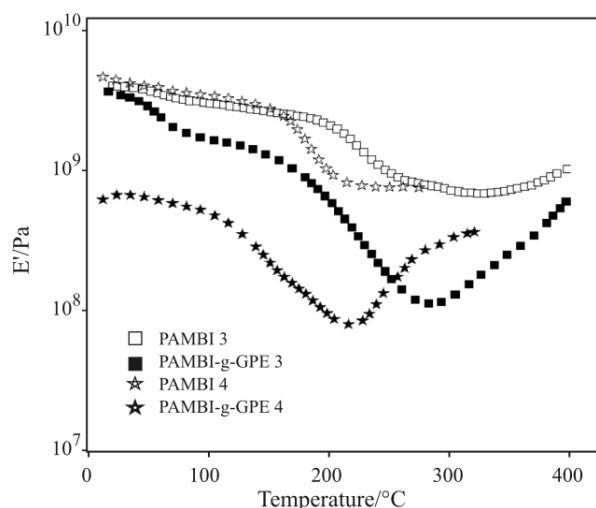
Going back to the viscoelastic behaviour of PAMBI 1, it should be stressed that the diamine A-2 has a high nucleophilicity. The order of nucleophilicity of the amines involved in synthesis decreases in the series: A-1>A-2>A-3>A-4. Undoubtedly, during multi-step thermal curing included in film preparation, the reactive secondary amine groups of A-2 favoured crosslinking processes. This explains the small and broad decrease of  $E'$  in the glass transition range, that spans a temperature range of 90°C. Notice that further increase in temperature does not bring about additional rigidity, therefore no supplementary growing of  $E'$  is observed till 400°C. This is an indication for the absence of homopolymerization of maleimide groups in the DMA oven. The presence of few free maleimide groups can not be excluded, but it is very probable that they can not reach each other for homopolymerization because of limited mobility of the network.

The PAMBI-g-GPE 1 compound has the storage modulus  $E'$  at room temperature lower than the corresponding unmodified compound PAMBI 1. The  $\beta$  transition is noticed at room temperature and is more important than the one of PAMBI 1 due to the presence of GPE as pendent group. An increase in  $E'$  is remarked over 65°C that is associated with the removal of water. It was reported that polybismaleimide resins absorb water as high as an amount

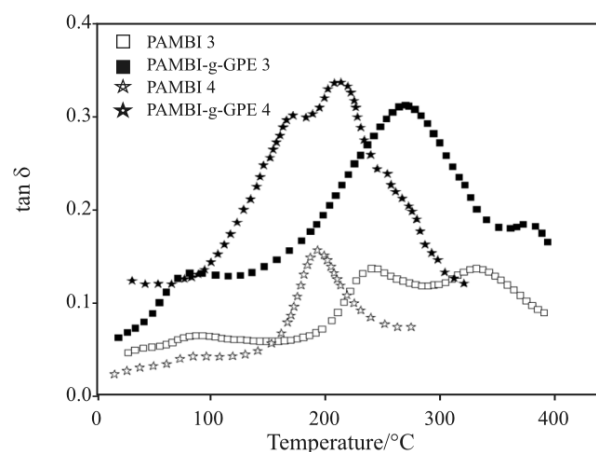
ranging between 1–4.8% [34]. The fall of  $E'$  corresponding to glass transition starts at a lower temperature than PAMBI 1 (140°C) and the descent is small and large. The  $\tan\delta$  curve shows a shoulder on the ascending side, at 200°C, and a very large peak centred at 230°C. Similarly, additional reactions between secondary amine groups and unreacted maleimide groups generate crosslinkings that augment the inhomogeneity of the resin. Despite the presence of pendent GPE groups, they do not diminish the stiffness induced by these crosslinkings. Moreover, the storage modulus has an ascending trend after 250°C, contrary to its unmodified homologue. More probable this extra-rigidity can be attributed to the etherification of hydroxyl groups. It was mentioned for a maleimide-epoxy resin that 255°C corresponds to the temperature of the etherification reaction [35].

The resin PAMBI 2 exhibits a distinctive variation of the viscoelastic parameters. The glass transition includes two steps: 150–200 and 200–300°C. The change in slope during glass transition process is seen at 200°C and thereafter the  $E'-T$  curve became less steep up to a new break point at 300°C ( $E'=0.042$  GPa). To account for this behaviour the nucleophilicity of amines will be considered. The nucleophilicity of amine A-2 is higher than the one of the amine A-3. Consequently, during the cure of the films at 240°C in the preparatory steps, the probability of Michael addition between unreacted maleimide groups and secondary amine groups is bigger for PAMBI 1 than for PAMBI 2. Accordingly, the PAMBI 2 film contains more reactive groups that are capable of forming crosslinkings during the DMA experiment. In addition, the amine A-3 is more flexible than the amine A-1 and it is very likely that the reactive groups of PAMBI 2 approach and react in the middle of the glass transition process when coordinated movements of long chain segments occur. The  $\tan\delta$  curve denotes the two-step glass transition as a peak and a shoulder (200 and 265°C). Over 300°C a faint gain in  $E'$ , attributed to the additional crosslinking as a result of homopolymerization of maleimide groups, is consistent with the previous rationale.

The variation of the viscoelastic parameters ( $E'$  and  $\tan\delta$ ) with temperature for the samples PAMBI 3, PAMBI-g-GPE 3, PAMBI 4, PAMBI-g-GPE 4 is represented in Figs 3 and 4. The storage modulus  $E'$  at room temperature diminishes in the order: PAMBI 4 (3.75 GPa)  $\cong$  PAMBI 3 (3.7 GPa) > PAMBI-g-GPE 3 (3 GPa)  $\gg$  PAMBI-g-GPE 4 (0.65 GPa). There is no important difference between the storage modulus  $E'$  of the unmodified compounds PAMBI 3 and PAMBI 4 at room temperature.



**Fig. 3** Variation of the storage modulus with temperature for PAMBI 3, PAMBI-g-GPE 3, PAMBI 4 and PAMBI-g-GPE 4



**Fig. 4** Variation of the loss factor with temperature for PAMBI 3, PAMBI-g-GPE 3, PAMBI 4 and PAMBI-g-GPE 4

On the contrary, the introduction of GPE as pendent groups causes a decrease of  $E'$  at room temperature, more important for PAMBI-g-GPE 4. This observation will be commented in the later discussion of results. Before a detailed examination of this category of polybismaleimides, it is worth to notice that PAMBI 3 and PAMBI 2 have symmetric structures (Table 1). However, the values of  $E'$  for the two compounds point out that PAMBI 3 (Fig. 2) is more rigid than PAMBI 2 (Fig. 1). The nucleophilic character of the amine A-2 is higher than that of the amine A-3. On that account, more crosslinkings are formed during the cure in the preparatory step that impart more stiffness to the PAMBI 3 film.

Going back to Fig. 2, the  $E'$  variation for PAMBI 3 indicates a large  $\beta$  transition that generates at 50°C a small decrease of  $E'$  till 2.5 GPa at 150°C. The corresponding  $\tan\delta$  indication of this transition is

a very large peak centered at 90°C. The one-step glass transition region starts at 180°C and stretches up to 268°C, where  $E'$  is 0.79 GPa. The middle point of  $\tan\delta$  peak is 245°C. The small drop in the storage modulus indicates that this structure is a tightly crosslinked one. The breadth of the transitions suggests a substantial heterogeneous structure. Only when the temperature exceeds 325°C, there is a small upward of storage modulus and an increase in  $\tan\delta$ . From visual observations of the film at the end of the DMA experiment, these events are associated with degradation.

The first striking characteristic of the  $E'-T$  curve for PAMBI-g-GPE 3 is the presence of an important  $\beta$  transition with  $\tan\delta$  peak centered at 75°C. The storage modulus decreases till 1.5 GPa. A very large glass transition temperature ranges between 140 and 280°C, as can be seen from the  $E'$  variation and the  $\tan\delta$  peak is extremely broad. After 290°C, a very abrupt increment of the storage modulus is consistent with a highly crosslinked resin. The origin of these crosslinkings seems to be the etherification reaction. Setting aside the very small  $\beta$  transition, the first fall of  $E'$  for PAMBI 4 occurs at a lower temperature (165°C) than the corresponding temperature of PAMBI 3 (180°C).

Considering that the two amines A-2 and A-4 have almost the same flexibility, the dominating factor behind the onset of the glass transition temperature is the smaller nucleophilicity of the amine A-4. The few crosslinkings formed in the preparatory step make the PAMBI 4 structure more flexible than that of PAMBI 3 and the glass transition temperature is decreased. It is important to notice that no supplementary crosslinkings are formed during DMA experiment due to the small nucleophilicity of the amine. The experiment was stopped at 275°C and no increasing in  $E'$  is noticed till then.

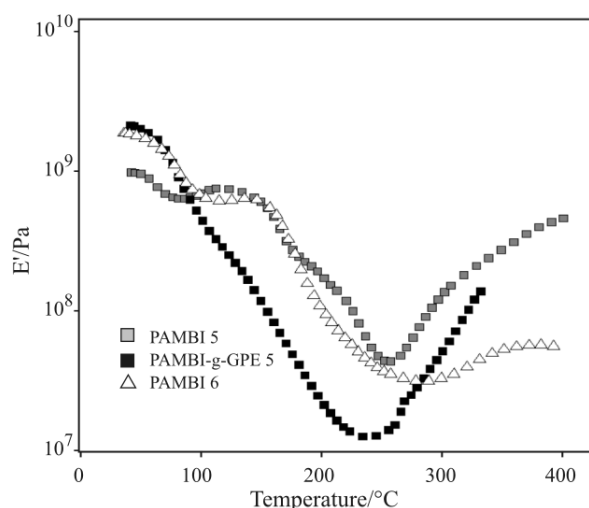
In the case of PAMBI-g-GPE 4 the onset of glass transition shifts to a lower temperature (115°C) than the unmodified PAMBI 4. Quite impressive is the broadness of the  $\tan\delta$  peak that is an explicitly sign for the huge inhomogeneity of this sample. The presence of the electron-withdrawing sulfone group in the diamine reduces the basic character. As a consequence the amine is less reactive, few crosslinkings are formed during the preparation of film and the sample is not so rigid before DMA experiment. Moreover, additional softness is supposed to be imparted by GPE pendent chains. At 210°C, where the storage modulus reaches 0.09 GPa, the descent trend of  $E'$  ceases and a steep upturn begins at 225°C. Miscellaneous processes overlap in this temperature region: maleimide – primary/secondary amine reactions, homopolymerization, etherification. Despite

the upward course of  $E'-T$  curve, the occurrence of the glass transition is not ruled out. Nevertheless, the crosslinking effects outweigh the contribution of the resin softening, resulting in an enhancement of  $E'$ .

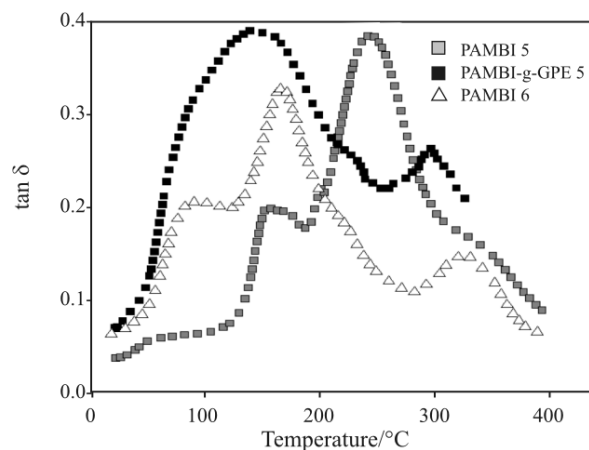
Further experiments were performed on polybismaleimide resins derived from very flexible structural units (Figs 5 and 6).

At the first glance it seems surprisingly the values of the storage modulus at room temperature: PAMBI-g-GPE 5 (1.9 GPa) > PAMBI 6 (1.67 GPa) > PAMBI 5 (0.9 GPa).

The polymer PAMBI 5 displays a small and broad decrement of  $E'$ , between 40 and 65°C, interrelated with  $\beta$  transition. This is followed by a faint increase that suggests water loss, similar with the one encountered for the polymer PAMBI-g-GPE 1. Further, in the glass transition range,  $E'$  modulus decreases in three steps: 125–165; 165–210; 210–240°C. The first represents the glass transition range of the compound resulted from



**Fig. 5** Variation of the storage modulus with temperature for PAMBI 5, PAMBI-g-GPE 5 and PAMBI 6



**Fig. 6** Variation of the loss factor with temperature for PAMBI 5, PAMBI-g-GPE 5 and PAMBI 6

synthesis, after processing. At 165°C the slope becomes less steep, i.e. the rigidity of the sample is increased as result of additional crosslinking determined by varied Michael addition reactions, as mentioned before. Around 210°C a new break point in  $E'-T$  variation signs the glass transition of the advanced crosslinked compound. The entirely drop of  $E'$  is a little bit more than one order of magnitude that is consistent with the presence of constraints represented by crosslinkings. The increasing edge of the  $\tan\delta$  peak corresponding to the glass transition of the initial samples interrupts the raising around 155°C and flattens out due to convergence with curing reactions. The  $\tan\delta$  peak corresponding to the glass transition of the crosslinked compound is centered at 250°C. The important increase of  $E'$  over 250°C suggests the occurrence of further curing as result of homopolymerization. It is meaningful to compare the room temperature storage modulus of the compounds: PAMBI 5 (0.9 GPa) and PAMBI 2 (1.33 GPa). Likewise, the onset of glass transition temperature is smaller in the case of PAMBI 5. All these happen due to the presence of hexamethylene units that confer a very high flexibility to PAMBI 5. The higher storage modulus of the modified compound (PAMBI-g-GPE 5) can be accounted for by the following explanation. The hexamethylene segments convey suppleness to polymer chains and allow the hydroxyl groups to get in touch easily and to be involved in an intermacromolecular etherification reaction. This process may occur even in the oven, during initial polymer film curing. Therefore ether-type crosslinkings are formed and they confer extrarigidity to the modified compound PAMBI-g-GPE 5 as compared to the unmodified one, PAMBI 5. The compound PAMBI-g-GPE 5 is characterized at 40°C by the onset of a broad fall of  $E'$  that continues out to 220°C, where the value of  $E'$  is less than the one for the PAMBI 5 compound. There are perceptible some changes of the slope, but they are extremely faint. It is evident that the glass transition comes out immediately after the  $\beta$  transition. It is no levelling plateau between them. The extended broadness of  $\tan\delta$  peak indicates a large distribution of the relaxation times between 50 and 200°C that corresponds to an inhomogeneous morphology. This behavior denotes that the compound resembles a loose crosslinked network. Over 225°C the storage modulus increases indicating an increment in the rigidity of the sample because of thermal homopolymerization. In order to unravel the higher  $E'$  of PAMBI 6 as compared to PAMBI 5, one should consider the highest nucleophilicity of the amine A-1 and, consequently, the very high probability to form numerous crosslinkings as a result of the reaction between the

reactive secondary amine group and the unreacted maleimide rings during the curing at 240°C in the preparatory stage.

The  $\beta$  transition of PAMBI 6 almost coincides with the one for PAMBI 5, but is larger. This is explained by the presence of hexamethylene groups both in amine and BMI segments. After  $E'$  levelling at 0.58 GPa, an important glass transition is registered between 140 and 250°C. The peak and shoulder noticed on  $\tan\delta$  curve (170 and 230°C) indicate the existence of two glass transition domains: one for the initial compound and, after 200°C, the one for a loose crosslinked compound. The secondary reaction between the secondary amine and the maleimide groups occurs also in the DMA oven, during the experiment. The increase in  $E'$  modulus after 250°C is less important.

## Conclusions

Polyaminobismaleimides and their derivatives grafted with pendent GPE units have been synthesized. The values of storage modulus and glass transition depend both on the flexibility of the chain segments and on the nucleophilicity of the diamine involved in the synthesis. All the compounds have high storage modulus at room temperature. There are no big differences between the values of the storage modulus at room temperature because in the case of these specific structures the two factors compensate each other to a certain extent.

The amine with the highest flexibility (A-1) is the most reactive. Therefore it induces the formation of quite highly crosslinked systems, but with relatively long chain segments between the joints that soften the constraints of the network. The GPE attached to the polymeric chain lessens the stiffness to a certain extent; even so it determines over 230°C etherification reaction that increases the rigidity of the compounds.

Glass transition processes are broad and the small drop in the storage modulus (around one order of magnitude) is consistent with the crosslinked structures. The curing reactions continue during the DMA experiment and this is emphasized by multistep glass transition processes, with changes in the slope of the  $E'$  variation. The  $\tan\delta$  peaks are broad and reflect large composition fluctuations in the network and restrictions of segmental motions. According to the peak value  $\tan\delta$  ( $E''/E'$ ) all samples exhibit viscoelastic solid-like behavior. It is important to mention that the grafting of GPE to PAMBI improves the damping properties of the compounds.

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