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Polyurethane and unsaturated polyester hybrid networks: 2. Influence of hard domains on mechanical properties

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Abstract

The influence of hard domains on the mechanical and thermomechanical properties of polyurethane and unsaturated polyester hybrid networks has been investigated. The hybrid networks consist of a polyurethane linkage formed by reacting unsaturated polyester polyol with polymeric 4,4′-diphenylmethane diisocyanate (MDI) and free-radical crosslinking through styrene monomer and vinylene groups in the unsaturated polyester. Hard segments were formed by condensing two different types of chain extender, ethylene glycol (EG) and 1,6-hexanediol (HD), with MDI. Incorporation of chain extenders in the hybrid networks varied from 0% to 12% by weight based on the weight of unsaturated polyester polyol. The thermomechanical properties of the polyurethane and unsaturated polyester hybrid networks were characterized by heat distortion analysis and by dynamic mechanical analysis. Flexural three-point bend tests and unnotched Izod impact analysis were used to investigate mechanical properties at ambient temperature. Hybrid networks with hard segments formed by MDI and EG showed an increase in the glass transition temperature. A second glass transition was found with incorporation of more than 6 wt% EG due to the formation of phase-separated hard domains. The rubber plateau of the hybrid networks decreased owing to the lower crosslinking density when chain extenders were incorporated. Phase-separated hard domains enhanced the rubber plateau by acting as physical crosslinks in the hybrid network until the glass transition was reached. The hybrid network had improved mechanical properties when more hard segments were added into it without creating the phase-separated hard domains. A dramatic drop in mechanical properties was observed for the sample with a two-phase structure. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Unsaturated polyester; Polyurethane; Hybrid networks

1. Introduction

Unsaturated polyester resins are one of the most widely used thermosetting materials in the composites industry. They offer reasonably good mechanical properties and are relatively inexpensive. The properties of the cured resins can be enhanced by adding various additives to the unsaturated polyester. The fracture properties of cured resins can be improved by blending these materials with reactive liquid rubbers [1,2]. The shrinkage that occurs during the crosslinking reaction of the unsaturated polyester resins with styrene can be eliminated by the incorporation of low-shrinkage or low-profile agents [3,4]. Improvements in the thermal properties and elastic modulus have been investigated recently by creating a polymer network of unsaturated polyester and bismaleimide resins [5]. The mechanical properties of the unsaturated polyester resin can be greatly improved by incorporating the polyurethane linkage into the polymer network. The mechanical properties of polyurethane and unsaturated polyester hybrid networks also can be altered with the techniques used in segmented polyurethanes. Segmented polyester polyurethanes are well-known materials that have been studied extensively by Cooper and co-workers [6–11] as well as other researchers [12–14]. The polyurethane and unsaturated polyester hybrid networks consist of soft segments from the crosslinked unsaturated polyester and hard segments from the extension of a diisocyanate with a low-molecular-weight diol. The structures of hybrid networks are different from those of segmented polyurethanes. The polyurethane and unsaturated polyester hybrid networks are thermosetting materials, while segmented polyester polyurethanes are usually thermoplastics.

The unique structure of the polyurethane and unsaturated polyester hybrid networks mentioned in this study was discussed in a previous paper [15]. The soft segment is composed of a styrene/unsaturated polyester crosslinking network and forms the continuous phase for most of the

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samples. The hard segment comprises a polymeric 4,4′-diphenylmethane diisocyanate (MDI) condensed either with ethylene glycol (EG) or 1,6-hexanediol (HD). The hard segment can be either the overall polyurethane segment or simply the chain-extended polyurethane [15]. If two or more hard segments stay next to each other through hydrogen bonding, they could form a region rich in hard segments called a hard domain. The hard domains may be dispersed in the soft domain, forming a phase-mixed structure, or they may coagulate and create phase-separated hard domains. The phase-separated hard domains may also contain soft segments because they are linked to the hard segments through urethane linkages in the hybrid network.

The previous study investigated the influence of hard domains on phase structure and its influence on thermal properties [15]. This paper aims to determine the influence of hard domains on the mechanical behaviour of polyurethane and unsaturated polyester hybrid networks. Flexural tests and impact analysis were run at ambient temperature. Thermomechanical properties were investigated by heat deflection analysis and dynamic mechanical analysis.

The elastic behaviour of polymer networks can be described by either the affine or the phantom network model. For the affine network model [16], the shear modulus is given by:

$$G_{\mathrm{aff}} = \nu RT \tag{1}$$

where ν is the molar number of elastic chains per unit volume of network, R is the gas constant and T is absolute temperature. The phantom network [17] also considers the effect of elastically active junctions. The shear modulus of the phantom network is lower than that of an affine network and is given by:

$$G_{\mathrm{phant}} = (\nu - \mu)RT \tag{2}$$

where μ is the molar number of elastically active junctions per unit volume of the network. The phantom network usually describes the elasticity of perfect networks.

Table 1
Composition of the samples used in this study

Chain extender	Wt%[a]	Sample name	Molar ratio[b]
None	0	REF	(1:0.81:0)
EG	1.5	EG1.5	(1:1.02:0.27)
	3	EG3	(1:1.25:0.55)
	4.5	EG4.5	(1:1.48:0.84)
	6	EG6	(1:1.72:1.14)
	8	EG8	(1:2.04:1.54)
	10	EG10	(1:2.38:1.96)
	12	EG12	(1:2.74:2.42)
HD	3	HD3	(1:1.05:0.28)
	6	HD6	(1:1.29:0.6)
	10	HD10	(1:1.63:1.04)

[a] Wt% calculated with respect to the unsaturated polyester polyol solution.
[b] Molar ratio based on pure products (without styrene): $(x{:}y{:}z)$ = unsaturated polyester resin:modified MDI:chain extender.

However, most of the networks have less than perfect elasticity in real networks. Non-idealities such as pendant chains will decrease ν and entrapped entanglements will increase ν [18]. The molecular chains will also interact with each other and reduce the junction fluctuations. In the case of strong interactions, the junctions do not fluctuate at all and are displaced affinely with macroscopic strain [19]. The shear modulus is equal to G_{aff}.

Because strong interaction among molecular chains exists in the hybrid network, the shear modulus G of the hybrid network will be correlated by the affine network model as:

$$G = \frac{\rho RT}{\langle M_c \rangle} \tag{3}$$

where ρ is the network density at the given temperature T and $\langle M_c \rangle$ is the number-average molecular weight between crosslinks.

2. Experimental

2.1. Materials

Polyurethane and unsaturated polyester hybrid networks were made with the same materials as described in a previous paper [15]. The unsaturated polyester polyol resin was made by reacting an excess of diethylene glycol with 50 mol% of isophthalic acid and 50 mol% of maleic anhydride. It was dissolved in styrene monomer with a 76% solids content. The modified 4,4′-diphenylmethane diisocyanate (MDI) was provided as a 90% solids content solution in styrene. The isocyanate content of the MDI solution was 20.5%. Chain extenders were two α,ω-aliphatic diols: ethylene glycol (EG) and 1,6-hexanediol (HD). Various amounts of chain extender were blended into the unsaturated polyester polyol in styrene solution before preparing the hybrid network. All materials were used as-received without further purification.

The polyurethane and unsaturated polyester hybrid networks were prepared by reacting the unsaturated polyester polyol solution with MDI solution and about 1.5 wt% of benzoyl peroxide at ambient temperature. The reaction between MDI and hydroxyl groups took place first, forming the polyurethane linkage. The crosslinking reaction eventually occurred through the unsaturated polyester and styrene monomer. Two sets of samples were prepared with various EG or HD contents and their compositions are listed in Table 1. Clear castings about 3 mm in thickness were prepared by moulding the samples between two glass plates. The clear castings were cured at ambient temperature for 24 h to convert the isocyanate groups fully and then postcured at 120°C for 1 day to complete the unsaturated polyester/styrene crosslinking reaction. The clear castings were cooled slowly for 2 h to ambient temperature after postcure. Quenched samples were prepared by heating postcured samples to 230°C and then quickly cooling them in cold water.

2.2. Heat distortion analysis (h.d.a.)

A Tinius Olsen model HD 94 automatic deflection temperature tester was used to measure the heat deflection temperature. A beam, 127 mm × 12.7 mm × 3.2 mm in size, was cut from the cast panel. The beam was placed in the test set-up, which consists of two supports with 102 mm span and a loading nose midway between the supports. The set-up was submerged in an oil bath, and the oil bath heated from 25°C to 200°C with an initial soak time of 5 min at a heating rate of 2°C min^{-1}. The heat distortion temperature (HDT) was detected by a linear variable displacement transducer as the temperature at which a 0.254 mm deflection (2%) under a load of 1.8 MPa occurred. The reported HDT was an average of two measurements. Experimental variation was usually lower than ± 1°C.

2.3. Dynamic mechanical analysis (d.m.a.)

A Rheometrics dynamic analyser RDA II in the oscillatory mode was used to measure the storage shear modulus (G'), the loss shear modulus (G'') and the phase angle as expressed by tan δ. Torsion bars about 40 mm × 12 mm × 2 mm in size were cut from the cast panel. D.m.a. tests were conducted at a constant frequency of 1.1 Hz and a strain of 0.05 or 0.2%. The first series of tests was run from − 140°C to 250°C in 5°C steps to get an overview of the thermomechanical behaviour of the polyurethane and unsaturated polyester hybrid networks. Each sample was soaked for 1 min at the measuring temperature before each measurement was taken, to allow the torsion bar to reach thermal equilibrium at the measuring temperature. A second measurement was conducted from ambient temperature to 220°C in 4°C steps to provide better resolution. The averages of results from both measurements are used in the discussion.

In order to apply the time–temperature superposition principle and to build master curves, d.m.a. tests were also conducted at the frequency range from 1 Hz to 100 Hz and the temperatures from 46°C to 146°C. Ten data points were measured for each frequency decade, and the temperature step was 10°C. Data were shifted according to the Williams–Landel–Ferry equation to form a master curve with a frequency range from 10^{-2} Hz to 10^{12} Hz. Data shifts were based on a reference temperature of 106°C. The storage shear modulus was chosen as the shifting variable. Data shifts were completely automated by the computer software provided by the Rheometrics RDA II in the Guess shift mode.

2.4. Unnotched Izod impact test

The unnotched Izod impact strength of each sample was tested following the test procedures described in ASTM D 256-88 [20]. All samples were tested unnotched so they would be more sensitive to the transition between ductility and brittleness. As mentioned by Nielsen [21], a notch tends to decrease the apparent ductility of a material and often has a greater effect on ductile materials than on brittle ones. Specimens about 64 mm × 13 mm × 3 mm in size were tested at ambient temperature (23°C). The specimen was held as a cantilever beam and was broken by the single swing of a pendulum. A 2 lb pendulum was used for most of the samples, but samples with higher impact resistance were tested with a 10 lb pendulum. At least 10 specimens were tested for each of the samples to ensure the accuracy of the results. The fracture surface of the tested samples was examined under an optical microscope and micrographs were taken with a video imaging system.

2.5. Flexural three-point bend test

The standard flexural test method, ASTM D 790-86 [22], was used to determine the flexural properties of the hybrid networks on an Instron Universal Tester model 1125. Specimens were cut and tested at ambient temperature (23°C). A constant crosshead speed of 1.3 mm min^{-1} was used with a sampling rate of 3 points s^{-1}. At least five specimens were tested for each sample. Stress at yield and strain at yield were defined at the maximum load point. Calculation of the flexural Young's modulus was performed by the computer software provided by Instron from the initial linear region of the testing curve.

3. Results and discussion

3.1. Thermomechanical analysis

Plots of tan δ and storage shear modulus G' as a function of temperature for the polyurethane and unsaturated polyester hybrid networks with EG incorporation are shown in Fig. 1(a), Fig. 1(b). Four peaks were observed on the tan δ curve: α, β, γ_a, and γ_b, listed in order of appearance with decreasing temperature, as described in Fig. 1(a). Two small relaxations, γ_a and γ_b, were present at about − 80°C and − 140°C respectively for all samples. The lower-temperature relaxation, γ_b, was assigned to localized motion in the methylene sequences [9,23], whereas the higher-temperature relaxation, γ_a, was related to some motion of the phenyl groups in the styrene sequences [24]. The β transition was due to the glass transition of the soft domain. The high-temperature α transition was from the phase-separated hard domains, which existed in hybrid networks with EG contents above 6 wt% only. The higher the amount of EG incorporated, the bigger the shoulder from the α transition.

The transition temperatures determined by h.d.a., d.m.a. and modulated differential scanning calorimetry (d.s.c.) [15] are listed in Table 2. The glass transition temperature determined by the β peak of tan δ was about 20°C higher than the T_g found by modulated d.s.c. for all samples. However, the temperature of the β peak of loss modulus G'' was very close to the T_g determined by modulated d.s.c. and by h.d.a. This temperature also represented the yield point of storage modulus G'. The α transition temperature of tan δ measured by d.m.a. agreed with the second T_g from the phase-separated hard domain as measured by modulated d.s.c. [15]. EG increased the β transition temperature of the hybrid network by 16.8°C between REF and EG12, whereas HD-extended segments showed an increase of less than 1°C between REF and HD10. A greater increase in the β transition temperature was observed before the phase-separated hard domain was formed than after the phase-separated hard domain was formed. A 10.3°C increase was observed between REF and EG6, while the increase between EG6 and EG12 was only 6.5°C. The phase-separated hard domains act as crosslinking and/or filler for the soft domain until the temperature is higher than its glass transition [25]. This could explain the increase of the β transition temperature even when the weight fraction of hard segments dissolved in the soft domain remained constant [15].

Plots of the storage shear modulus G' vs. temperature for various EG samples are given in Fig. 1(b). The glassy

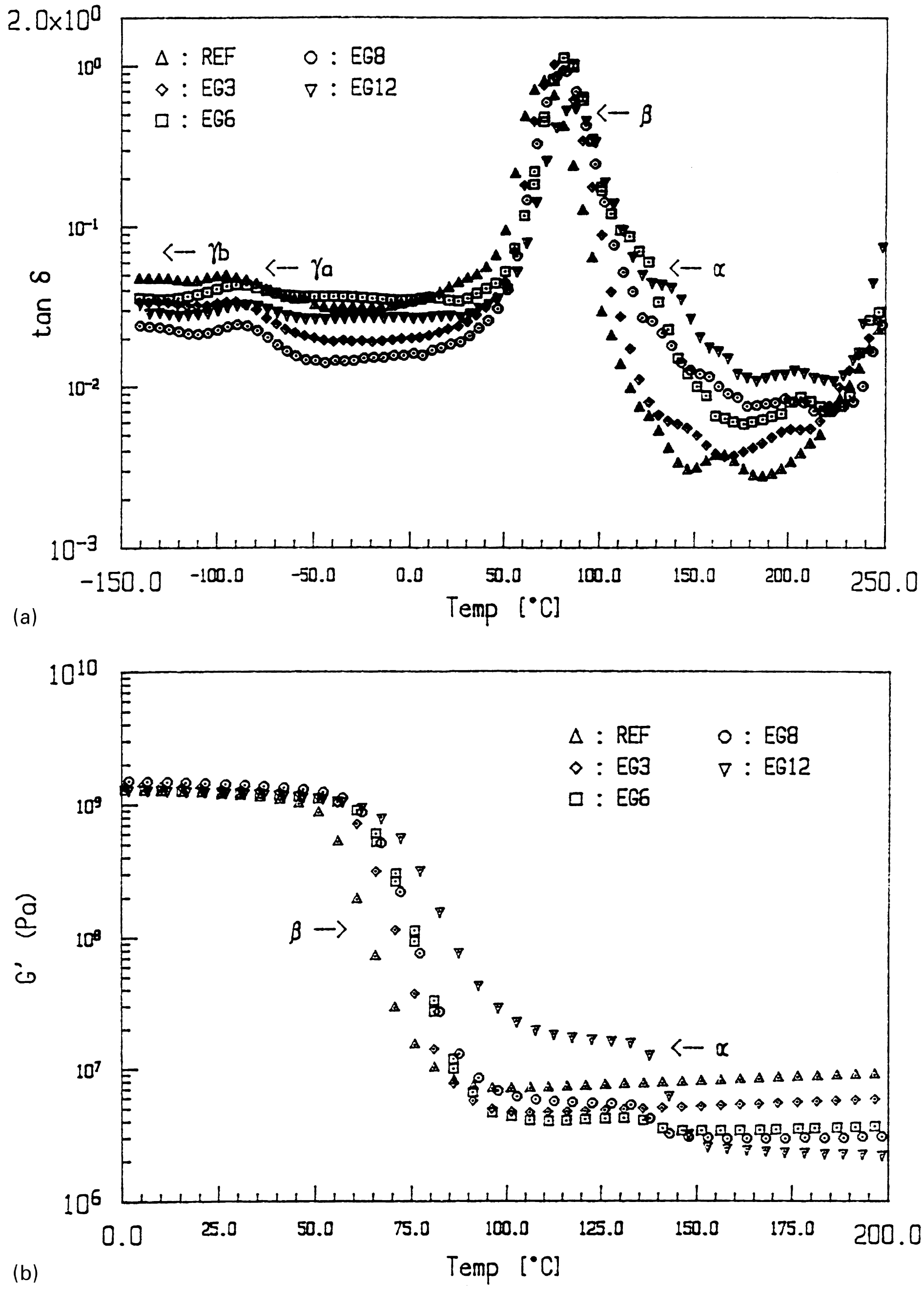

Fig. 1. D.m.a. curves of REF, EG3, EG6, EG8 and EG12: (a) tan δ; (b) storage shear modulus, G'.

Table 2
Transition temperatures determined by h.d.a., d.m.a. and modulated d.s.c. (in °C)

	HDT	D.m.a.					D.s.c.
		Peak β of tan δ	Peak α of tan δ	Peak β of G''	Peak α of G''	Peak height of β trans. in tan δ	T_g
REF	54	70.8	—	55	—	0.89	50.2
EG1.5	53.5	72.5	—	57	—	0.92	52.4
EG3	59	75.9	—	65	—	1.04	56.5
EG4.5	55	77.6	—	62	—	1.07	60.2
EG6	63	81.1	125	65	125	1.03	62.5
EG8	61.5	82.5	130	67	130	0.87	62.5 130.0[a]
EG10	71	86.4	135	72	132	0.62	65.0 136.6[a]
EG12	69	87.6	138	72	133	0.56	67.2 134.6[a]
HD3	52	71.1	—	55	—	0.9	51.6
HD6	55	71	—	60	—	1.01	52.7
HD10	58	71.4	—	60	—	1.04	52.2

[a] Second T_g.

plateau was a constant for all HD and EG samples at 1.5 GPa. This value agrees with the storage shear modulus of segmented polyurethanes found in the literature [26,27]. The G' rubber plateau varied with the content of hard segments. The more chain extender incorporated, the lower was the ultimate rubber plateau due to the change in crosslinking density. The weight fraction of unsaturated polyester polyol in the resin mixture decreased when more chain extender was added to the system. Since crosslinks come from the reaction between unsaturated polyester and styrene, a lower crosslinking density is expected with higher incorporation of chain extender. To correlate the rubber plateau modulus with the hybrid resin composition, the number-average molecular weight between crosslinks, $\langle M_c \rangle$, was chosen for the calculation. $\langle M_c \rangle$ was calculated from:

$$\langle M_c \rangle = \frac{422.4}{w_{\mathrm{UPR}}} \tag{4}$$

where w_{UPR} is the weight fraction of pure unsaturated polyester polyol resin. The value of 422.4 is the number-average molecular weight between unsaturations as calculated from the polymer composition. Eq. (4) does not consider the effect of pendant chains which exist in the hybrid network. Table 3 lists the $\langle M_c \rangle$ values of all samples calculated from Eq. (4).

Table 3
Average-number molecular weight between crosslinks, $\langle M_c \rangle$ (in g)

Incorporation of chain extender (wt%)	EG	HD
0[a]	745	745
1.5	808	
3	873	823
4.5	940	
6	1009	905
8	1104	
10	1203	1024
12	1307	

Number-average of molecular weight between unsaturations for pure unsaturated polyester polyol = 422 g/C=C.
[a] REF.

The relationship between G at the rubber plateau and $\langle M_c \rangle$ as given by Eq. (3) was examined at 120 and 180°C. The entire hybrid network was in the rubbery state at 180°C, while only the soft domain of the phase-separated hybrid network reached the rubbery state at 120°C. The hybrid network density was calculated from the specific thermal expansion of $5 \times 10^{-4}\,\mathrm{cm}^3\,\mathrm{g}^{-1}\,\mathrm{K}^{-1}$ [28] and a network density of $1.20\ \mathrm{g\,cm}^{-3}$ at 25°C. The calculated hybrid network density was equal to $1.14\ \mathrm{g\,cm}^{-3}$ at 120°C and $1.10\ \mathrm{g\,cm}^{-3}$ at 180°C. The rubber storage shear modulus, G'', was used in the comparison since the phase angle was small at both temperatures. The comparisons of measured and calculated rubber storage shear modulus, G', as a function of $1/\langle M_c \rangle$ are shown in Fig. 2. A very good correlation between the measured and calculated results was observed for the phase-mixed system. However, the predicted results were slightly higher than the experimental results. The difference is due to pendant chains which were not included in the $\langle M_c \rangle$ calculation. The pendant chains should decrease ν and result in a lower G'' as described by Patel et al. [18]. The intermediate storage shear modulus measured at 120°C for phase-separated samples was much higher than the value predicted by Eq. (3). This is due to the existence of phase-separated hard domains. The phase-separated hard domains act like physical crosslinks within the rubber soft domain when the temperature is lower than their T_g. Fedors described the phenomenon as ‘virtual crosslinking’, although no chemical crosslinks are present [29]. Therefore, the number-average molecular weight between crosslinks was smaller than the value calculated by Eq. (4).

The phase structure of the hybrid network can be changed by quenching the sample from the rubbery state to the glassy

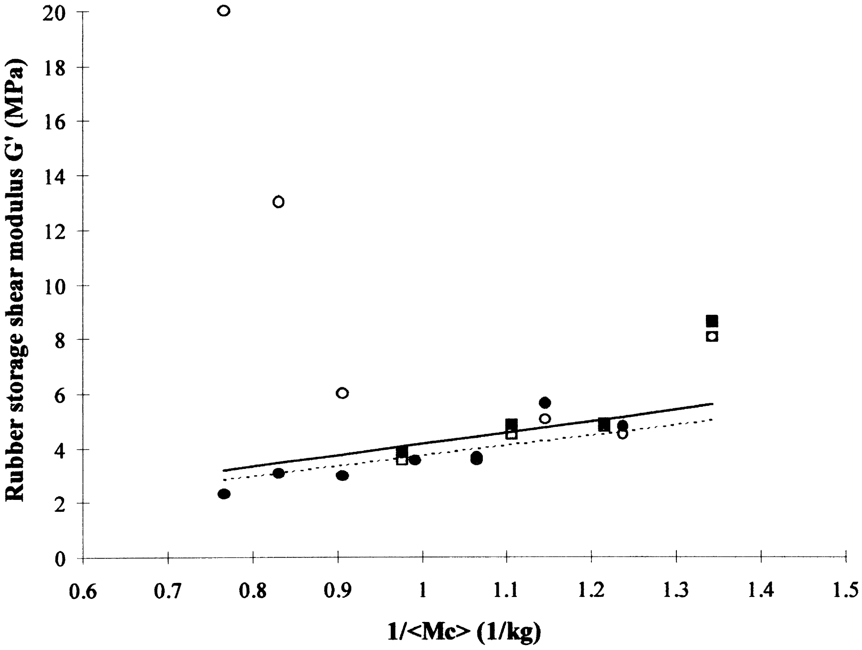

Fig. 2. Rubber storage shear modulus, G', vs. $1/\langle M_c\rangle$: (○) EG at 120°C; (□) HD at 120°C; (●) EG at 180°C; (■) HD at 180°C; (- - -) extrapolation of G' by Eq. (3) at 120°C ($\rho T = 448$ g K cm^{-3}); (——) extrapolation of G' by Eq. (3) at 180°C($\rho T = 496$ g K cm^{-3}).

state as described in the previous paper [15]. Fig. 3 shows G' and tan δ vs. temperature for EG12 before and after quenching. The hybrid network changed from a phase-separated system into a phase-mixed system after quenching. The high-temperature α transition was not present on G' nor tan δ curves after quenching. G' yield as well as tan δ peak were much broader for the quenched samples. The half-height width of the tan δ peak changed from 40°C to 60°C for EG12 after quenching. The height of the tan δ peak also increased after quenching. These results indicate that the volume fraction of the soft phase was higher since the hard domains were dissolved in the soft domain instead of forming phase-separated hard domains.

The dynamic mechanical properties of these samples were also investigated by creating master curves of shear storage modulus and tan δ vs. frequency following the time–temperature superposition (TTS) principle [30] using 106°C as the reference temperature. The shift factor, a_T, is defined by the Williams–Landel–Ferry (WLF)

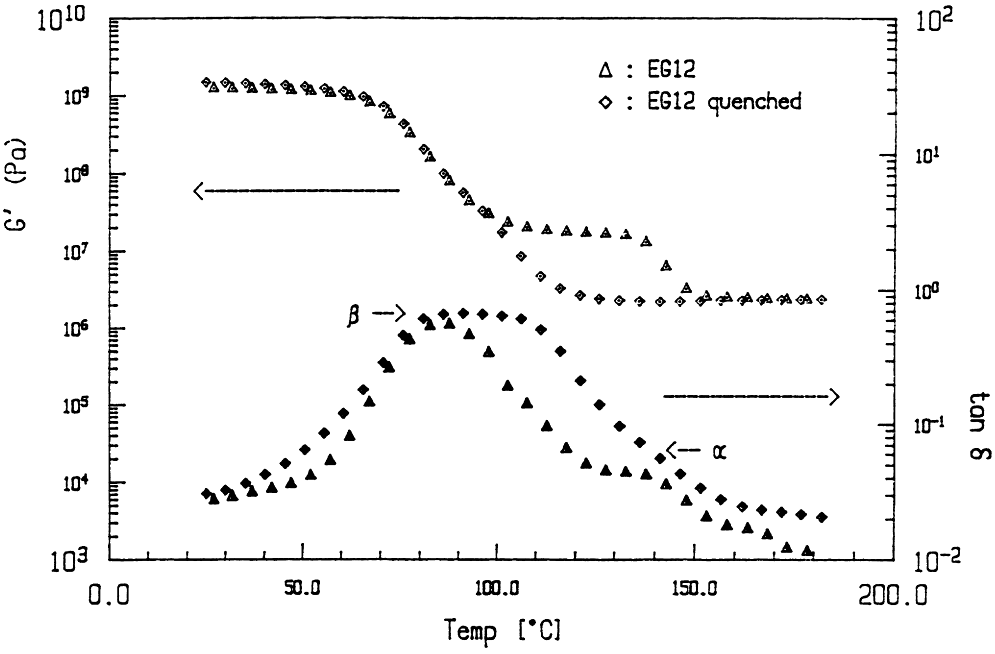

Fig. 3. Storage shear modulus G' and tan δ of EG12 before and after quenching.

equation as shown below:

$$\log a_T = \frac{-c_1^0(T - T_0)}{(c_2^0 + T - T_0)} \quad (5)$$

where c_1^0 and c_2^0 are the shift coefficients and T_0 the shift reference temperature. c_1^0 and c_2^0 appeared to be constant for a given chain extender within experimental error. c_1^0 and c_2^0 were 14.3 and 168.4°C respectively for hybrid networks with EG incorporation, and 12.9 and 165.6°C for hybrid networks with HD as chain extender. They are of the same order of magnitude as those found in the literature [30,31]. The activation energy, E_a, of the shift factor was calculated by the Rheometrics software using an Arrhenius equation of the form:

$$a_T = A_a \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where a_T is the shift factor and A_a is a constant. All samples showed good correlation, with a correlation factor r^2 between 0.85 and 0.97. The average activation energy for polyurethane and unsaturated polyester hybrid networks, $\langle E_a \rangle_{EG}$, was 282 kJ mol^{-1} with EG incorporation. The average activation energy for hybrid networks with HD as chain extender, $\langle E_a \rangle_{HD}$, was 242 kJ mol^{-1}. This is in the same range of activation energy found for polyurethane systems by Senich and MacKnight [26] and by Hartmann and coworkers [31,32].

Changes in the dominant relaxation frequency of the master curves, f_0, have been shown to be directly related to changes in T_g determined by the maximum of tan δ [33]. For a phase-mixed polymer system the relationship between $\log(f_0)$ and $1/T_g$ is linear. Samples with a higher f_0 have a lower T_g. Experimental results are given in Fig. 4 showing $\log(f_0)$ plotted against $1/T_g$. The β transition of tan δ in d.m.a. tests was used as the T_g to be consistent with the method. All HD samples were almost superimposed because they had about the same T_g. Polyurethane and unsaturated polyester hybrid networks with low contents of EG as chain extender, i.e., before phase separation, followed a linear relationship. When the system was phase-separated, experimental results did not agree with the linear correlation. f_0 increased as the T_g of each sample increased. The deviation is due to the inhomogenity of the phase-separated hybrid network. To clarify this point, the same tests were conducted for quenched samples with higher EG contents. In this case, a higher T_g led to a lower f_0 and agreed with the theoretical expectation. A linear relationship was found among all phase-mixed samples. The results of hybrid networks with HD as the chain extender, with EG incorporation lower than 6 wt%, or quenched samples with higher EG incorporation, could be extrapolated by a single straight line.

Fig. 5 shows storage shear modulus at the rubber plateau, G_0, vs. the weight fraction of hard segments in the hybrid network. Data obtained from time–temperature superposition experiments gave good confirmation of the results of d.m.a. tests. G_0 decreased as the hard segment fraction increased. However, we can note that after phase separation, G_0 determined from shifted data was much larger. This means that G_0 was not the ultimate rubber plateau but the intermediate rubber plateau. The TTS principle can be used only with a phase-mixed system, which was not the case for the hybrid network with high content of EG. When the tests were conducted with quenched samples, the experimental results agreed with expectation. All values can be described by a decreasing line as the weight fraction of hard segments increases. No significant difference in G_0 was found between EG and HD hard segments.

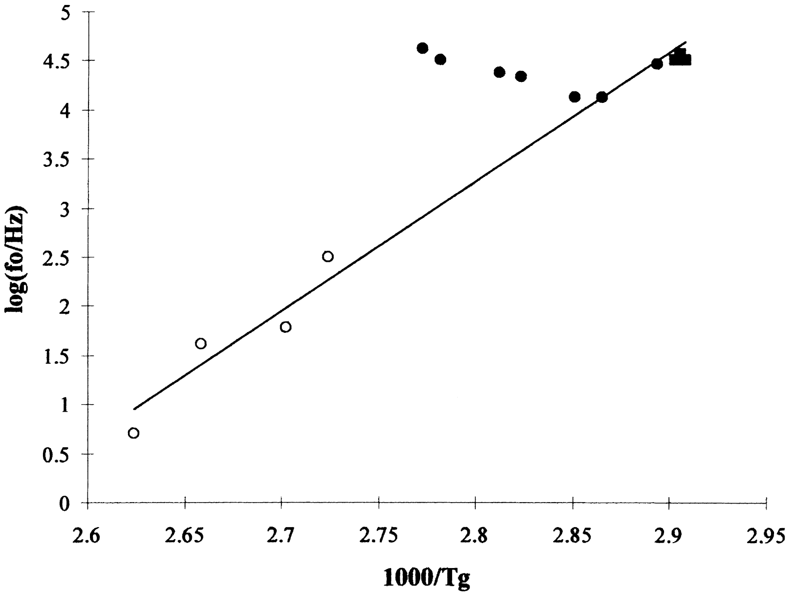

Fig. 4. Log(f_0/Hz) vs. 1000/T_g: (●) EG; (○) EG quenched; (■) HD.

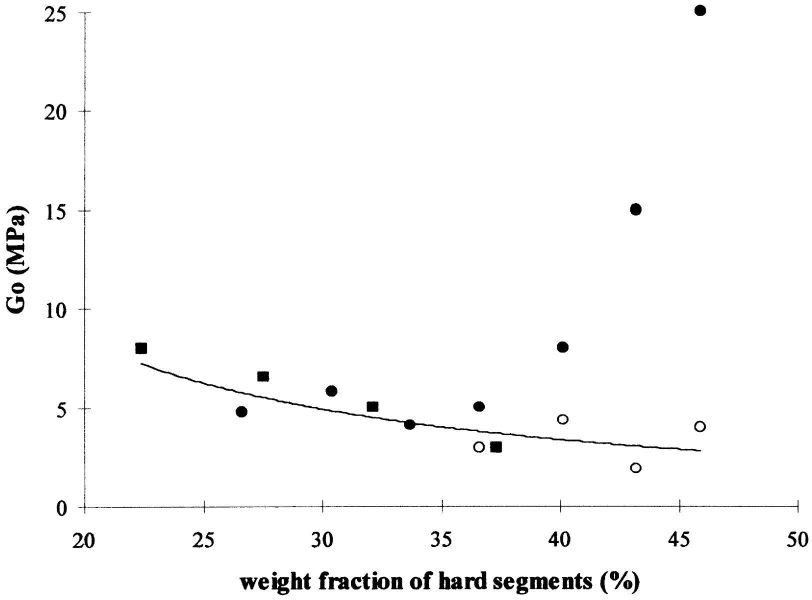

Fig. 5. Rubber plateau of storage modulus (G_0) vs. wt% of hard segments: (●) EG; (○) EG quenched; (■) HD.

3.2. Mechanical properties

Typical polyurethane block copolymers are rubbery at ambient temperature. Their mechanical properties are similar to those of elastomeric materials. The modulus is typically of the order of MPa, and the elongation is generally between 500% and 1000% at break [34,35]. The polyurethane and unsaturated polyester hybrid networks are glassy at ambient temperature, and therefore their mechanical properties are different from those of the polyurethane block copolymers.

Comparison of results from the Izod impact resistance tests of unnotched specimens is shown in Fig. 6. Hybrid networks with HD incorporation showed an improvement in impact resistance of nearly 20% for increasing content of chain extender from 0 to 10% by weight. Micrographs of the unnotched Izod fracture surface of HD3 and HD10 are shown in Fig. 7(A), Fig. 7(B), respectively. As the HD content increased, the smooth fracture initiation region became smaller while the rough secondary fracture region grew. Secondary cracks were shown throughout the secondary fracture region. The secondary cracks consumed more energy than the smooth initiation region. As the amount of

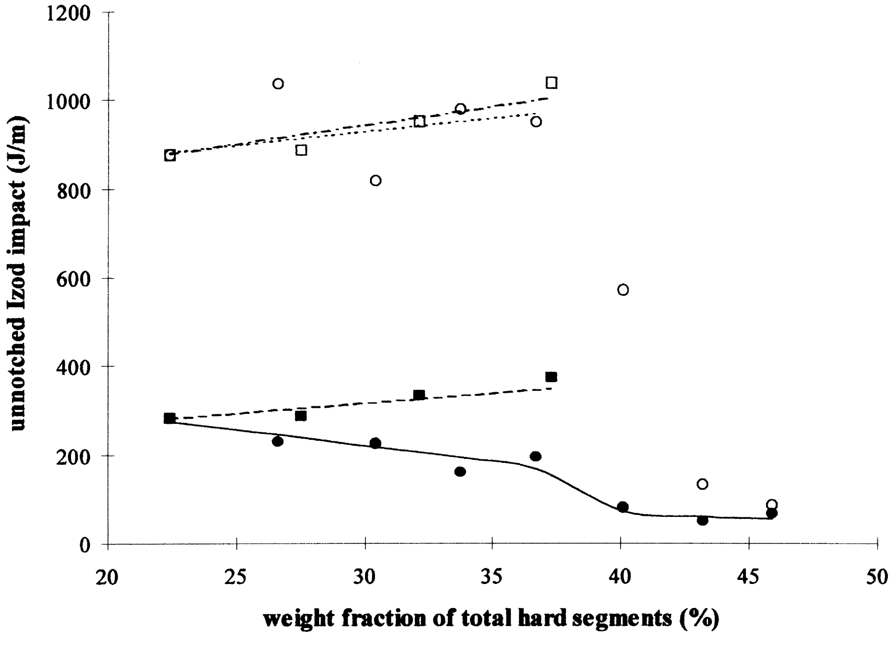

Fig. 6. Izod impact analysis (unnotched specimens) vs. wt% of hard segments: (– • –) EG; (· · ·○ · · ·) EG quenched; (- - -■ - - -) HD; (— – — □ — – —) HD quenched.

HD incorporated increased, larger fibrils were pulled out of the secondary fracture surface.

On the contrary, the impact resistance decreased for all samples with EG incorporation. A bigger drop in impact strength was observed when phase-separated hard domains were formed. Since both the soft domains and hard domains exist in the hybrid network, the impact resistance is controlled by the more brittle phase, formed by hard domains. Fig. 7(C), Fig. 7(D) show micrographs of the unnotched Izod fracture surface of EG3 and EG12, respectively. The fracture surface of the polyurethane and unsaturated polyester hybrid networks with EG incorporation, before phase separation occurred, was similar to that of hybrid networks with HD as chain extender as shown in Fig. 7(C), Fig. 7(A). However, Fig. 7(C) shows fewer secondary cracks and smaller fibrils pulled out compared with the fracture surface of the HD samples. Since less energy was consumed by the secondary cracks, hybrid networks with EG as a chain extender had a lower impact resistance. Fig. 7(D) shows that the fracture initiation region was larger and the secondary fracture region was very smooth after phase separation occurred. No fibril pull-out was observed on the fracture surface, which agreed with the very low impact resistance for these samples. The chain length of the chain extender plays an important role in determining the impact resistance of hybrid networks. A more flexible, long chain extender gives higher impact strength, while a more rigid, short chain extender decreases the impact strength.

Quenched samples had a much higher impact resistance and the impact resistance increased with incorporation of the chain extender, with the exception of samples that were initially phase-separated. Results for materials with HD or EG as chain extender were about the same for a given weight fraction of hard segments, within experimental error. The fracture surface of quenched samples showed a small smooth fracture initiation region and a large rough secondary fracture region with both cracks and fibril pull-out. Samples that had a two-phase structure before quenching showed a very sharp drop in impact strength. This was due to the flat, round cracks that formed from internal stresses within the materials during quenching. The higher the incorporation of EG, the more numerous the cracks. The flat round cracks were between 1 and 5 mm in diameter. Stresses may appear at the interface of the soft and hard domains because of a differential thermal expansivity. The cracks developed from weak areas of the material in order to release internal stresses and thus formed the flat round geometry.

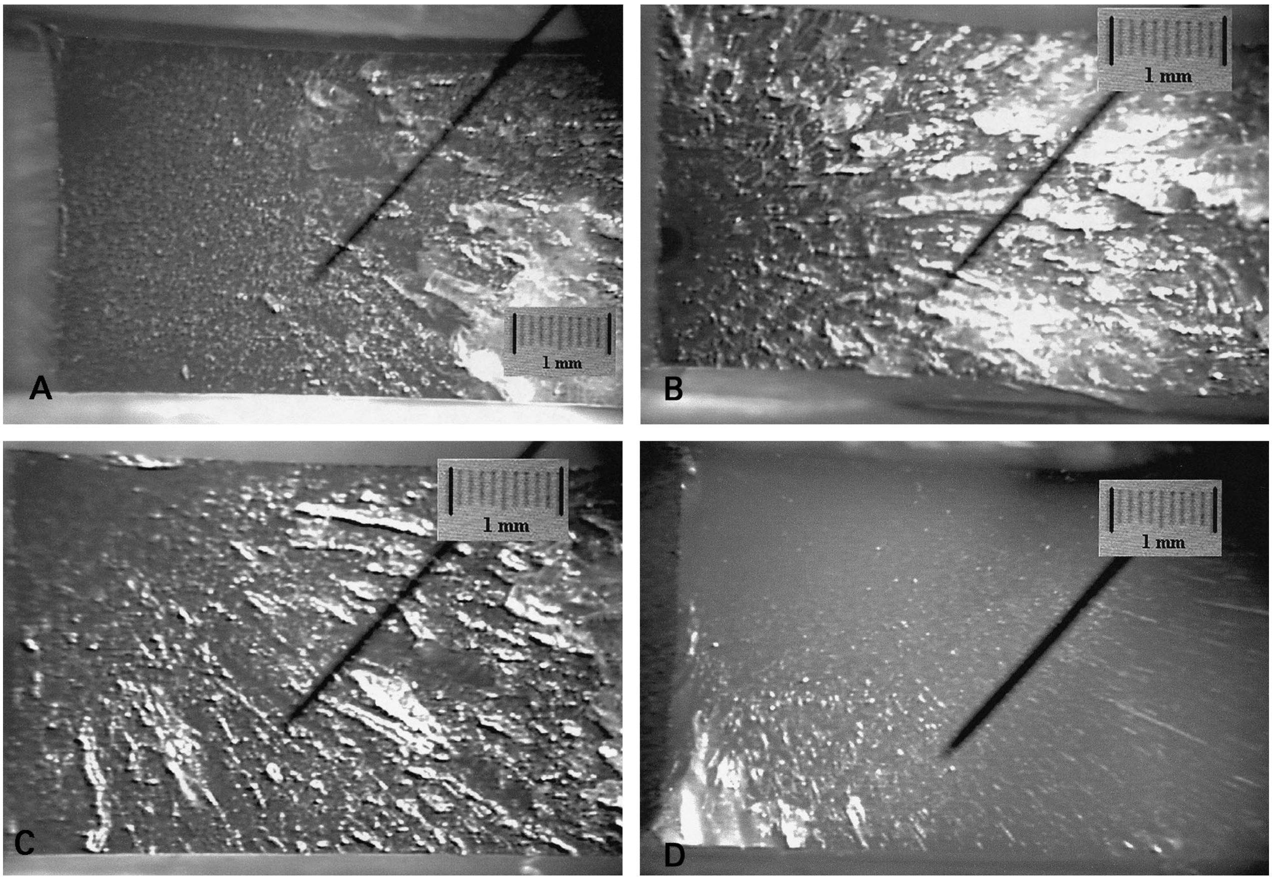

Fig. 7. Micrographs of the unnotched Izod fracture surface of: (A) HD3; (B) HD10; (C) EG3; (D) EG10.

The flexural modulus of hybrid networks vs. weight fraction of total hard segments is given in Fig. 8. The modulus of samples with HD as the chain extender decreased slightly when the HD content increased, while the modulus of samples with EG as the chain extender increased with increasing EG content. As previously discussed, this is due to the chain length of the chain extender. A significant increase in flexural modulus was observed for the samples with phase-separated hard domains. In this case, hard domains form a co-continuous phase with soft domains as described by Ophir and Wilkes [14] and give a higher flexural modulus. The quenched samples had a lower flexural modulus and the modulus decreased as the incorporation of chain extender increased for both sets of samples. Because hard segments do not form a phase-separated hard domain in quenched samples, the apparent flexural modulus of hybrid networks of quenched samples was controlled by the soft domain.

Fig. 9(a), Fig. 9(b) show the stress at yield and strain at yield as a function of the weight fraction of hard segments. Both the flexural stress and strain at yield increased slightly for samples with low incorporation of chain extender. For higher amounts of chain extender, both flexural stress and strain at yield decreased, especially after phase separation. Mekhilef and Verhoogt explained the fact that the co-continuous structure of polymer blends usually possesses weak mechanical properties by virtue of the weak interfacial interaction between the two polymers, although both components are continuous and thus could fully contribute to the properties of the blend [36]. However, quenched samples showed a decrease in yield stress and an increase in yield strength as the content of chain extender increased. Shifts in the flexural stress and strain at yield were also observed before and after quenching. Quenched samples had a lower yield stress and a higher strain than unquenched samples. Flat round cracks were found in quenched samples that had previously been phase-separated. The cracks decreased the flexural stress and stain at yield dramatically.

4. Conclusion

The thermomechanical properties of polyurethane and unsaturated polyester hybrid networks have been investigated by heat distortion analysis and dynamic mechanical analysis. Transition temperatures agreed with the results measured by modulated d.s.c. as reported in a previous study. Multiple transitions shown by d.m.a. for samples with EG contents above 6 wt% were related to the phase-separated structure. The α transition was related to the phase-separated hard domain and the β transition was related to the soft domain. The rubber plateau of the storage shear modulus was correlated to the crosslinking density. However, theoretical predictions at temperatures lower than the glass transition temperature of the hard domains did not agree with experimental results for the phase-separated hybrid networks. The phase-separated hard domains acted as ‘virtual crosslinks’ and reduced the number-average molecular weight between crosslinks. Mechanical properties at room temperature were generally improved by the incorporation of a chain extender. HD increased the flexibility of polymer chains, resulting in higher deformation and impact resistance of the hybrid networks. Hybrid networks with EG as the chain extender were stiffer by virtue of the rigid hard domains. Hybrid networks with an EG content greater than 6 wt% showed a high

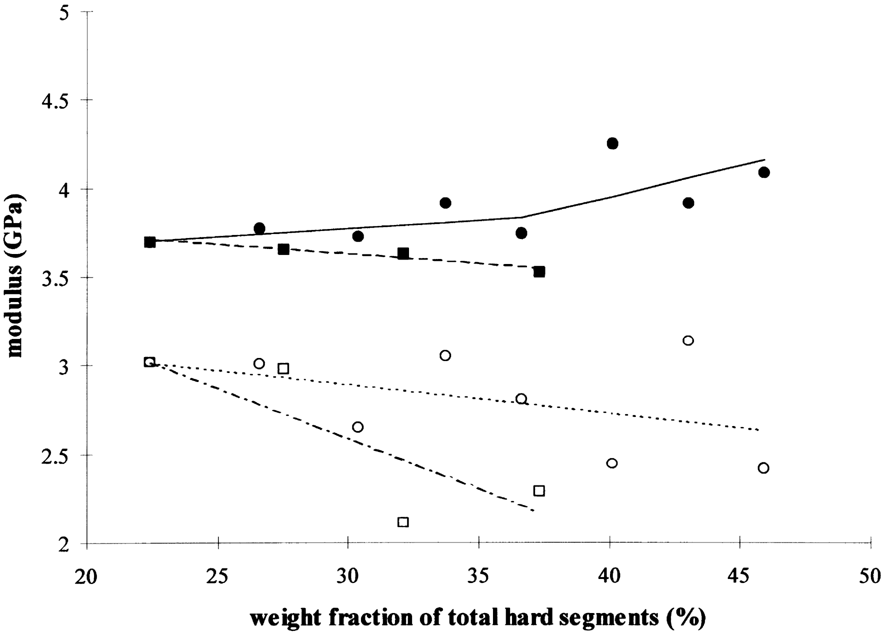

Fig. 8. Flexural modulus vs. wt% of hard segments: (– • –) EG; (· · ·○ · · ·) EG quenched; (- - -■ - - -) HD; (— – —□— – —) HD quenched.

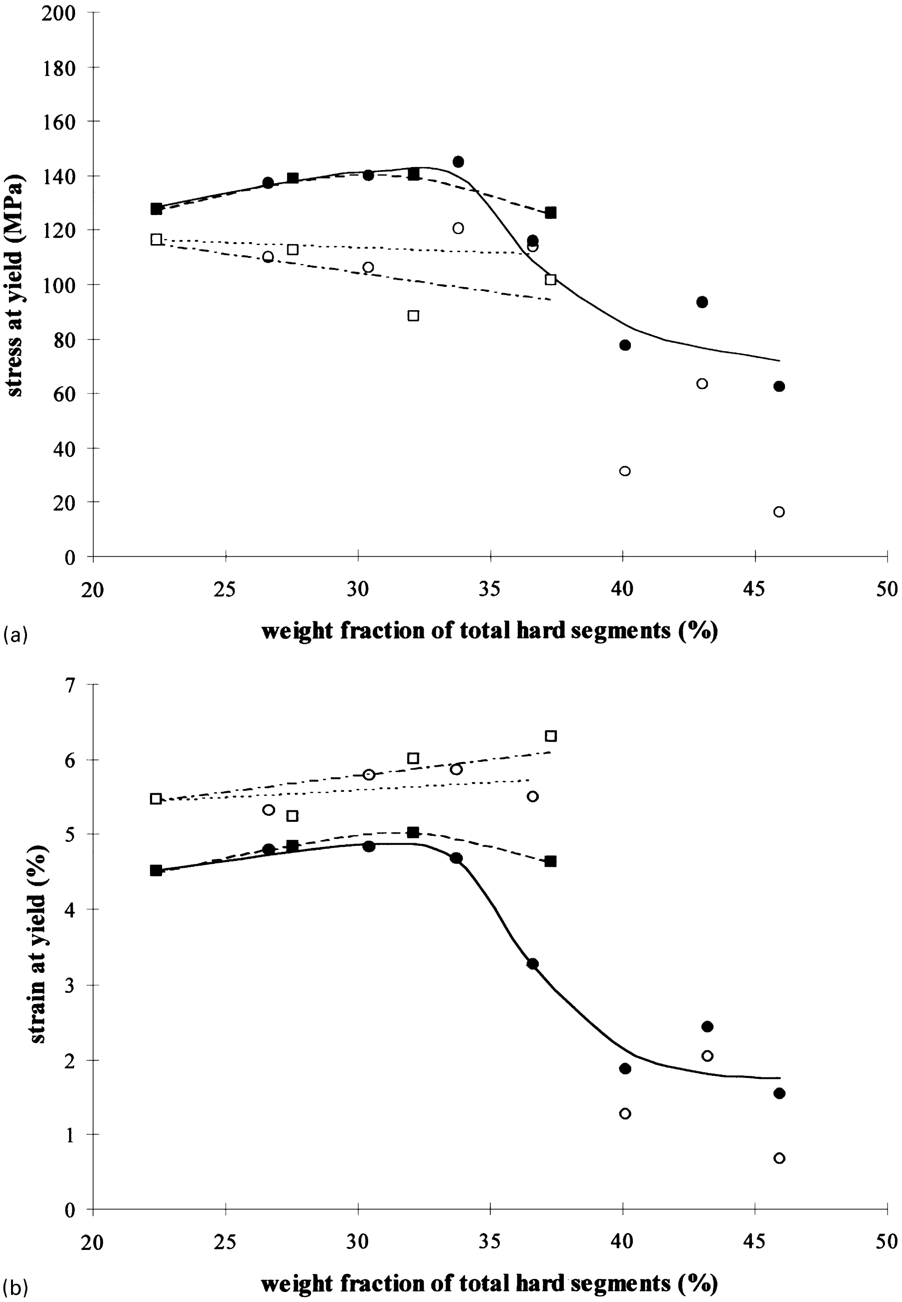

Fig. 9. (a) Stress at yield vs. weight fraction of hard segments and (b) strain at yield vs. weight fraction of hard segments: (– • –) EG; (· · ·O · · ·) EG quenched; (- - - ■ - - -) HD; (— — — □ — — —) HD quenched.

flexural modulus, but poor ultimate mechanical properties because of the formation of phase-separated hard domains.

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