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Use of rigid thermoplastics for toughening an optical network polymer

Masoud Frounchi *

Department of Chemical Engineering, Sharif University of Technology, Tehran, Iran

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Abstract

Blends of the thermoset poly(allyl diglycol carbonate) (PADC) with thermoplastic polymethacrylates have been prepared by dissolving polymethacrylates in allyl diglycol carbonate (ADC) monomer and subsequent polymerisation of ADC. The polymethacrylates formed separate phases in the blends as shown by scanning electron micrographs. The dynamic mechanical data showed two distinct high-temperature peaks corresponding to the glass transition temperatures of the PADC and polymethacrylates. Fracture toughness tests showed a significant increase in the critical intensity factor k_c of PADC by addition of only 10% (w/w) a ductile thermoplastic poly(ethyl methacrylate). Young's modulus at room temperature showed no reduction by addition of the thermoplastic component.

Keywords: Poly(allyl diglycol carbonate); Polymethacrylates; Blend; Toughening; Phase separation; CR-39

1. Introduction

The highly cross-linked micro-structure of network polymers often leads to low resistance to crack initiation and propagation [1,2]. It is important to increase the toughness of these materials without causing any major loss in their other desirable properties such as high modulus, high strength, and high glass transition temperature. The most common method to improve on the toughness of thermoset polymers involves the addition of elastomers [3,4]. However the rubbery inclusions often lower both the modulus and the use temperature of the thermoset resin [5]. Use of rigid thermoplastic tough, ductile polymers as an alternative method of toughening thermoset resins has had varying success in recent years [6–10]. It is envisaged that network polymers based on this method may be toughened without negatively affecting their other useful properties. The prevalent method in producing a thermoplastic second phase is to first dissolve the thermoplastic polymer into the thermoset monomer and later allow it to phase separate during the network formation process of the thermoset resin. A variety of morphologies can arise which may influence the final properties of resulting blends [5]. In this work we study the blends of the thermoset poly(allyl diglycol carbonate) (PADC) commercially known as CR-39 resin with thermoplastic polymethacrylates.

PADC is a cross-linked glassy polymer of excellent optical qualities [11]. It is made by bulk polymerisation of diethylene glycol bis-allyl carbonate monomer which is represented by the formula:

$$CH_2{=}CH{-}CH_2{-}O{-}CO{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CO{-}O{-}CH_2{-}CH{=}CH_2$$

The aim is to investigate the effect of these resulting morphologies on the fracture properties of PADC in order to find a way to enhance fracture resistance of this thermoset material. Apart from the optical transparency requirement in PADC modification, also the identification of the toughening mechanism operating in this polymer is of interest from the viewpoint of polymer fracture mechanics. In order to achieve a homogeneous

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* Tel.: +98-21-6005819; fax: +98-21-6022853.
E-mail address: frounchi@sina.sharif.ac.ir (M. Frounchi).

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blend before the gelation process of PADC, the allyl diglycol carbonate (ADC) monomer must be compatible with the thermoplastic modifier dissolved in a solvent. Polyetherimide [7] and poly(phenylene oxide) [10], which are very tough thermoplastics and very effective in toughening of highly cross-linked epoxies, were found to be totally immiscible with the ADC monomer. However, polymethacrylates are miscible with the ADC monomer and a proper selection of a tough polymethacrylate modifier may result in new strong optical plastics.

2. Experimental

Two grades of poly(methyl methacrylate) (PMMA) Elvacite 2009 and Elvacite 2021, and one grade of poly(ethyl methacrylate) (PEMA) Elvacite 2042, of DuPont company [12] were used in this study. These thermoplastic polymers are available as powder and their characterisation details have been listed in Table 1.

The polymethacrylates were dissolved in acetone and then mixed with the ADC monomer. Acetone was evaporated at room temperature in a vacuum chamber and a viscous transparent solution of polymethacrylates in PADC monomer was obtained. The solutions were transferred into a glass mould and then placed in a programmable oven in which the temperature was slowly increased from 50°C to 85°C over a period of 21 h. The samples were then removed from the mould and annealed at 110°C for 2 h. The completion of ADC polymerisation was determined by FT-IR spectroscopy through the absorption of the allyl groups overtone band at 6130 cm^{-1} [13]. The blends with 5% and 10% (w/w) thermoplastic polymers only were made because with increasing the thermoplastic content the viscosity was too high for moulding. In addition, it was found that around 10 wt.% thermoplastic content, phase inversion occurs and thus with further increase in thermoplastic content the continuous phase in the blend morphology will be the thermoplastic polymers.

Table 1
General properties of polymethacrylate at 23°C

	Polymer		
	PMMA		PEMA
	Elvacite 2009	Elvacite 2021	Elvacite 2042
Inherent viscosity ($\mathrm{ml\,g}^{-1}$)	0.39	0.5	0.8
Tensile strength (MPa)	41	50	23
Elongation at break (%)	1.8	3.5	45

The glass transition temperature for the various samples were determined by means of a DuPont 983 dynamic mechanical analyser at a heating rate of 20°C min^{-1} in resonant mode. Micrographs of the fracture surfaces of single-edge notch samples were examined by scanning electron microscope (SEM) using a Cambridge Stereoscan 360 electron microscope. The flexure modulus, E, and fracture toughness, K_c, were determined using an Instron tensiometer at a cross-head travel speed of 1 mm min^{-1} at room temperature. The flexure modulus was measured on $3.3 \times 14 \times 80$ mm^3 bars in three point flexure with a distance of 60 mm between supports. Fracture toughness was evaluated from the critical stress intensity factor K_c using single-edge notched tensile test specimens ($3.3 \times 15 \times 120$ mm^3). The notches which had a radius smaller than 10 µm were produced with a razor blade. Details of fracture testing were performed according to the methods described in Ref. [1].

3. Results and discussion

Phase separation in initially miscible blends of thermoplastic polymethacrylates–ADC monomer occurs during the reaction because the increase in the molecular weight of PADC diminishes the entropy of the blend. The final morphology results from the competition between the kinetics of reaction and phase separation. Scanning electron micrographs show that at thermoplastic concentration of 5% the thermoplastic phase is uniformly distributed as discrete spherical particles which are of average diameter of about 26 µm as shown in Fig. 1. At higher thermoplastic concentrations a co-continuous morphology is found as shown in Figs. 2–4. The domain sizes appear relatively large and the co-

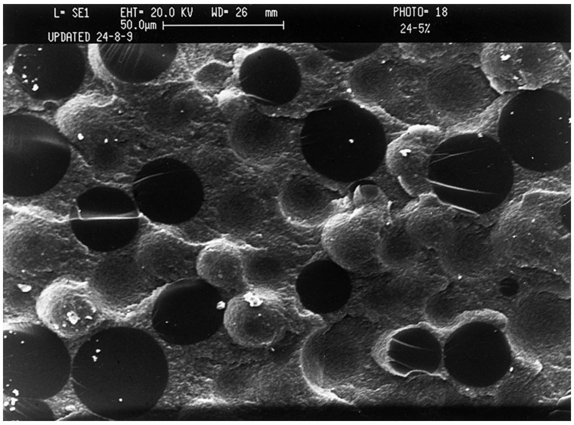

Fig. 1. Scanning electron micrograph of 5% PEMA/95% PADC; magnification 500×.

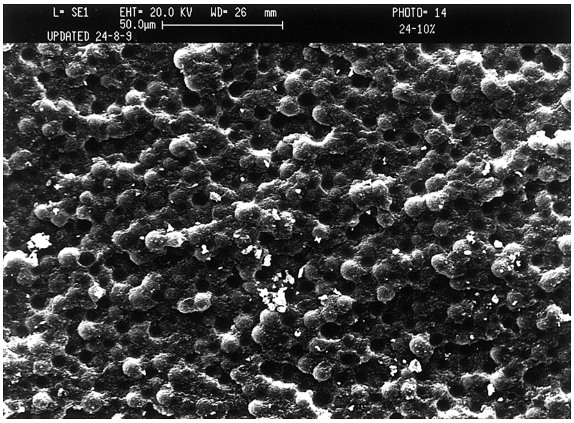

Fig. 2. Scanning electron micrograph of 10% PEMA/90% PADC; magnification 500×.

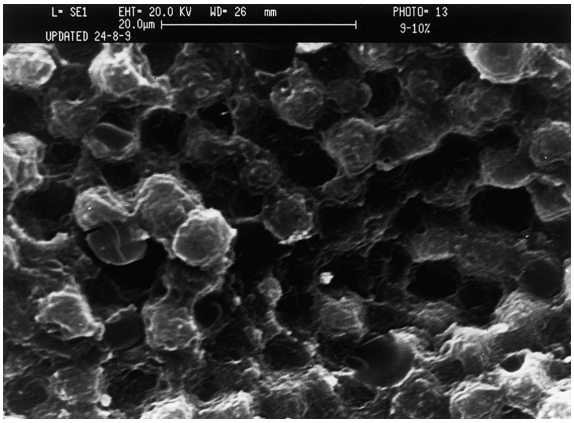

Fig. 3. Scanning electron micrograph of 10% PMMA/90% PADC (PMMA: Elvacite 2009); magnification 2000×.

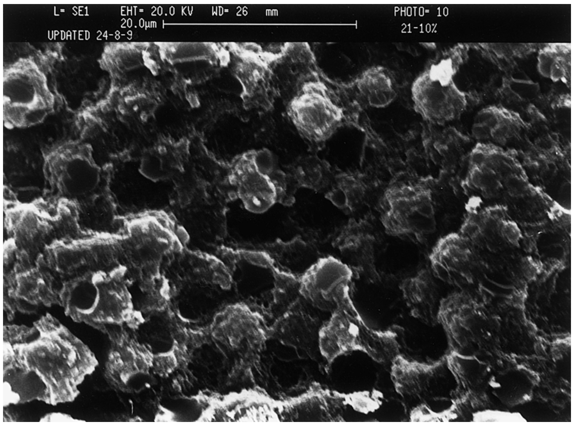

Fig. 4. Scanning electron micrograph of 10% PMMA/90% PADC (PMMA: Elvacite 2021); magnification 2000×.

continuous morphology suggests that phase inversion could occur at slightly higher amounts of thermoplastic modifier.

Dynamic mechanical thermograms for PADC and blends of 10 wt.% thermoplastic content are shown in Figs. 5–8. PADC shows a relaxation transition above room temperature. This transition occurs at 101°C on the E'' vs. temperature curve and about 130°C on the $\tan\delta$ vs. temperature curve. The blends show two transitions peaks above room temperature corresponding approximately to those in the unmixed component polymers. PADC transition peak in the blends shows a small amount of scatter around a mean value of 100°C, but remains effectively unchanged by the addition of polymethacrylates. Peak temperatures for polymethacrylates occur as shoulders prior to the PADC peak. The measured glass transition temperatures of the two-component polymers in the blends are presented in Table 2. It should be noted that the relaxation temperatures for polymethacrylates depend on: (i) the chemical side groups (i.e. methyl, ethyl or butyl); (ii) the method of measurement (ie. differential scanning calorimetry (DSC), DMA based on $\tan\delta$ or E''); (iii) and also the molecular weight. According to the typical data reported on the DuPont Elvacite technical bulletin [12], the relaxation temperatures for pure Elvacite 2009 (medium molecular weight PMMA) and 2024 (very high molecular weight polyethylmethacrylate) are 87°C, and 63°C, respectively, based on DSC measurement. Thus, to adopt a uniform approach on interpretation of experimental data, the discussion was based on the measurements from DMA E'' maxima. The occurrence of two single unshifted peaks on DMA E'' thermograms is showing that substantial demixing occurs during the PADC curing reaction. As mentioned earlier, the SEM micrographs show a two-phase micro-structure (Figs. 1–4), but the main feature of the dynamic mechanical data is to determine the degree of phase separation or thermodynamic miscibility. Thus, the fact that there is no significant shift in the transition temperature of PADC is evidence for a high degree of phase separation. It must be noted that the phase separation causes some degree of haziness. Indeed the haziness can disappear if the refractive indices of the two component polymers are very close [14]. The modification of PADC by urethane–acrylate resins [15] by the method of interpenetrating networks indicated no haziness owing to the similar refractive indices of two polymers. The flexure modulus data obtained for the blends (Table 3) suggest a slight increase from 2.4 GPa in the PADC to 2.66 GPa in the blends containing 10 wt.% thermoplastic. The slight increase in modulus is an advantage over more conventional rubber-toughening methods since the loss of modulus is an unavoidable consequence of adding rubber particles [5]. The measured fracture toughness data, K_c, of the blends is also shown in Table 3. The

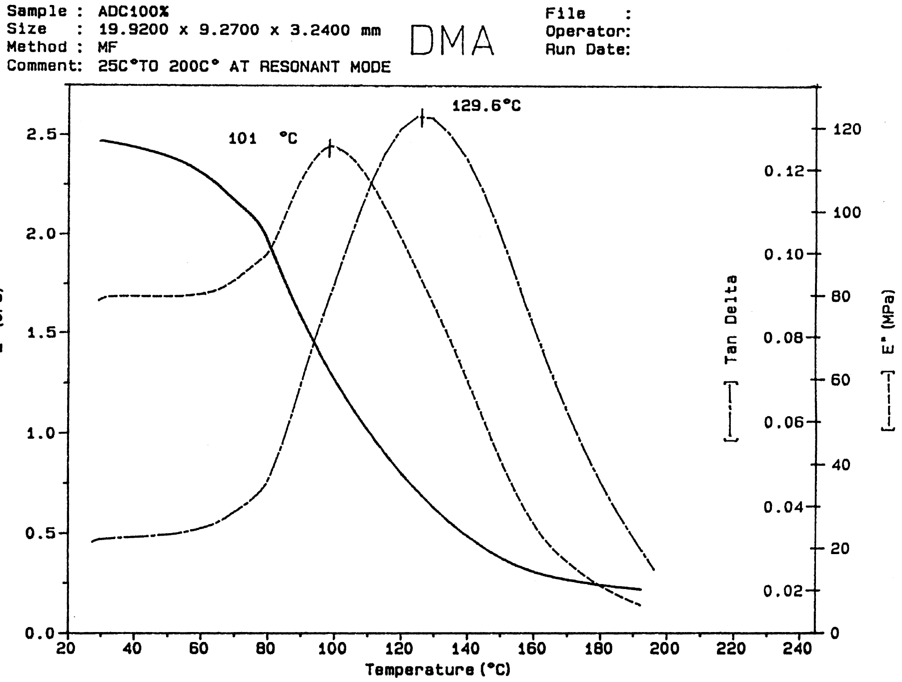

Fig. 5. Dynamic mechanical thermogram of PADC.

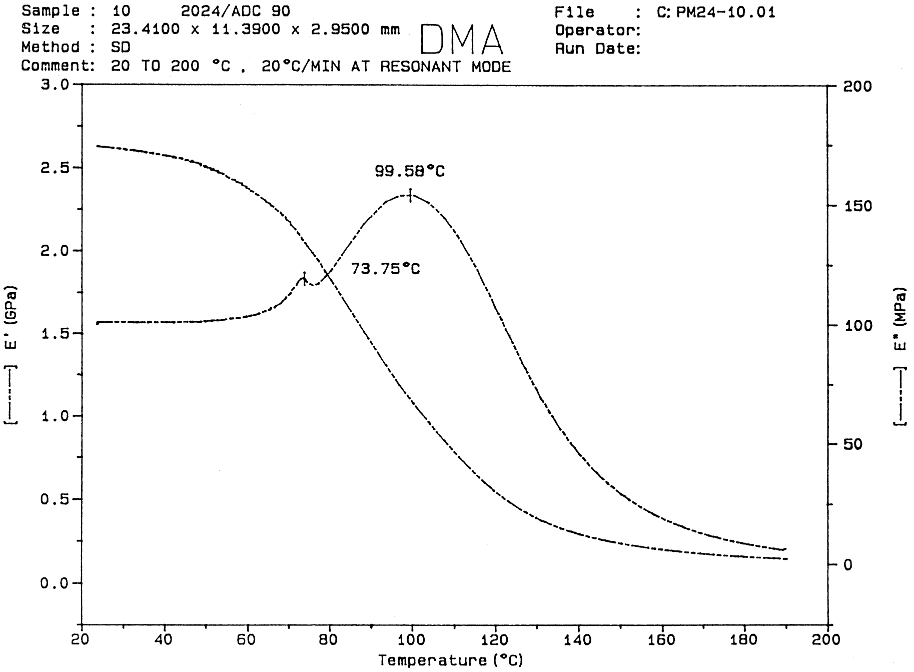

Fig. 6. Dynamic mechanical thermogram of 10% PEMA/90% PADC.

toughening effect of the PEMA was significant. This shows that the ductile PEMA contributes to the overall toughness of the two-component blends. Thus, it may be concluded that the first stage of fracture is brittle failure of the thermoset PADC phase leaving the more ductile PEMA bridging the gaps. The PMMAs which are more

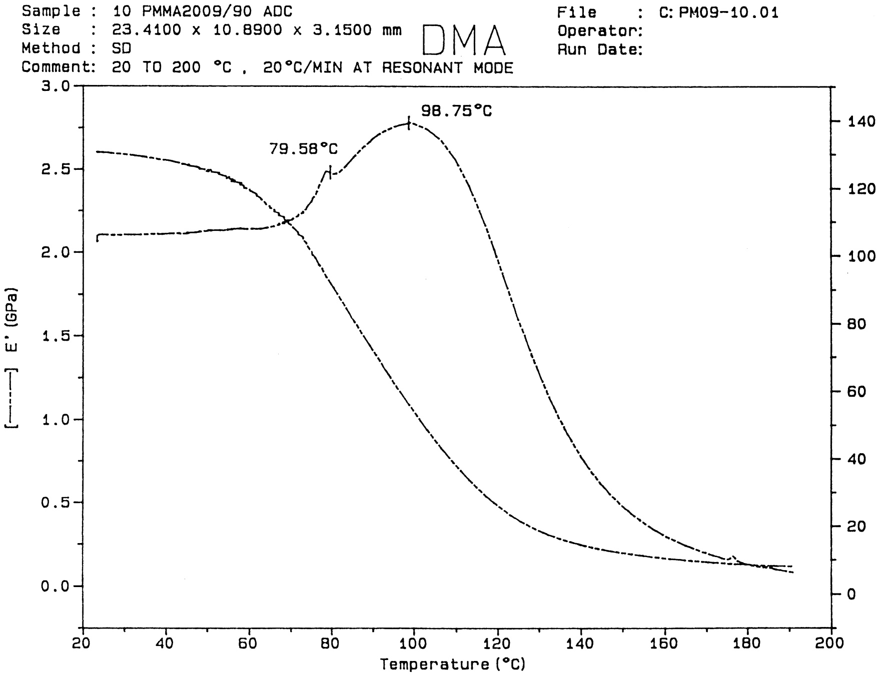

Fig. 7. Dynamic mechanical thermogram of 10% PMMA/90% PADC (PMMA: Elvacite 2009).

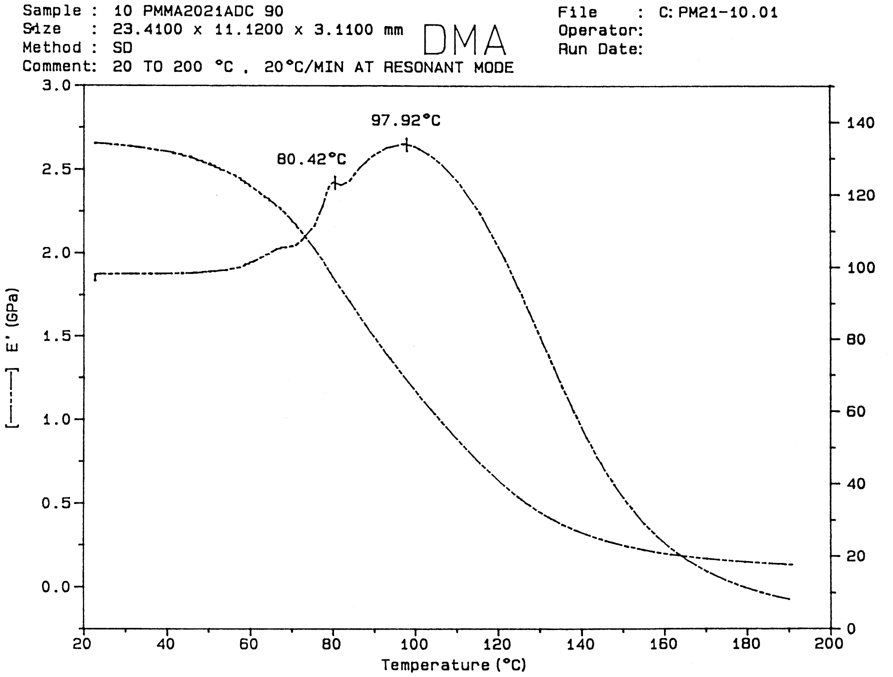

Fig. 8. Dynamic mechanical thermogram of 10% PMMA/90% PADC (PMMA: Elvacite 2021).

rigid, but much less ductile, than PEMA were not able to play a toughening role in the blends. The ductile tearing of the thermoplastic PEMA phase can occur when the PADC–thermoplastic interface is sufficiently strong. In the absence of reactive chemical groups between the two-component polymers, the interfacial

Table 2
Glass transition temperatures of the two-phase blends

Material	Lower glass transition temperature (°C)	Higher glass transition temperature (°C)
PADC	–	100.0
5% PEMA/90% PADC	65.00	100.0
10% PEMA/90% PADC	73.75	99.58
5% PMMA/90% PADC	73.92	99.58
10% PMMA/90% PADC (PMMA: Elvacite 2021)	80.42	97.92
10% PMMA/90% PADC (PMMA: Elvacite 2009)	79.58	98.75

Table 3
Mechanical properties of the blends

Material	Flexure modulus (GPa)	Fracture toughness, K_c (MPa m$^{1/2}$)
PADC	2.41	0.48
5% PEMA/90% PADC	2.66	0.69
10% PEMA/90% PADC	2.62	0.85
5% PMMA/90% PADC	2.64	0.48
10% PMMA/90% PADC (PMMA: Elvacite 2021)	2.65	0.49
10% PMMA/90% PADC (PMMA: Elvacite 2009)	2.60	0.37

strength must arise from physical entanglements between thermoplastic chains and PADC network. In rubber-toughened resins the principal mechanism is due to the yielding of the cross-linked matrix resin [16,17]. The rubber-toughening mechanism becomes progressively less effective as cross-link density is increased [5]. PADC is a highly cross-linked thermoset polymer which will not permit adequate yielding [15,17]. Thus, it may be concluded that the operating toughening mechanism in PADC/PEMA blends involves a drawing mechanism in the thermoplastic component polymer.

4. Conclusions

This work has shown that addition of a properly selected thermoplastic can increase the fracture toughness of a highly cross-linked thermosetting polymer without loss in modulus of the thermoset polymer. Addition of polymethacrylates into the PADC forms phase-separated blends. The scanning electron micrographs and dynamic mechanical data show that there is little, if any, miscibility between the two components after the network forming polymerisation of ADC. The toughening mechanism in the blends appears to depend upon the ductile drawing of the thermoplastic component polymer. PEMA, which is a rigid ductile thermoplastic, was shown to play an effective toughening role in the blends.

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