Mechanical Behavior of Gradient Polymers*

G. C. MARTIN, *Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13210*, E. ENSSANI and M. SHEN, *Department of Chemical Engineering, University of California, Berkeley, California 94720*

Synopsis

Gradient polymers are multicomponent networks which contain a spatial gradient in the concentration of the components in the blend. In this study, the properties of a system of gradient polymers consisting of a rubbery addition to a glassy matrix [poly(methyl methacrylate)] and a glassy addition to a rubbery matrix [poly(2-chloroethyl acrylate)] were investigated. Dynamic mechanical spectroscopy was used to characterize the compatibility of the polymers. The PMMA matrix gradients were found to be incompatible, while the PClEA matrix gradients and the interpenetrating network exhibited compatibility. The tensile properties and the fracture strength of the polymers were measured and interpreted in terms of the composition and the deformation mechanism of the materials.

INTRODUCTION

Because of their heterogeneous nature and adaptability, polymer blends are receiving increased attention and application. One novel type of polymer blend consists of multicomponent networks which contain a spatial variation or gradient in the concentration of the components. These materials are called gradient polymers and are similar to interpenetrating networks in which the polymers are completely interspersed together. Because of the unique nature of the gradient and its effect on the polymer structure, these materials may be utilized in a diverse range of applications such as fuel tanks, structural components, biomedical implants, noise dampeners, and packaging materials.[1-4]

Several systems of gradient polymers including poly(methyl acrylate) in poly(methyl methacrylate) (PMMA) and polyacrylonitrile in polystyrene,[5] poly(hydroxyethyl methacrylate) in silicone rubber,[2] hydrogels in poly(ether–urethane),[4] and poly(2-chloroethyl acrylate) in PMMA[6] have been studied. In general, the gradient materials have been found to display enhanced physical properties, such as toughness and resistance to environmental degradation, over the homopolymers and interpenetrating networks with similar composition.

In this study, the system of gradient polymers formed from poly(2-chloroethyl acrylate) (PClEA) and PMMA were extensively investigated. Since PClEA has a low glass transition temperature (whereas PMMA is glassy), the effects of adding a rubbery component to a glassy matrix (PMMA) and a glassy addition to a rubbery matrix (PClEA) could be explored. The specific objectives were:

(1) to determine the effects of processing conditions on the synthesis and transport properties of the materials,

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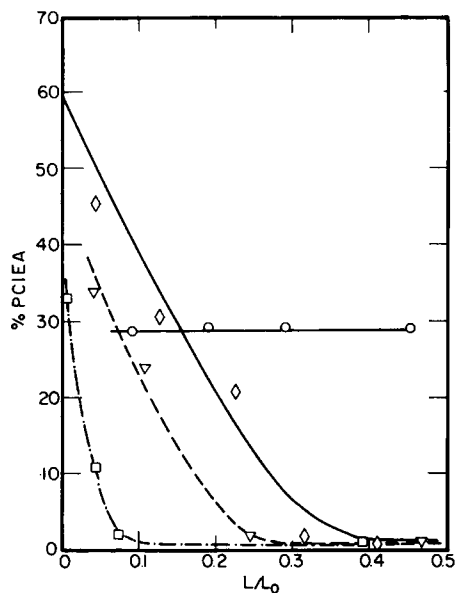CCC 0021-8995/81/051465-09$01.00

Fig. 1. Gradient profile: wt % PClEA as function of reduced thickness for the PMMA/PClEA blends. (-□-) PMMA/GRAD PClEA, (10%); (-▽-) PMMA/GRAD PClEA, (20%); (-◇-) PMMA/GRAD PClEA, (30%); (-○-) PMMA/GRAD IPN, (30%).

(2) to investigate the effect of composition and the nature of the gradient on phase separation in the blends,

    (3) to examine the enhanced mechanical properties of the gradients, and

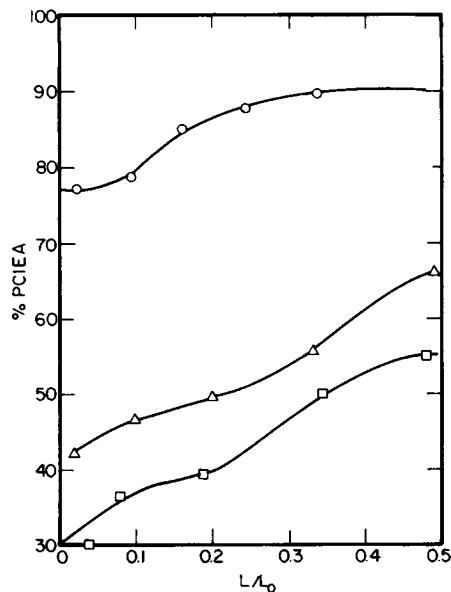   (4) to elucidate the deformation mechanism in the polymers.

Fig. 2. Gradient profile: wt % PClEA as function of reduced thickness for the PClEA/PMMA blends. (-○-) PClEA/GRAD PMMA, (10%); (-△-) PClEA/GRAD PMMA, (30%); (-□-) PClEA/GRAD PMMA, (50%).
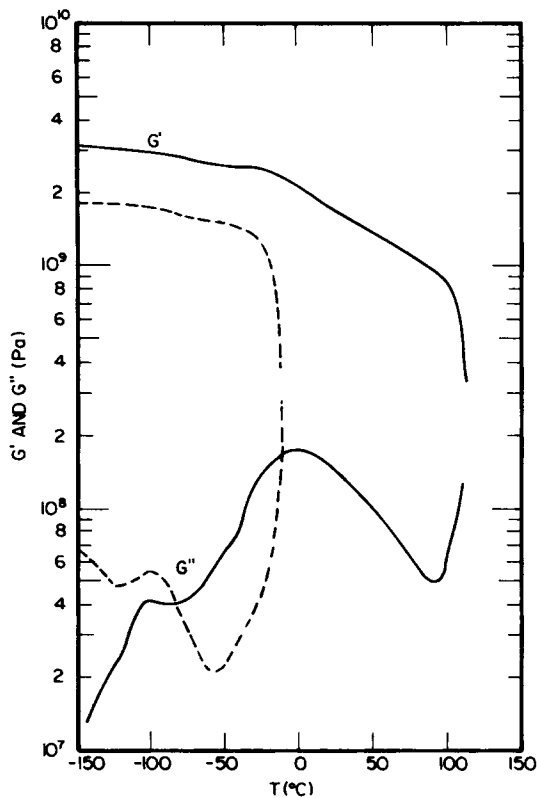
Fig. 3. Dynamic moduli of PMMA and PClEA at 1 Hz.   (—) PMMA, 1 Hz; (- - -) PClEA, 1 Hz.

EXPERIMENTAL

Polymer blends were prepared by the nonequilibrium swelling of a network (matrix) polymer with a network-forming monomer which was subsequently polymerized in place.   The polymerizations were conducted by photopolymerization with ultraviolet light using benzoin *sec*-butyl ether as the initiator and ethylene glycol dimethacrylate with a concentration of 1.4 wt % as the crosslinking monomer.

The experimental procedure consisted of the synthesis of the host polymer, the diffusion of the second monomer, and the polymerization of the penetrant into the gradient configuration.   Some of the processing variables in gradient polymer synthesis are the transport properties of the host network polymer and the penetrant, the geometry of the swelling apparatus (i.e., diffusion through one side or both sides of the matrix), the temperature and the pressure, and the annealing time after swelling.   In this study, the diffusion of 2-chloroethyl acrylate into PMMA was conducted at 60°C, 1 atm, while the swelling of PClEA with methyl methacrylate was conducted at 0°C, 1 atm.   The samples were stored in a vacuum oven to remove unreacted monomer after each polymerization step.

The gradient configuration was determined by chemical analysis of the chlorine concentration across the thickness of the material.   Compositions from 0 to 30 wt % PClEA in PMMA and from 0 to 50 wt % PMMA in PClEA were prepared.
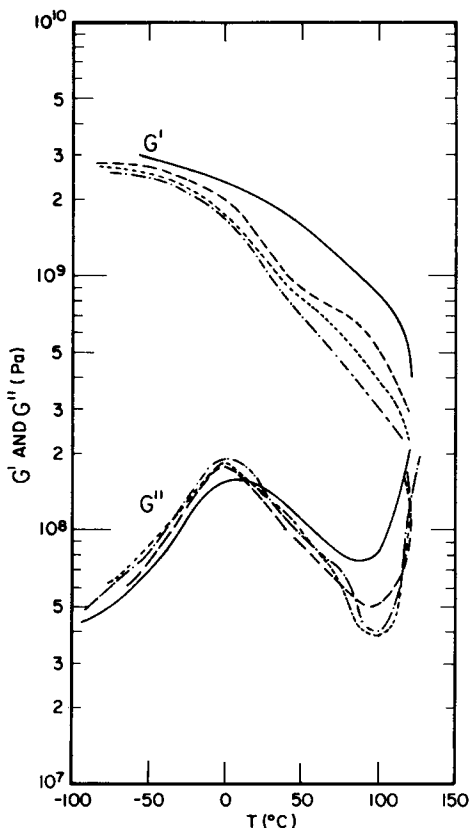
Fig. 4. Dynamic moduli of the PMMA matrix gradients at 1 Hz for concentrations of PClEA from 0 to 30 wt %. (—) PMMA; (- - -) PMMA/GRAD PClEA, (10%); (—·—) PMMA/GRAD PClEA, (20%); (- - -) PMMA/GRAD PClEA, (30%); 1 Hz.

In addition, the properties of the IPN material prepared in a previous study[6] were investigated. The configurations of the gradient polymers are shown in Figures 1 and 2. Further details of the gradient synthesis procedure are given by Jasso et al.[6] and by Ensanni.[7]

A free torsional oscillator was used to characterize the materials. This instrument had a frequency range of 0.1 to 10.0 Hz and used an optical transducer[8] for damping detection. The dynamic mechanical tests were conducted on rectangular bars at a frequency of 1.0 ± 0.1 Hz over a temperature range of −150 to 110°C.

RESULTS AND DISCUSSION

As shown in Figures 1 and 2, the transport of the penetrant monomer into the host polymer is described by non-Fickian kinetics. The shape of the concentration profiles in the PMMA matrix gradients indicates that case II transport occurs, while, in the PClEA gradients in which the methyl methacrylate penetrated into a rubbery matrix, the transport process could be approximated by Fickian kinetics.[9-11]

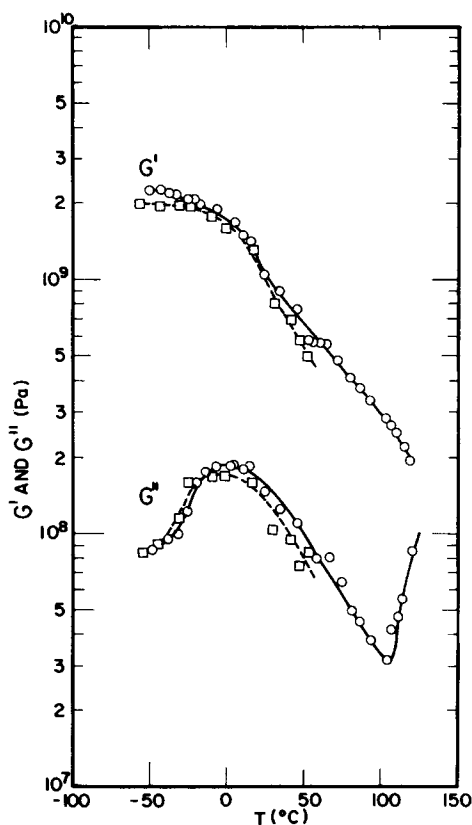The dynamic moduli at 1 Hz of PMMA and PClEA are shown in Figure 3.

Fig. 5. Comparison of the dynamic moduli of the gradient and the IPN blends containing 30 wt % PClEA. (-□-) PMMA/IPN PClEA, (30%); (-●-) PMMA/GRAD PClEA, (30%); 1 Hz.

Although the glass transition temperature of PMMA increases with crosslinking, the effect of crosslinking, at a concentration of 1.4 wt % ethylene glycol dimethacrylate, on the dynamic moduli is slight. The β transition of PMMA at 7°C is apparent as well as a γ transition at -100°C which has been attributed to the presence of adsorbed water in the polymer.[12]

In PClEA, the glass transition occurs at -10°C, the β transition at -100°C, and the γ transition near -150°C. These results are in agreement with those of Waterman et al.[13] and Huff et al.[14] on poly(2-chloroethyl methacrylate) in that the glass transition temperature of PClEA is between the glass transition temperatures of poly(methyl acrylate) and poly(ethyl acrylate) while the glass transition temperature of PClEMA is between that of PMMA and of poly(ethyl methacrylate). The γ transition in PClEA corresponds with the γ loss peak in PClEMA indicating that the transition may be due to the motions of the 2-chloroethyl group. The source of the β peak is unclear; it may be caused by the rotation of the side group about the main chain as in poly(methyl acrylate)[15] or by the presence of absorbed water in the polymer.

The dynamic mechanical properties of the gradient polymers were measured in order to determine the compatibility or miscibility of the materials. If the polymers are incompatible, i.e., a heterogenous structure is present, loss peaks corresponding to the glass transitions of the respective homopolymers should
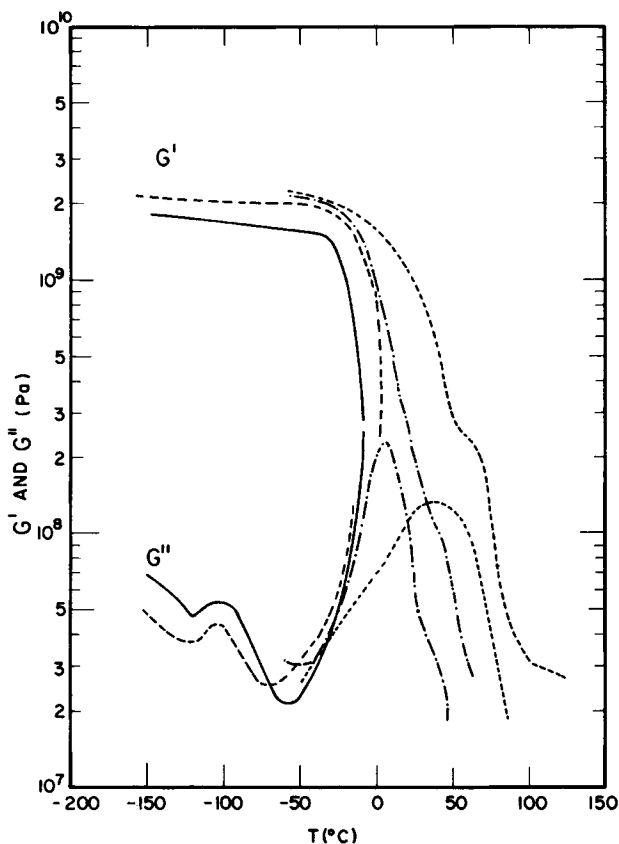
Fig. 6. Dynamic moduli of the PClEA matrix gradients at 1 Hz for concentrations of PMMA from 0 to 50 wt %. (—) PClEA; (- - -) PClEA/GRAD PMMA, (10%); (-··-) PClEA/GRAD PMMA, (30%); (- - -) PClEA/GRAD PMMA, (50%); 1 Hz.

TABLE I
Fracture Results

Temperature, °C	Material	K_{I_c}, MP$_a$ − m$^{1/2}$
25	Uncrosslinked PMMA	1.48
	Crosslinked PMMA (ref. 19)	1.28
	PMMA/Grad PClEA (12%)	1.20
50	Uncrosslinked PMMA	2.40
	Crosslinked PMMA (ref. 19)	1.75
	PMMA/Grad PClEA (12%)	1.21

be apparent.   If the polymers are miscible, the material behaves as a single-phase system and the glass transition occurs at a temperature between the glass transition temperatures of the homopolymers.[16]

As shown in Figure 4, transitions corresponding to the glass transitions of PMMA at 110°C and PClEA at −10°C appear in the dynamic spectra of the gradient polymers with a PMMA matrix.   This indicates incompatibility and phase separation of the polymers over the range of concentrations studied.   One of the effects of blending is to increase and broaden the temperature range of high damping values as shown in the PMMA/30% PClEA gradient material.
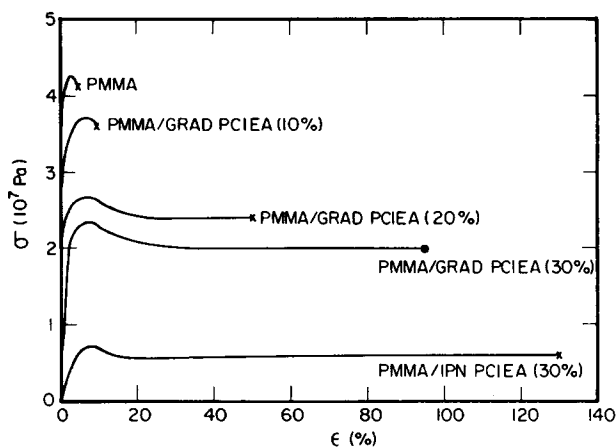
Fig. 7. Stress–strain behavior of the PMMA/PClEA blends at 60°C and a strain rate of 0.042 sec^{-1}.

The IPN material containing 30% PClEA exhibits much different behavior as shown in Figure 5. In the IPN material, a single transition occurs at 10°C indicating a compatible material and no phase separation. This result agrees with those of Huelck et al.[17] who studied a poly(ethyl acrylate)/52.9% PMMA IPN. Since these results were obtained for only one composition, the differences between the IPN and the gradient are inconclusive at this time and further work is necessary in order to elucidate the relationship between the gradient structure and the compatibility of the components.

Whereas the PMMA matrix gradients indicate incompatibility, the PClEA matrix gradients exhibited compatibility at concentrations to 50% PMMA. For
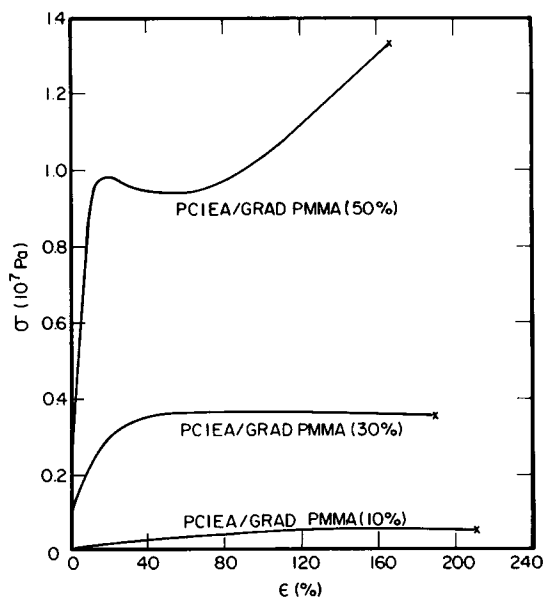

Fig. 8. Stress–strain behavior of the PClEA/PMMA blends at 60°C and a strain rate of 0.042 sec^{-1}.
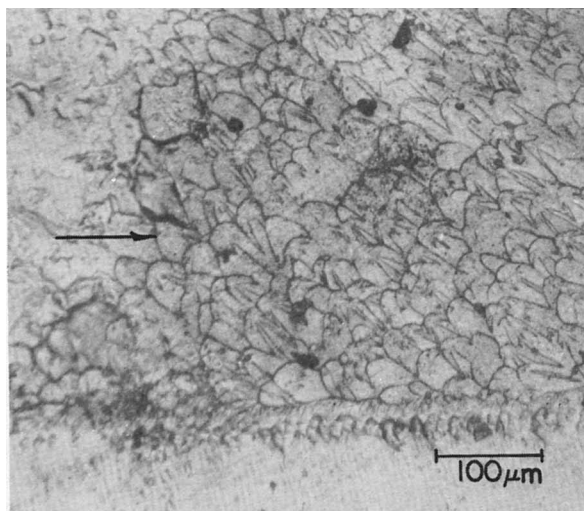
Fig. 9. Micrograph of the fracture surface of PMMA/PClEA gradient containing 12 wt % PClEA at 25°C showing the transition between the glassy matrix (upper part of the figure) and the rubbery layer. The arrow indicates the direction of the crack growth.

these materials, the glass transition temperatures of the blend are between the glass transition temperatures of the homopolymers as shown in the dynamic spectra of Figure 6. The glass transition temperature of the gradient T_g can be approximated by the Fox relationship[18]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

where W_1 and W_2 are the mass fractions and T_{g1} and T_{g2} are the glass transition temperatures of the components. The miscibility results for the two matrix polymers may be a consequence of the concentration dependence of the phase separation[16,17] and the transport process in the materials. Since the transport of the penetrant monomers occurred by different kinetics (as shown in Figures 1 and 2), if the compatibility is concentration dependent, different miscibility behavior may be observed in the materials.

The stress–strain behavior for the PMMA matrix gradients is shown in Figure 7 and for the PClEA matrix gradients, in Figure 8. The data shown were obtained at 60°C and a strain rate of 4% sec^{-1}; similar behavior was observed at 21 and 80°C. As previously reported by Jasso et al.,[6] the PMMA matrix gradients exhibit enhanced fracture strain and energy to break over the PMMA homopolymer and the IPN material. The PClEA matrix materials also display higher mechanical strength than the PClEA which is a very weak rubber. Similar behavior has been reported in elastomeric IPN materials.[17]

The presence of the gradient structure appears to have a synergistic effect similar to that observed in rubber-toughened polymers. The high strength of the glassy polymer and the high elongation of the elastomer are retained in the gradient materials. Several mechanisms have been proposed to interpret this behavior. One approach is to consider the gradient as an infinite series of layers of varying composition and modulus. Since the strain is constant over all of the layers upon deformation, each layer supports stress according to its modulus.

This stress distribution may cause the material to yield rather than to deform brittlely, thereby resulting in an increase in the fracture strain and the energy to break.[6]

Another proposed mechanism is that the mechanical strength may be enhanced by a reduction in imperfections on the surface of the materials. In the PMMA matrix materials, a high concentration of PClEA exists on the material surface. This rubbery region may prevent craze and crack initiation on the material surface and, thus, increase the mechanical strength of the material.

This mechanism was supported by the fracture toughness tests on the PMMA matrix materials. In a precracked sample, the craze can initiate at the notch and a reduction in surface imperfections has no effect. The fracture toughness of the gradients was measured over a temperature range of -100 to $60°C$. It was found that the gradient materials displayed lower K_{I_c} values than the PMMA homopolymer or the crosslinked PMMA as shown in the data at 25 and $-50°C$ in Table I.

Microscopy of the fracture surfaces indicates a region of rubbery deformation near the surface and a region of typical glassy fracture near the center as shown in the micrograph of the fracture surface in Figure 9. The upper part of the micrograph shows the glassy zone with a high concentration of PMMA with parabolas caused by secondary crack fronts while the lower part of the micrograph displays the rubbery region with a high concentration of PClEA. Consequently, it appears that the presence of the rubbery layer on the surface of the gradients may inhibit crack growth and increase the stress for craze initiation. Polymers with a gradient structure may have greater resistance to stress corrosion and environmental degradation than the respective homopolymers.

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