

# Latex Interpenetrating Polymer Networks Based on Acrylic Polymers. II. The Influence of the Degree of Network Compatibility on Morphology

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## Synopsis

Two latex interpenetrating polymer networks, one prepared from a pair of supposedly compatible polymers and the other from an incompatible pair, were investigated using transmission electron microscopy and dynamic mechanical analysis. From the results, it was proposed that both interpenetrating polymer networks consisted of latex particles with essentially core-shell morphologies. Evidence for a core-shell structure was more marked for the materials synthesised from the incompatible polymers. The other polymer pair showed indications of a significant amount of mixing.

## INTRODUCTION

Latex interpenetrating polymer networks (LIPNs) are a unique type of polymer blend synthesised by emulsion polymerization.<sup>1-5</sup> Initially a cross-linked seed latex (polymer 1) is made and then a second monomer together with a crosslinker and initiator are added to the polymer 1 latex and polymerized. Because of the deliberate omission of new emulsifier in the second polymerization, it is assumed that no or very few new particles are formed and that the growth occurs on or in the already established seed particles, resulting in particles containing both networks. No experimental evidence was found to suggest that any significant number of latex particles containing only polymer 2 was formed.

In general, the LIPNs exhibit varying degrees of phase separation depending, principally, on the compatibilities of the constituent polymers. With highly incompatible polymers,<sup>6</sup> the thermodynamics of phase separation dominate and substantial separation occurs before crosslinking can prevent it. With intermediate degrees of compatibility or semicompatibility,<sup>4</sup> complex behavior results which is reflected in the ultimate properties of the LIPN.

The predicted and observed compatibility behaviors of a series of acrylic polymer pairs were presented in Part I of this series.<sup>7</sup> Two LIPNs, with widely differing predicted degrees of compatibility, were selected for further study. They are the supposedly compatible<sup>7</sup> system E, based on poly(ethyl acrylate) (PEA) and poly(ethyl methacrylate) (PEMA), and the supposedly incompatible system F, based on PEA and poly(*t*-butyl acrylate) (PtBA).

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## EXPERIMENTAL

The experimental details of the synthetic procedure and the preparation of sheet specimens are described in Part 1.<sup>7</sup> The polymer 1 to polymer 2 weight ratio was maintained at 1:1 for both systems E and F.

A Hitachi HU-IIB transmission electron microscope was used to obtain the electron micrographs. In order to achieve contrast between the components, 1 mole % of isoprene was added with the second monomer. Sheet samples were microtomed and stained with osmium tetroxide vapor prior to microscopic examination. Isoprene acts as a comonomer and facilitates osmium tetroxide staining because of its olefinic structure.

A Polymer Laboratories Dynamic Mechanical Thermal Analyzer was employed for the dynamic mechanical measurements. The temperature range studied was from  $-40$  to  $120^{\circ}\text{C}$  for system E and  $-40$  to  $100^{\circ}\text{C}$  for system F. The heating rate was  $2^{\circ}\text{C}/\text{min}$  and the frequency employed was 10 Hz.

## RESULTS AND DISCUSSION

LIPNs show complex morphologies including core-shell and cellular structures.<sup>8-11</sup> If the polymers are incompatible, the degree of phase separation is increased. Such incompatibility not only prevents polymer 2 formed at the seed particle interface and the established core from mixing, but also causes phase separation of the monomer polymerised within the core, yielding microcellular structures.<sup>6</sup> On the other hand, if the polymers are more compatible, and there was sufficient time for the second monomer to completely swell the polymer 1 particles, a less distinct core-shell morphology is observed.<sup>4</sup>

Electron micrographs of systems E and F are shown in Figures 1 and 2, respectively. Both systems show stained and unstained areas which is indicative of a two-phase morphology. However, phase separation is more distinct in system F than in system E. In system F, the darker regions are polymer 2 (PtBA) rich regions. The lighter background appears to be continuous. On closer examination of this continuous phase, it is apparent that

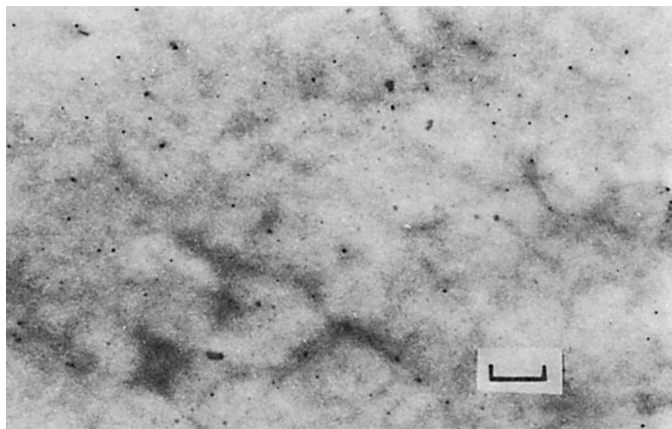


Fig. 1. Transmission electron micrograph of the PEA/PEMA LIPN (system E). The scale mark represents 500 nm.

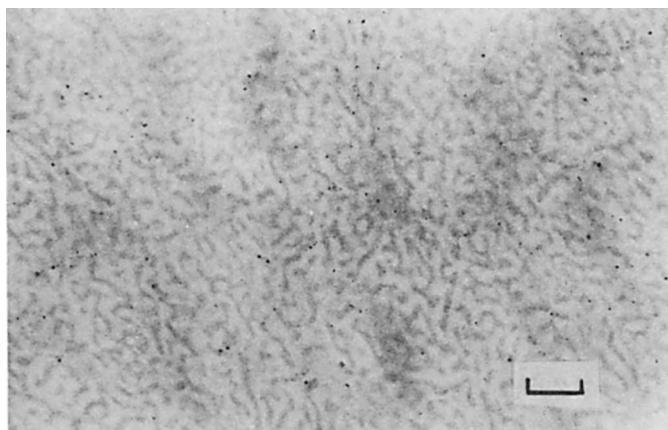


Fig. 2. Transmission electron micrograph of the PEA/PtBA LIPN (system F). The scale mark represents 500 nm.

it consists of a very fine cell-like structure, which is characteristic of two-phase morphology in LIPNs. Unlike system F, system E shows a low level of cellular structure. The reason for this could be the more compatible nature<sup>7</sup> of the two components, PEA and PEMA, resulting in some degree of molecular mixing.

The  $\tan \delta$  vs. temperature plots for systems E and F are shown in Figures 3 and 4. The peak positions of the corresponding homopolymers, represented by broken lines, are also shown. The glass transition temperatures ( $T_g$ ) obtained from the above plots are shown in Table I. Both systems E and F show two well-defined  $\tan \delta$  peaks. In the case of system E, the position of the first and second network peaks, in comparison to their homopolymer positions, are shifted to higher and lower temperatures, respectively. Although the higher temperature shift in the case of the first formed network (PEA) is quite small, a substantial lowering in temperature is seen for the second formed network (PEMA). These shifts are not observed for system F. The inward shifting of the peaks in polymer-polymer blends has been

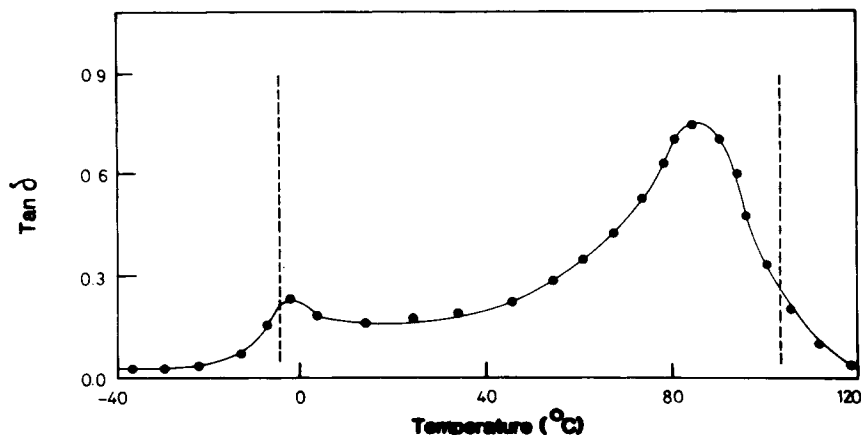


Fig. 3.  $\tan \delta$ -temperature curve for system E (PEA/PEMA) at 10 Hz. The broken lines indicate the peak positions of the corresponding homopolymer networks.

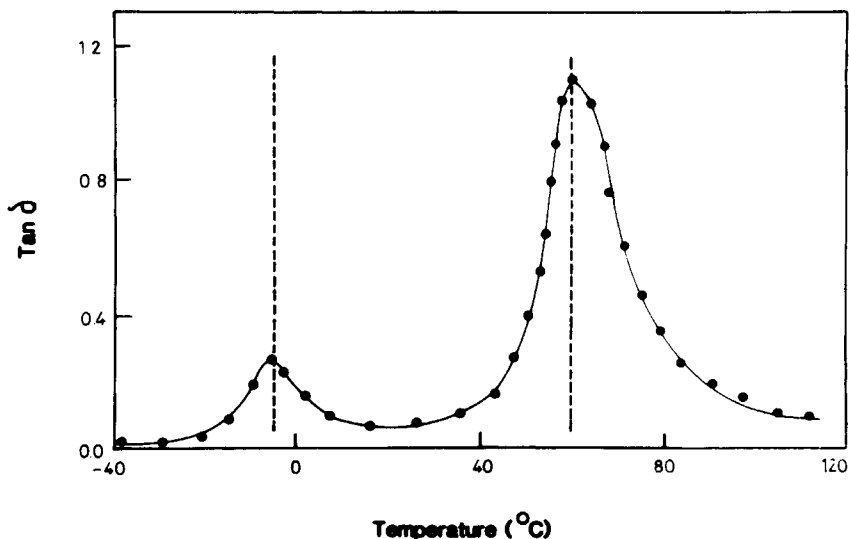


Fig. 4.  $\text{Tan } \delta$ -temperature curve for system F (PEA/PtBA) at 10 Hz. The broken lines indicate the peak positions of the corresponding homopolymer networks.

shown by many workers to be an indication of some level of molecular mixing.<sup>1-4,12</sup> Accordingly, it could be said that in system E some mixing is taking place, while for system F there is no evidence for this.

The dynamic storage ( $E'$ ) and dynamic loss ( $E''$ ) modulus vs. temperature plots for systems E and F are shown in Figures 5 and 6. System F shows two well-defined transitions in  $E'$  separated by a plateau and two distinct  $E''$  peaks corresponding fairly closely to the homopolymer network glass transitions. For system E, although two  $E'$  transitions are seen, they are not as clearly separated as in the case of system F. As for the  $E''$  plots, system E shows only one well-defined low temperature peak while the high temperature peak is broadened appreciably into a shoulder. The presence of two distinct  $E'$  and  $E''$  transitions in system F is again clearly indicative of the absence, to any significant extent, of molecular mixing, but the gradual merging of the peaks in system E suggests the presence of a certain degree of miscibility.

It is important to note that, although in systems E and F a 1:1 weight ratio was maintained, it is observed from Figures 3-6 that the second

TABLE I  
Glass Transition Temperatures of the LIPNs and their Homopolymer Networks (10 Hz)

Polymer	$T_g$ (°C)		
	Homopolymer	Network 1	Network 2
PEA	-4		
PEMA	104		
PtBa	58		
System E, PEA/PEMA		-2	84
System F, PEA/PtBA		-2	58

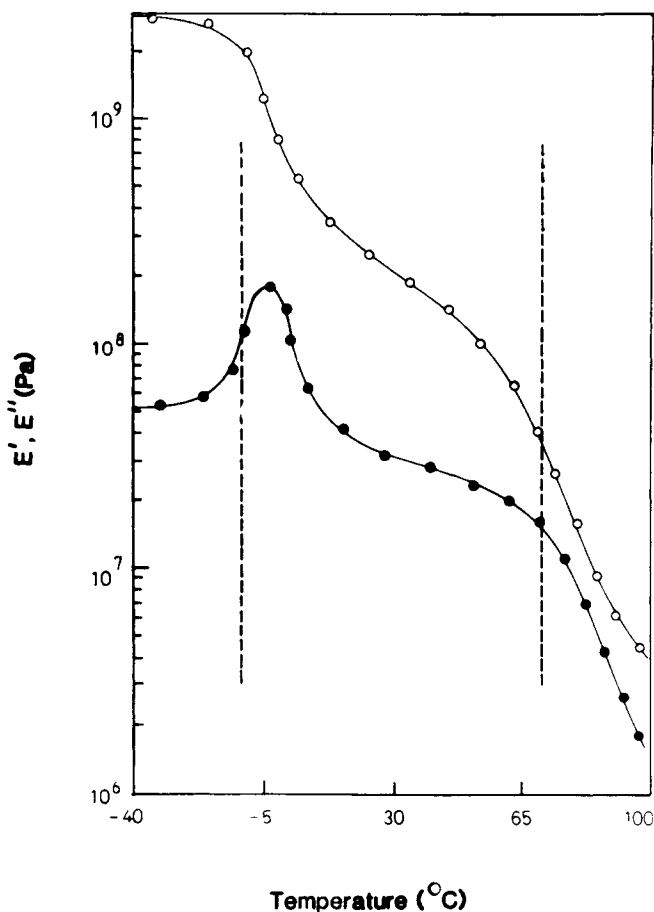


Fig. 5.  $E'$  (○) and  $E''$  (●)-temperature plots for system E (PEA/PEMA) at 10 Hz. The broken lines indicate the positions of the  $E''$  peaks of the homopolymer networks.

network exhibits the predominant contribution to both the storage modulus and  $\tan \delta$  values. If the second network is present as a shell on the outside of each particle, then, when the latex is coagulated and hot pressed into sheets, that network will form the more continuous phase. Thus, the information contained in Figures 3–6 may be taken as evidence of core-shell type of morphology in both systems. However, it must be remembered that should rubbery polymer 1 segments be trapped in glassy polymer 2 domains, the former may be highly constrained and only contribute to loss processes when polymer 2 goes through its glass transition. This mechanism could be making a contribution in system E where the evidence cited so far indicated some degree of mixing. However, it does not seem to be applicable to system F.

Apart from the already mentioned criteria, there exist other indices of mixing in polymer blends. Some of these methods were employed to support the results already discussed. The width of an  $E''$  peak at half maximum height has been shown<sup>18</sup> to provide a semiquantitative guide to the amount of segmental mixing in polymer blends. An increase in the  $E''$  half peak

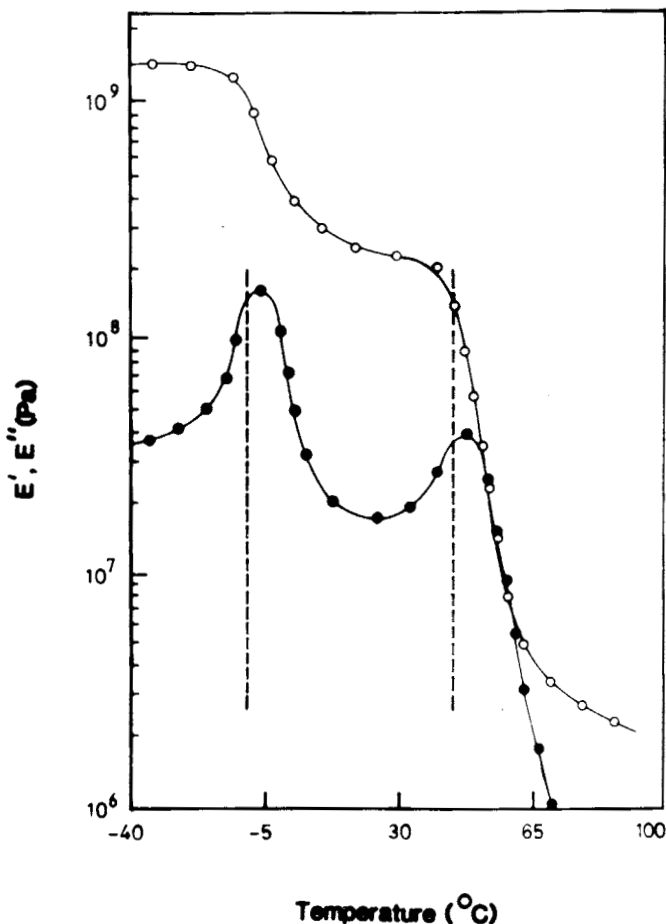


Fig. 6.  $E'$  (○) and  $E''$  (●)—temperature plots for system F (PEA/PtBA) at 10 Hz. The broken lines indicate the positions of the  $E''$  peaks of the homopolymer networks.

width is an index of mixing. The  $E''$  half peak widths for both systems are shown in Table II. Also shown in the same table are the respective values for the homopolymer networks. It is seen that the  $E''$  half peak width for the first network of system E has increased in comparison with the PEA homonetwork value. However, in the case of system F, both the first and the second network  $E''$  half peak width values remain unchanged in relation to those of the homopolymer networks.

TABLE II  
The Half Peak Width Values for Systems E and F and Their Homopolymer Networks

Polymer	$E''$ half peak width (°C)	
	Network 1	Network 2
PEA	13	
PtBA		21
System E, PEA/PEMA	16	—
System F, PEA/PtBA	13	21

TABLE III  
The Intertransition  $\tan \delta$  Values and the Valley Depth Measure for Systems E and F

System	Intertransition $\tan \delta$ value	Trough depth
System E, PEA/PEMA	0.17	0.58
System F, PEA/PtBA	0.07	1.08

Another very useful qualitative index<sup>14</sup> of the extent of mixing is the magnitude of  $\tan \delta$  at an intermediate temperature between the two glass transitions.<sup>14</sup> The minimum value of  $\tan \delta$  may be used. If mixing occurs and there is, therefore, an overlap of the relaxation time distributions of the components, these intertransition values of  $\tan \delta$  should be larger than for the case where no such mixing occurs. Table III shows the  $\tan \delta$  values at 20°C for both systems. It is seen that system F has a very small  $\tan \delta$  value, while system E shows a relatively high value, supporting the contention that some mixing occurs in system E.

The decrease in depth of trough between the two  $\tan \delta$  transitions has also been used<sup>15</sup> as an index of mixing. Table III shows the results of this measure. System F shows a high value indicating the probable absence of mixing, while system E shows a relatively low value indicating some degree of mixing.

With the evidence so far cited, it can be concluded that some molecular mixing between polymer 1 and polymer 2 is present in system E and essentially absent in system F.

Core-shell models for two stage emulsion systems have been cited<sup>13,16-18</sup> by many workers. In this study, too, an attempt has been made to explain the observations using the core-shell model. Two schematic core-shell models of systems E and F, based on the experimental evidence, are postulated in Figure 7.

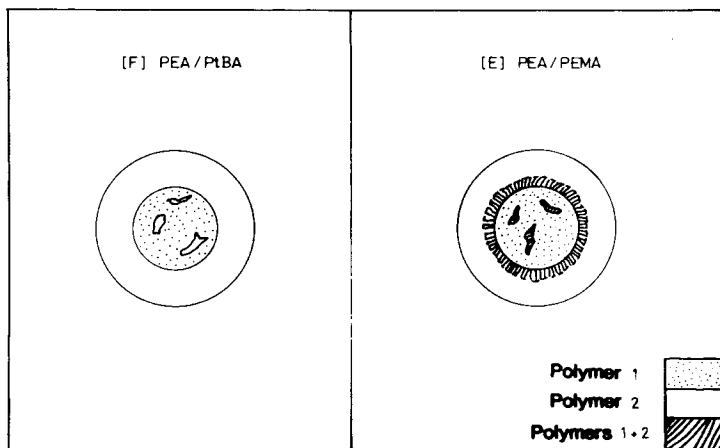


Fig. 7. Schematic diagrams of the core-shell models suggested for the morphologies of the latex particles of systems E and F.

For the incompatible system F, where two distinct  $E''$  peaks are observed, a definite polymer 2 shell surrounding the polymer 1 core seems best to fit the experimental observations. The PtBA inclusions within the core region can be postulated to arise from second monomer which penetrates into the interior of the polymer 1 seek particles, and, upon polymerization, phase separates. In system E, where the dynamic mechanical measurements showed evidence of mixing, a graded core-shell morphology could fit the observations. As shown in Figure 7, the polymer 1 rich core and the polymer 2 rich shell can be visualized as being separated by a mixed region consisting of both polymers. It could also be that the system E latex particles have a gradation of polymer 2 (PEMA) content increasing from pure PEA near the centre of the core to pure PEMA at the outside of the shell.

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