

Latex Interpenetrating Polymer Networks Based on Acrylic Polymers. IV. The Influence on Mechanical Properties of the Time of Swelling the Seed Particles with the Second Monomer

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Synopsis

Two latex interpenetrating polymer networks, one based on a partially compatible pair and the other based on an incompatible pair of polymers, were prepared by a two-stage emulsion polymerization. To investigate the effect of swelling the first formed polymer particles with the second monomer, the second stage of the synthesis was conducted after allowing the second monomer to be in contact with the seed latex for specified periods of time. Fabricated samples of these interpenetrating polymer networks were subjected to hardness, stress-strain, and dynamic mechanical measurements. The results showed an enhancement in mixing of the two networks in the case of the partially compatible pair and a detectable increase in the level of mixing for the incompatible pair.

INTRODUCTION

Latex interpenetrating polymer networks (LIPNs) are a unique type of polymer blend prepared by two-stage polymerization methods.¹⁻³ The preparation involves making a seed latex of a crosslinked polymer (polymer 1), and then introducing into the reaction vessel the second monomer (monomer 2) together with its crosslinking agent. Monomer 2 is then polymerized. Since no fresh emulsifier is added during the second stage of the polymerization, it is assumed that no new nucleation takes place during monomer 2 polymerization. Hence, growth occurs on the already established latex particles. Many studies have claimed⁴⁻⁷ that with this type of polymerization method the morphology of the resulting particles ranges from homogeneous through the simple domain type to the core-shell morphology. Among other criteria, the particle morphology depends⁶ on the miscibility of monomer 2 in polymer 1. The mutual compatibility⁸ of polymers 1 and 2, the crosslink density of the networks and the relative hydrophilicities⁷ of the polymers are also involved.

Previous papers^{9,10} in this series discussed LIPNs based on poly(ethylacrylate) and poly(ethyl methacrylate) (PEA/PEMA), denoted as system E, and poly(ethyl acrylate) and poly(*t*-butyl acrylate) (PEA/PtBA), denoted as

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system F. From morphological and mechanical properties studies, an essentially core-shell model was proposed.⁹ Further investigations of the properties of these LIPNs were carried out by altering some of the conditions of synthesis. The effects of altering the composition of the LIPN and of the inverting the order of synthesis were reported¹⁰ earlier. The influence of the time that monomer 2 is allowed to swell polymer 1 is the subject of this paper.

In a two-stage polymerization, the time allowed for the second monomer to be in contact with the seed polymer has been shown¹¹⁻¹⁵ to have important consequences on the morphology and mechanical properties of the end product. In this study, investigations of the effect of swelling time on the mechanical properties of the LIPN systems E and F were conducted. The second monomer in each case was allowed to be in contact with the seed polymer for times ranging from 0 to 240 h before the second stage polymerization was carried out. The resulting latexes were coagulated and fabricated into sheets for hardness, stress-strain, and dynamic mechanical measurements.

EXPERIMENTAL

The seed latex of the LIPNs was prepared using the method described previously.⁸ Once the seed latex was prepared, it was then cooled to room temperature (20°C) and monomer 2, together with crosslinker, but no initiator, were added. Care was taken that all outlets of the reaction vessel were properly sealed in order to prevent any monomer escaping from the system. The reaction vessel containing the seed latex plus monomer 2 was then allowed to stand under stirring at 20°C for time intervals of 0, 15, 30, 60, 120, and 240 h, before the second polymerization was initiated.⁸ Hot pressed samples from the coagulated latex were obtained for mechanical measurements. All samples had a 1 : 1 composition ratio. Hardness, stress-strain, and dynamic mechanical measurements were conducted as described¹⁰ earlier.

RESULTS AND DISCUSSION

Hardness Measurements

The Shore (type D) hardness numbers¹⁰ as a function of swelling times are shown in Table I. It is seen that up to a swelling time of 60 h, neither system shows any significant change in hardness. However, as swelling time is increased, system E, to a large extent, and system F, to a much smaller extent,

TABLE I
Hardness Numbers for Systems E and F as a Function of Swelling Time

Swelling time (h)	Shore hardness (type D)	
	System E (PEA/PEMA)	System F (PEA/PtBA)
0	55	49
15	56	50
30	56	50
60	55	49
120	50	45
240	43	44

TABLE II
Stress-Strain Properties of System E and F at 20°C as a Function of Swelling Time

Swelling time (h)	Initial modulus (MN/m ²)	Strain at break (%)
System E: PEA/PEMA		
0	76.0	211
15	56.4	185
30	42.3	200
60	35.8	230
120	35.0	260
240	34.0	310
System F: PEA/PtBA		
0	88.8	169
15	66.8	233
30	42.4	248
60	25.3	287
120	34.2	347
240	34.5	352

show lowering in hardness. This implies that the two networks in the LIPNs are more mixed when the seed polymer is left in contact with the monomer 2 for sufficiently long periods of time. The higher degree of softening in system E might be attributed to the partial compatibility of the two polymers PEA and PEMA as discussed previously.^{9,10}

Stress-Strain Measurements

The initial modulus and the strain at break values from the stress-strain plots for systems E and F are shown in Table II. In both the LIPNs the PEA

TABLE III
Glass Transition Temperatures of Systems E and F as a Function of Swelling Time

Swelling time (h)	T_g (°C) ^a	
	Network 1	Network 2
System E: PEA/PEMA		
0	-2	84
15	-1	82
30	-1	82
60	0	82
120	0	81
240	1	80
System F: PEA/PtBA		
0	-4	58
15	-4	58
30	-4	58
60	-4	58
120	-2	55
240	-2	55

^aThe experimental frequency was 10 Hz. T_g 's of homopolymers¹⁰ are PEA = -4°C, PEMA = 104°C, and PtBA = 58°C.

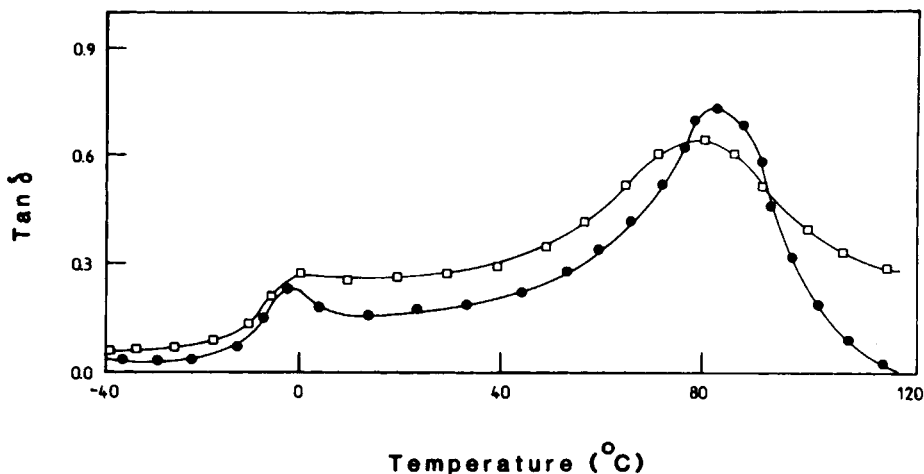


Fig. 1. $\tan \delta$ -temperature curves (10 Hz) for system E at swelling times of 0 h (●) and 240 h (□).

seed latex is a rubbery network while the second formed polymer, PEMA in system E and PtBA in system F, constitutes a glassy polymer network. Since the compositions of the two LIPNs were maintained at a ratio of 1:1, it would be expected that the second formed glassy component would dominate^{3,10} the stress-strain behaviour of the hot pressed sheet samples. However, it is seen from Table II, that in both systems the initial modulus decreases and the strain at break increases as a function of swelling time, indicating that the LIPNs are becoming more rubbery in nature. This result suggests that there is an increasing degree of mixing between the two networks, when monomer 2 is allowed time in contact with the seed polymer. It is also interesting that the initial modulus values for 120 and 240 h swelling times do not differ substantially, probably suggesting that complete or saturation swelling of the seed polymer has taken place by about 120 h.

Dynamic Mechanical Analysis

The glass transition temperatures (T_g) of systems E and F, as a function of swelling time, are shown in Table III. These values were obtained from $\tan \delta$ vs. temperature plots. Also shown in Figures 1 and 2 are two of these plots at swelling times of 0 and 240 h. In the previous papers of this series,^{9,10} comment was made on the inward shifting of the transitions in relation to their respective homopolymer T_g values. Such shifts are commonly taken as an indication of mixing between the polymers. On this basis some degree of mixing is present in system E and is essentially absent in system F.

Using the same criterion, it can be seen from Table III that the T_g values of both systems E and F show small inward shifts as a function of increased swelling time. This implies that, in the case of system E, the extent of mixing between the polymer 1 and polymer 2 networks becomes more pronounced with increasing swelling time. For system F, although mixing was essentially absent in the zero swelling time sample, evidence of a certain level of mixing is

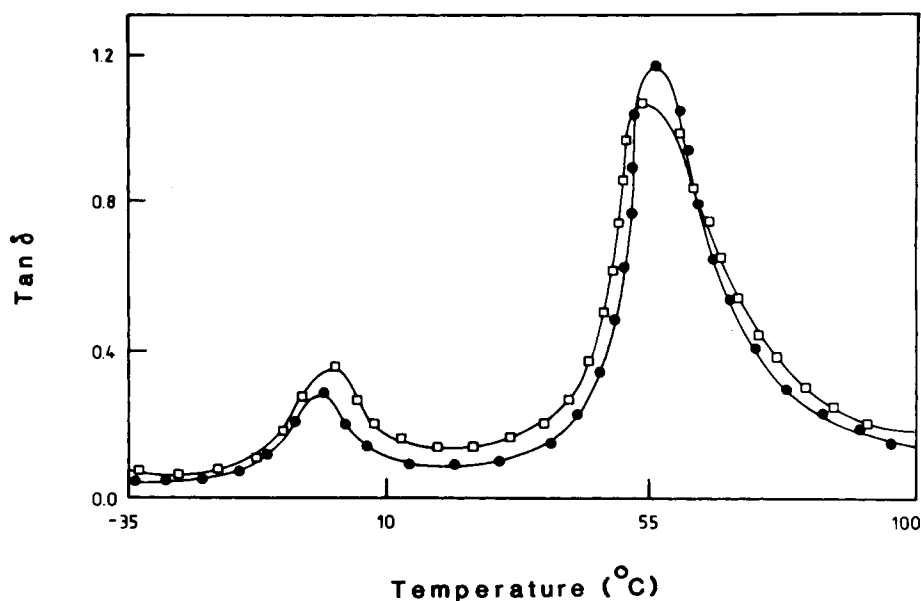


Fig. 2. $\tan \delta$ -temperature curves (10 Hz) for system F at swelling times of 0 h (●) and 240 h (□).

seen when polymer 1 is allowed to be in contact with monomer 2 for a sufficient length of time.

An increase in the width of the $\tan \delta$ peak, which is usually measured at half-peak height, has been employed¹⁰ as an index of the extent of mixing between the two polymer components. The $\tan \delta$ half-peak widths for systems E and F are shown in Table IV. An increase is observed for both systems at swelling times greater than 60 h. At 240 h swelling time, a half-peak width increase of 22°C for system E and of 6°C for system F were observed. This, again, indicates that the degree of network mixing in especially system E is enhanced by allowing the seed polymer to be in contact with monomer 2 for protracted periods.

Another useful qualitative index⁹ of the extent of mixing is the magnitude of $\tan \delta$ in the region between the two glass transitions. These $\tan \delta$ intertran-

TABLE IV
 $\tan \delta$ Half-Peak Widths of the Higher Temperature Transitions of the LIPNs as a Function of Swelling Time

Swelling time (h)	$\tan \delta$ half-peak width (°C)	
	System E (PEA/PEMA)	System F (PEA/PtBA)
0	38	19
15	39	20
30	39	21
60	50	20
120	54	22
240	60	25

TABLE V
Intertransition Tan δ Values for the LIPNs as a Function of Swelling Time

Swelling time (h)	Intertransition value	
	System E (PEA/PEMA)	System F (PEA/PtBA)
0	0.17	0.07
15	0.17	0.08
30	0.16	0.08
60	0.20	0.09
120	0.22	0.10
240	0.26	0.11

sition values, as a function of swelling times, are shown in Table V. An increase in the intertransition value with increasing swelling time is seen for both systems, indicating some degree of enhanced network mixing.

The loss modulus (E'') vs. temperature plots for systems E and F at 0 and 240 h swelling times are shown in Figures 3 and 4. As discussed in earlier

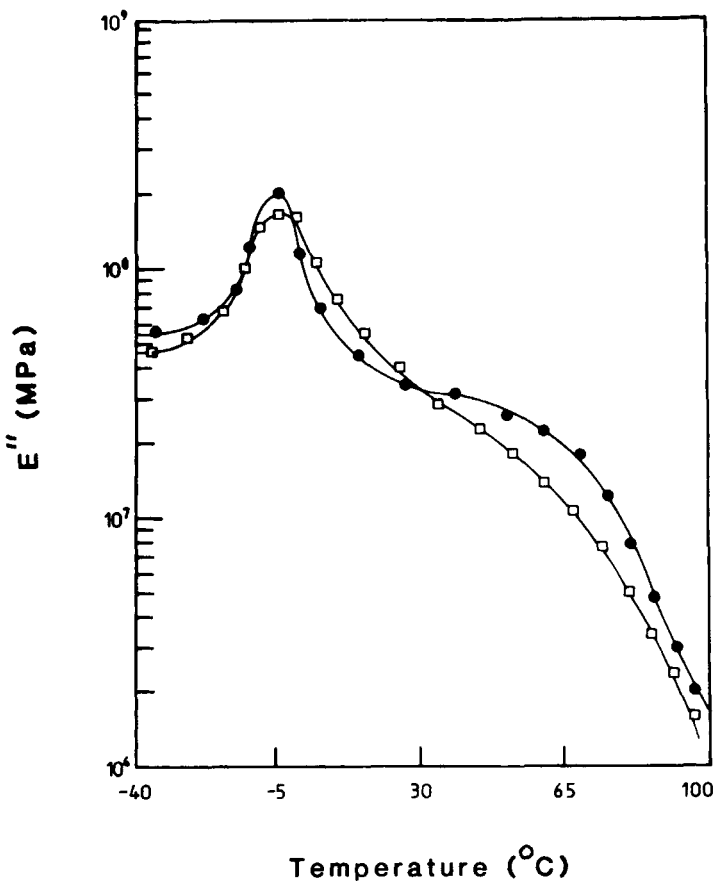


Fig. 3. Loss modulus (E'')-temperature curves (10 Hz) for system E at swelling times of 0 h (●) and 240 h (□).

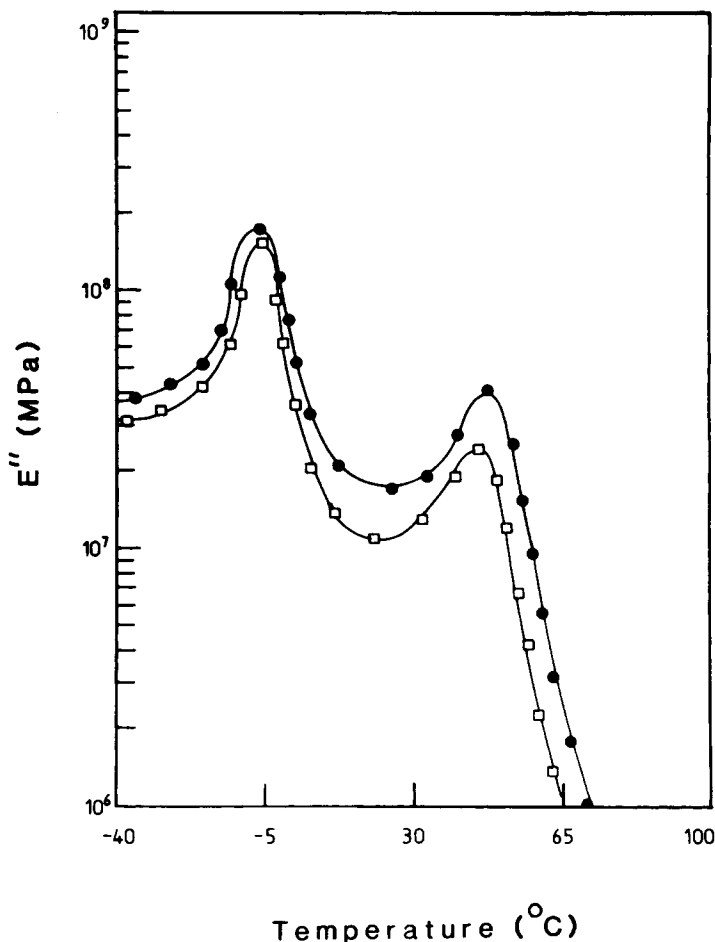


Fig. 4. Loss modulus (E'')-temperature curves (10 Hz) for system F at swelling times of 0 h (●) and 240 h (□).

papers,^{9,10} the nature and the shape of these plots are indicative of the extent of network mixing. The presence of only one well-defined transition for system E at 0 h indicates a substantial amount of mixing between the two networks. It is also seen from Figure 3 that the presence of a single well-resolved loss modulus transition is even more exaggerated for the sample which was swollen for 240 h, suggesting an enhancement of mixing between the two networks. In system F (Fig. 4), however, although the 240 h sample exhibits two loss modulus transitions the second network transition is broadened in relation to that of the zero time of swelling the sample, indicating a certain slight level of mixing.

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