Effect of decrosslinking and annealing on interpenetrating polymer networks prepared from poly(ethyl acrylate)/ polystyrene combinations

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Interpenetratino polymer networks, *IPN* polymers, were prepared from poly(ethyl acrylate), PEA, and polystyrene, PS. Part or all of the crosslinking monomer was acrylic acid anhydride, AAA, which was subsequently hydrolysed and the samples annealed. Modulus—temperature, modulus—time (during annealing) determinations, and transmission electron microscopy were performed on the freshly made samples, after hydrolysis, and after annealing. The studies show that the phase continuity of the PS component is increased relative to the PEA component on annealing, and the separation of the phases becomes more pronounced. A new morphology was observed with the totally decrosslinked, chemically induced blend, with the PEA showing both a continuous and a discontinuous aspect.

INTRODUCTION

During the past decade, interpenetrating polymer networks (*IPN* polymers) have been made in many ways. These include sequential[1-4], simultaneous[5-8], and gradient[9,10] syntheses of the two networks, and the preparation of materials with one or the other (but not both) of the polymers in the crosslinked state[2,11,12]. The subject has been reviewed recently[13-18].

The objectives of *IPN* studies are many. First, through the exploration of new molecular topologies, valuable novel applications may be achieved[19-21]. Second, the insights learned through studying the morphology and mechanical behaviour of *IPN* polymers may be applied to the broad classes of polymer blends[22-25], grafts[22,23], blocks[26], and AB crosslinked copolymers[27,28]. Certainly the several investigators have found the materials and structures 'fun to play with', as well as easy to model.

In this paper, we present the results of systematically decrosslinking and annealing *IPN* polymers prepared from poly(ethyl acrylate) and polystyrene, PEA/PS. Decrosslinking was achieved by employing greater or lesser quantities of acrylic acid anhydride (AAA), which can be hydrolysed through soaking in ammonia—water solutions. Both PEA[29] and PS[30] had been subjected to controlled decrosslinking separately with excellent indications that the hydrolysis of AAA is efficient and complete.

Previously, *IPN* polymers of PEA and PS had been studied by Huelck *et al.*[1], and had been found to exhibit significant phase separation with two identifiable glass transitions, one for each polymer. As with many other *IPN* polymers demixing was incomplete, with crosslinked polymer segments believed to be mechanically entrapped in the wrong phase. Controlled decrosslinking offers a new dimension in the art of preparing polymer blends with *IPN* polymers with unique morphologies and behaviour patterns.

There is yet another motive for this paper, for it represents a deliberate attempt to develop experimental examples of the use of mathematical group and ring theory concepts[30,31], as applied to multipolymer combinations. In the theoretical work, several tables of binary operations on elements are defined, which constitute a nomenclature scheme for multicomponent polymer materials. Several functions are also defined, which carry the elements about either within a table, or between two tables. These functions constitute a generalization of specific chemical reactions. Decrosslinking an *IPN* results in a chemically induced blend.

EXPERIMENTAL

Synthesis

(a) Poly(ethyl acrylate) (PEA): to each 100 ml ethyl acrylate was added 0.40 g benzoin as a photo-initiator, and 1.36 ml dodecane thiol as a chain transfer agent to counteract gelling due to side reactions. Various amounts of acrylic acid anhydride (AAA) and diethylene glycol dimethacrylate (DEGDM) were also added as crosslinking agents. Either 4.80 ml AAA or 9.24 ml DEGDM per 100 ml ethyl acrylate was taken to be 4% crosslinker on a molar basis. The mixture was polymerized with u.v. light for 48—72 h[29].

(b) Polystyrene (PS): to each 100 ml of styrene was added 0.30 g benzoin as a photoinitiator, and various amounts of divinyl benzene (DVB) as crosslinker. 4 ml of DVB per 100 ml styrene was taken to be 3.2% on a molar basis. The mixture was swelled into the PEA to approximately 50% by wt and polymerized with u.v. light for 48—72 h[1]. A table of the specimens prepared, indicating levels of crosslinker is shown in *Table 1*.

The AAA crosslinks may be hydrolysed, causing decrosslinking. This was accomplished when indicated by soaking in ammonium hydroxide for 24—48 h. It is important to realize that decrosslinking only involves the AAA linkages. For example, materials of specimen code 31 and 32 type still have half the original crosslink level in the PEA after decrosslinking by virtue of the DEGDM linkages. Annealing was carried out by heating the materials to 110°C for 24 h.

Table 1 Crosslink levels of PEA/PS *IPN* polymers

Specimen code number	PEA crosslinker (%)		PS crosslinker (%)
	AAA	DEGDM	DVB
11	4	0	0
21	3	1	0
31	2	2	0
A31	0	2	0
41	1	3	0
51	0	4	0
12	4	0	1.6
32	2	2	1.6
A32	0	2	1.6
13	4	0	3.2
43	1	3	3.2
53	0	4	3.2

Table 2 Strain to break

Specimen code	Deflection at break (in.)
11, freshly synthesized	>0.50
11, decrosslinked	0.05
11, decrosslinked and annealed	0.08
13, freshly synthesized	>0.50
13, decrosslinked	>0.50
13, decrosslinked and annealed	0.02
32, freshly synthesized	>0.50
32, decrosslinked and annealed	>0.50
A32, freshly synthesized	>0.50
A32, annealed	0.31

Characterization

Modulus (ten sec) was measured with a Gehman torsion apparatus. Impact strength was measured with a Charpy impact apparatus. In another experiment, stress in the configuration of a centre loaded beam was applied slowly to the various materials. The inside distance between the supports was 13/16 in. Values of deflection at break are shown in *Table 2*. The thickness of the specimens tested was about 0.15 in.

For electron microscopy, sections were made to the thickness indicated. A Philips 300 transmission electron microscope was used. For proper contrast, 2% isoprene was incorporated into the PEA during synthesis. The materials were stained with OsO_4 for one week, and embedded in epoxy for ultramicrotoming.

RESULTS

Immediately after synthesis, the 50/50 PEA/PS *IPN* polymers exhibited a translucent appearance indicative of a significant degree of phase separation. The appearance and qualitative behaviour of these specimens were, in fact, similar to those observed by Huelck *et al.*[1]. Two exceptions to this were specimen code A31 and A32 (see *Table 1* for description) which were milk white. After the decrosslinking step, their general appearance remained unchanged except for a yellowish cast and a noted increase in brittleness in some samples. After annealing, however, the materials became more opaque, suggesting important morphological changes had taken place.

Modulus—temperature

As the samples were freshly synthesized, the modulus—

temperature curves of all materials having 4% total crosslinker in the PEA were very similar, regardless of the amount of crosslinker in the PS. After decrosslinking, the modulus—temperature curves showed slight change except for an increase in modulus at the lower part of the transition region $(50° - 100°C)$ and a decrease in modulus of varying degree above this point *(Figure 1)*. At $110°C$, the modulus shows effects from both the residual crosslink level in the PEA *(Figure 2* at $t = 0)$, and the crosslink level in the PS *(Figure 3* at $t = 0)$. The modulus at $110°C$ of all freshly synthesized materials except specimen codes A31 and A32 was 1.74×10^7 dynes/cm^2. The greatest change observed after decrosslinking was in the specimen code 11 type, where the modu-
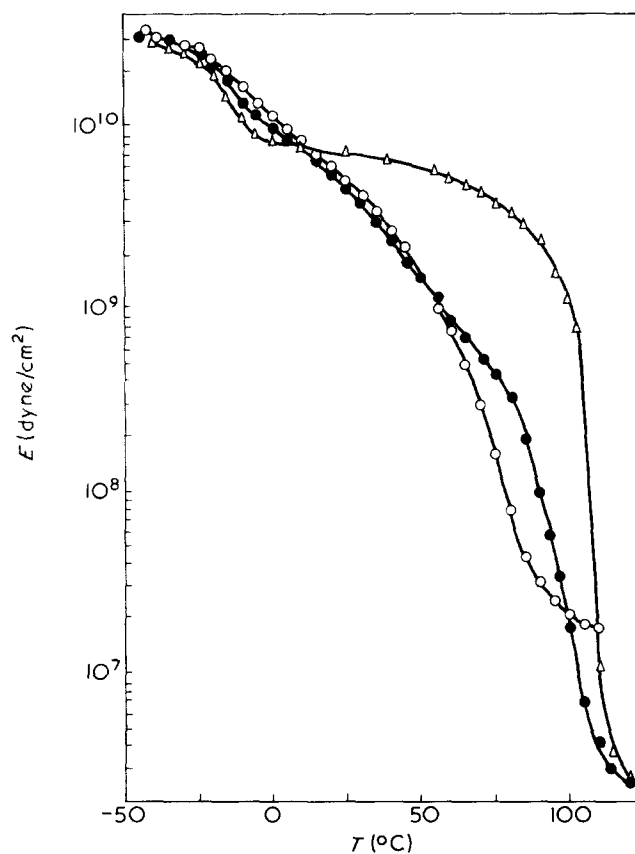

Figure 1 Modulus—temperature data, specimen code 21: O, freshly synthesized; ●, decrosslinked; △, decrosslinked and annealed
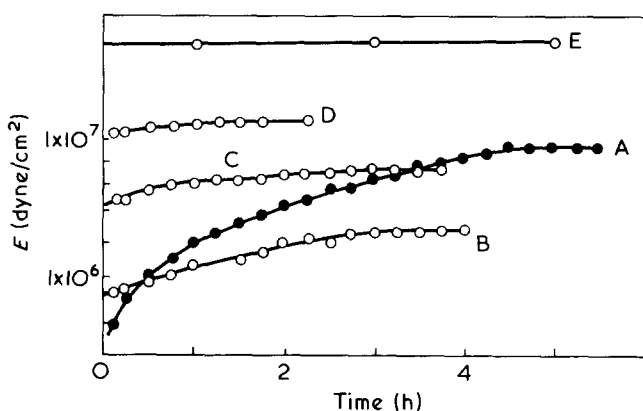

Figure 2 Modulus of decrosslinked specimens during annealing at $110°C$. Specimen codes: 11 (A), 21 (B), 31 (C), 41 (D), 51 (E), shown on Figure. At $t = 0$, no annealing has occurred
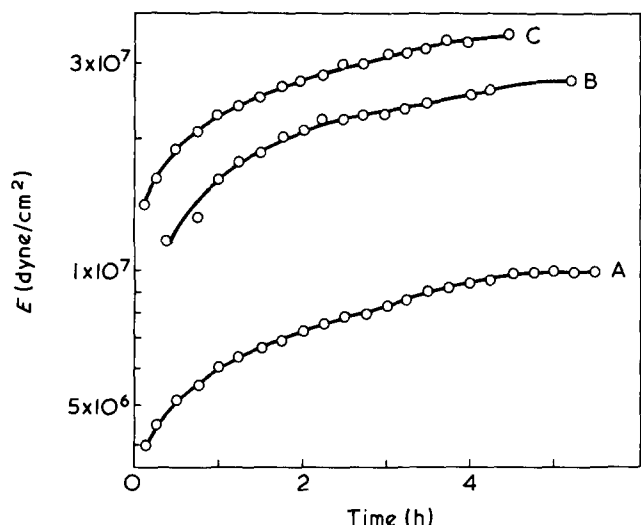
Figure 3 Modulus of decrosslinked specimens during annealing at 110°C. Specimen codes: 11 (A), 12 (B), 13 (C), shown on Figure. At t = 0 no annealing has occurred
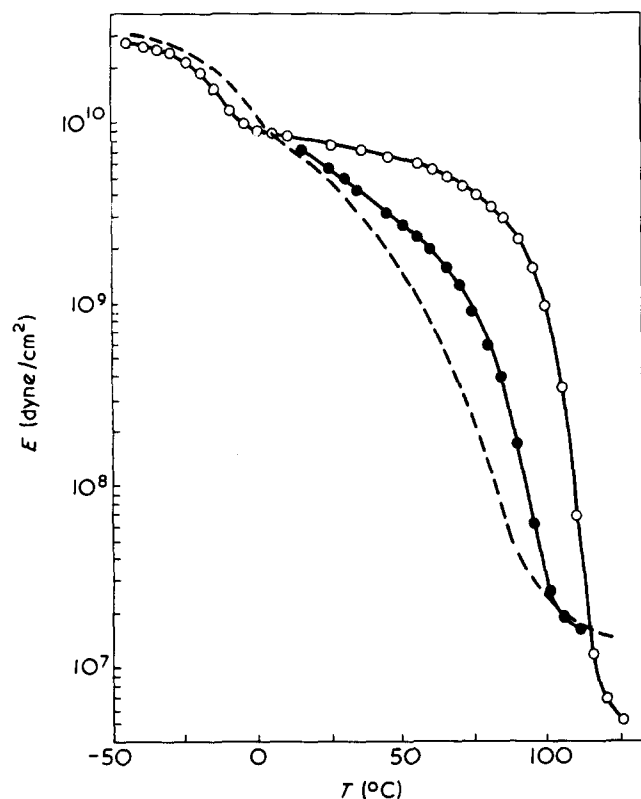

Figure 4 Modulus—temperature data: ― ― ―, typical, 4% cross-linker in PEA, 50/50 PEA/PS, freshly synthesized; ●, specimen code 53, annealed; ○, specimen code 13, decrosslinked and annealed

lus at 110°C had decreased about 80%. In this type, the PEA may be totally decrosslinked, and there is no crosslinker in the PS.

Annealing of the decrosslinked materials causes several results. As shown in *Figures 1* and *4*, the transition regions of both components become sharper. During annealing, the modulus at 110°C rises as shown in *Figures 2* and *3*. In the case of specimen code 12 and 13 materials, the resulting modulus at 110°C is even higher than the value just after synthesis, and also exceeds the modulus of either homo-polymer by a factor of about 2. The degree of annealing is

dependent on the degree of decrosslinking in the PEA and is relatively independent of the PS crosslink level. Annealing does occur to a small extent where no decrosslinking has occurred as in a specimen code 53 type material (*Figure 4*).

A comparison of specimen code 32 material after de-crosslinking and annealing and specimen code A32 material after annealing is shown in *Figure 5*. These two materials are identical as far as final crosslink levels in both components, but differ in synthesis route. Specimen code 32 originally had 4% crosslinker in the PEA, but the level was decreased to 2%, as in A32, upon decrosslinking.

Mechanical testing

Impact strength results are shown in *Table 3*. There is little change with decrosslinking or annealing except in the case of A31 and A32 materials where impact strength was decreased by over an order of magnitude by annealing. Typical values for nearly all materials tested were 0.10—0.20 ft lbs/in. of notch including A31 and A32 after annealing. However, A31 and A32 had values of about 2 ft lbs/in. of notch before annealing, indicating significant toughness.

Specimen code 11 material after decro..linking only and specimen code 13 material after decrosslinking and annealing exhibited brittle fracture in centre loading while 11 after de-crosslinking and annealing and A32 after annealing showed ductile fracture.
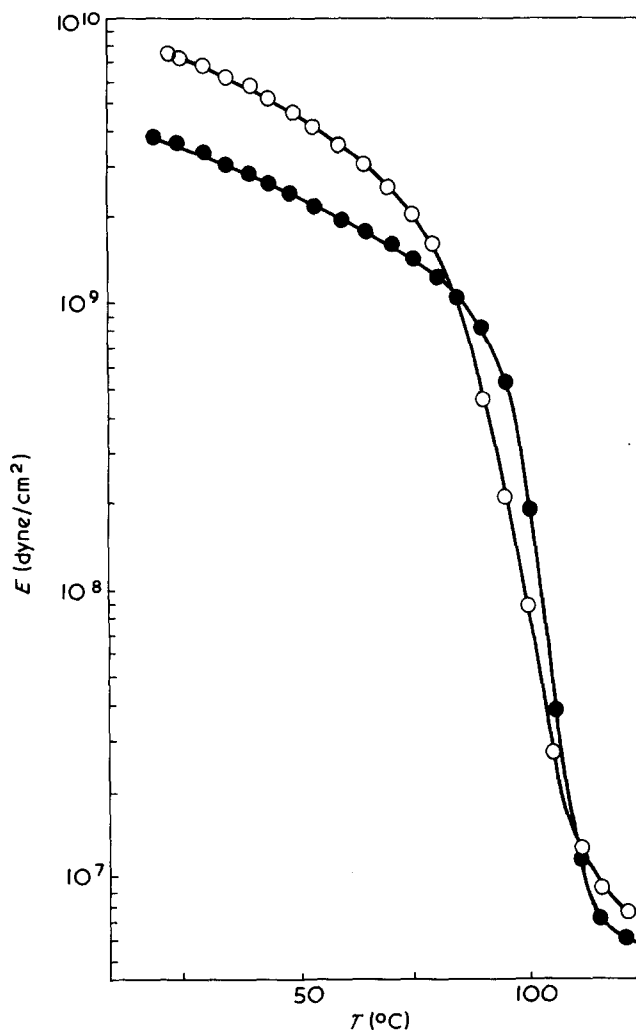

Figure 5 Modulus—temperature data: ●, specimen code A32, annealed; ○, specimen code 32, decrosslinked and annealed

Table 3 Impact Strength of *IPN* polymers (Charpy)

| Specimen Code	Impact value, (ft lbs/in. of notch)
11, freshly synthesized	0.09
11, decrosslinked	0.10
11, decrosslinked and annealed	0.19
13, decrosslinked	0.09
13, decrosslinked and annealed	0.10
31, freshly synthesized	0.11
31, decrosslinked and annealed	0.18
32, freshly synthesized	0.10
32, decrosslinked and annealed	0.14
A31, freshly synthesized	2.40
A31, annealed	0.15
A32, freshly synthesized	1.80
A32, annealed	0.10
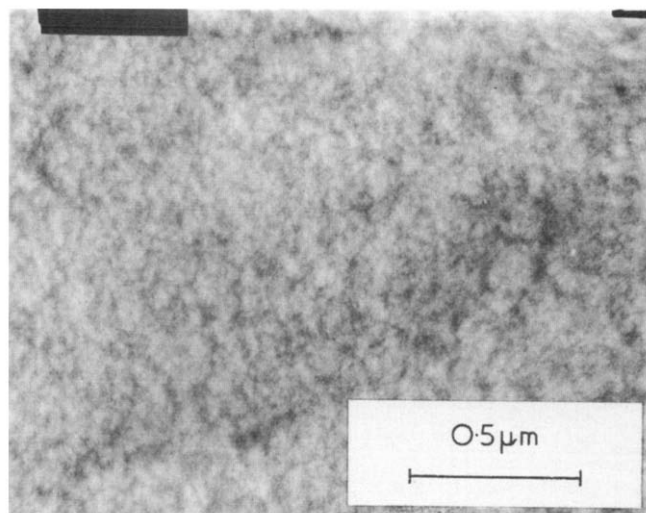
Figure 6 Electron micrograph 56 000 X specimen code 13, freshly synthesized

Electron microscopy

Results from electron microscopy are shown in *Figures 6–9*. Freshly synthesised materials of specimen code 13 in *Figure 6* show a fine structure of about 70 Å with coarser domains of about 700 Å. These materials resemble those of Huelck et al.[1], but the cellular structures are smaller and less well defined, probably due to the greater *IPN* crosslink density. After decrosslinking, the fine structure is coarser, about 170 Å, but the cellular structure remains unchanged, *Figure 7*. Annealing causes a larger increase in domain size, *Figure 8*, with domains ranging from 3000–10 000 Å. More important, fibrillar structures of the PEA component now appear, with an unusual orientation about the PS domains.

Figure 9 shows specimen code 11 after decrosslinking and annealing. The PS component is seen to have achieved significant phase continuity, while the PEA component has both continuous and discontinuous phase domains. The structures in *Figure 9* are much coarser than before decrosslinking and annealing.

Electron microscopy studies were also carried out on specimen code 32 for samples freshly synthesized, after decrosslinking, and after annealing. In each case the morphology resembled that already shown in *Figure 6*, with only modest changes in phase structure and size. However, noting that the hydrolysis should have produced only a partial

decrosslinking, the negative results obtained were in fact to be expected.

DISCUSSION AND CONCLUSIONS

Both electron microscopy and mechanical testing show modest changes after decrosslinking but much more extensive changes after annealing. Decrosslinking causes a slight enlargement in domain size, but no radical changes in structure. This is borne out by the modulus—temperature curves in *Figure 1* and a comparison of structure shown in *Figure 6–8* During annealing, domain size is enlarged greatly and the structure is highly altered in some cases. Two new morphologies have been encountered in *Figures 8* and *9*. *Figure 9* shows the PEA with both a continuous and a discontinuous aspect. In *Figure 8*, the PEA has achieved a fibrillar nature. After annealing the phase domains also appear larger and more distinct, probably due to molecular rearrangements possible after decrosslinking. It was found that the degree
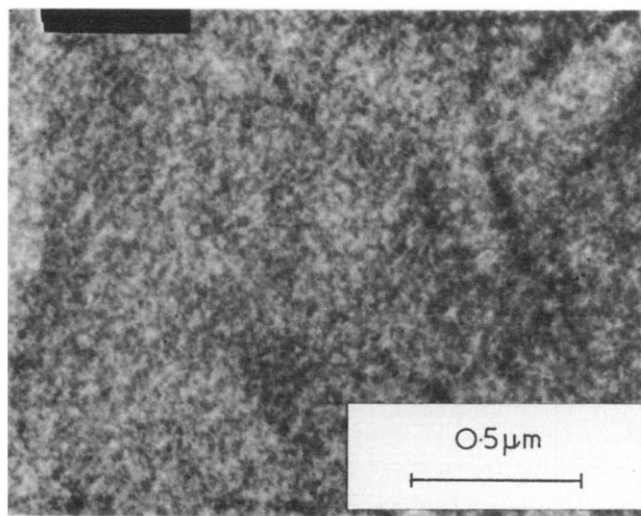

Figure 7 Electron micrograph 56 000 X specimen code 13, decrosslinked
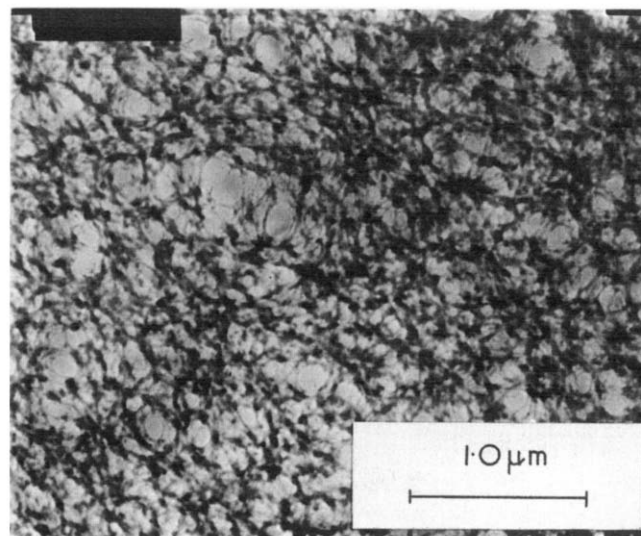

Figure 8 Electron micrograph 28 000 X specimen code 13, decrosslinked and annealed. Note the appearance of oriented or fibrillar PEA structures
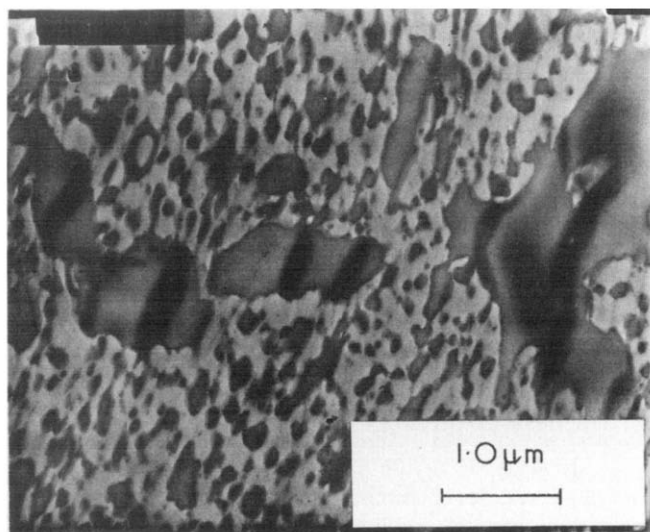
Figure 9 Electron micrograph 17 000 X specimen code 11, decrosslinked and annealed. While the PS now assumes a degree of continuity, the PEA has both continuous and discontinuous portions

of decrosslinking in the PEA controlled the degree of modulus change on annealing (*Figures 2* and *3*).

While most impact studies yielded low values, it should be noted that the values for specimen code A31 and A32 materials as freshly synthesized were much higher than would have been expected.

The degree of continuity in polymer 11 of an *IPN* is considered less than that of polymer 1, but the exact degree is uncertain[1,2]. The modulus data taken at constant temperature during annealing, *Figures 2* and *3*, suggest that the PS increases its degree of continuity.

Polymer structure theories usually assume that the polymer chains are in the same state in the mixtures as in the homopolymer. While this may be the case in a mechanical blend, it is not the case in an *IPN*[32]. In most *IPN* polymers, polymer I is strained because it has been swollen with monomer II during synthesis. Polymer II develops unstrained during synthesis. Apparently during annealing the domain structure is rearranged to equalize the strain in both polymers I and II yielding a minimum in the dual network free energy. Molecular rearrangement is facilitated by partial or total decrosslinking. In specimen code 11 material, both polymers I and II are probably unstrained after decrosslinking and annealing since they both exhibit a large degree of mobility. In a material like specimen code 32, polymers I and II are probably both strained after annealing.

The two pairs of materials 31, A31 and 32, A32 were prepared to demonstrate the use of decrosslinking to produce new types of materials. After decrosslinking and annealing, 31 and 32 are nominally identical to A31 and A32, after annealing respectively. After decrosslinking and annealing, the new materials 31 and 32 were superior to their counterparts, A31 and A32, in stiffness, toughness, and machining quality. In fact, when all properties were considered, specimen code 32, after decrosslinking and annealing, had the best material properties encountered.

Relating back to the ring theory concepts[30,31], it may be noted that moving a composition from the 'crosslinked' table to the 'blend' table causes a transformation in properties of great interest. According to ref 30, the decrosslinking may be expressed:

$$\beta S \big|_2 \rightarrow M_{12} \qquad \qquad (1)$$

for the specimen code 11 sample. The other reactions can be expressed similarly. Reactions by stages, however, such as partial decrosslinking rather than total decrosslinking yields insight into the mechanism of annealing.

ACKNOWLEDGEMENT

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