

Studies on Semi-interpenetrating Polymer Networks from Poly(vinyl chloride-co-vinyl acetate) and Poly(butyl acrylate)

ANNAKUTTY MATHEW and P. C. DEB

Naval Chemical and Metallurgical Laboratory, Post Bag No. 10012, G.P.O., Bombay 400001, India

SYNOPSIS

A series of semi-interpenetrating polymer networks (semi-IPN) based on linear poly(vinyl chloride-co-vinyl acetate) and cross-linked poly(butyl acrylate) were synthesized. The copolymer was swelled in butyl acrylate monomer containing azobisisobutyronitrile (AIBN) initiator and tetraethylene glycol dimethacrylate cross-linker and later polymerized *in situ*. Variation in composition of the IPN was achieved by varying the copolymer/monomer ratio. The semi-IPN was found to exhibit two distinct glass transitions as measured by differential scanning calorimetry and dynamic mechanical analysis. The $\tan \delta$ values were found to be dependent on the composition. The tensile strength was found to be higher for semi-IPNs containing a higher percentage of copolymer.

INTRODUCTION

The development of polymer blends and grafts have added new dimensions to the use of more common polymers for speciality applications. Interpenetrating polymer networks (IPNs) belong to the category of polymer blends with special characteristics such as damping of vibrations¹⁻⁹ and impact resistance modification^{10,11} over a wide temperature range not realized for conventional homopolymers or blends. Most IPNs exhibit a greater or lesser degree of phase separation. However, new morphologies and properties arising out of domain size and numerous cross-links are recently being attempted for specific and desired applications. It seems possible that by controlling the process parameters and proper selection of constituents one can obtain network structures with phases smaller than macromolecular end-to-end distances. Moreover, the introduction of cross-links in both polymers in a full IPN restricts domain size and enhances the molecular mixing. The effect is a bit less pronounced in semi-IPN where cross-linking of one component only takes place. However, with proper selection of polymers, an appreciably high extent of mixing can be obtained.

The present study deals with the synthesis and characterization of semi-IPNs based on linear poly(vinyl chloride-co-vinyl acetate) (PVC-VA) copolymer and cross-linked poly(butyl acrylate) (PBA). The combination is expected to afford interesting characteristics because the copolymer is a resin having a glass transition temperature (T_g) of about 69°C, whereas the acrylate has a T_g of -55°C, behaving as a pseudoelastomer at room temperature.

EXPERIMENTAL

Materials

The PVC-VA, 85/15 w/w (Union Carbide, U.S.A.) was used without further purification. Butyl acrylate monomer (Fluka) was freed from inhibitor and distilled under reduced pressure before use. Tetraethylene glycol dimethacrylate (TEGDM) (Fluka) was used as such. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. The carbon black used was HAF (Rubochem Industries Pvt. Ltd., India).

Synthesis

Semi-IPNs of PBA/PVC-VA have been prepared as follows: 10 g PVC-VA resin powder was thor-

oughly mixed with 18 mL butyl acrylate monomer containing 0.03 g AIBN and 0.4 mL TEGDM. The mixture was allowed to stand at room temperature for 4 h and the viscous mass obtained was poured into a stainless-steel mold ($1.5 \times 100 \times 150 \text{ mm}^3$) held between two stainless-steel plates. It was then polymerized at 80°C under a pressure of 150 psi for 1 h. The IPN sheet was then kept under reduced pressure at 80°C for 24 h to remove small molecules. This ensured complete polymerization of acrylate and no further weight loss. Composition of the above IPN was found to be 50% PVC-VA and 50% PBA by weight. Some butyl acrylate monomer was lost during the polymerization and also during the complete removal of residual monomer in vacuum. Since the weight of PVC-VA remains constant during all these stages, the actual composition has been calculated by knowing the total weight of IPN. IPNs of various compositions were prepared by varying the PVC-VA/butyl acrylate monomer ratio. Also, samples of different dimensions were made by changing the mold dimensions.

IPNs containing carbon black filler were synthesized by first mixing the PVC-VA powder with carbon black and later mixing with the monomer as described earlier. Carbon black, 7.5 parts, per 100 parts of IPN, was used in all the filled IPNs.

Cross-linked PBA was prepared by taking 30 mL

butyl acrylate monomer containing 0.6 mL TEGDM and 0.02 g AIBN into a glass mold. The mold consisted of two $3 \times 200 \times 200 \text{ mm}^3$ glass plates separated by rubber strips of 5 mm thickness and was kept at 60°C for 4 h and then at 80°C for 8 h. The residual monomer was completely removed by keeping it in a vacuum oven at 80°C for 12 h. The cross-linked PBA obtained was very soft and sticky, having a very low tearing strength. Sheets of PVC-VA were prepared as follows: 20 g PVC-VA powder was taken in the same stainless-steel mold used for IPNs and kept at 100°C for 10 min. Transparent sheets of 1.5 mm thickness were obtained that were cut to the required size at the same temperature. On cooling, the sheet was tough and brittle.

Thermal Analysis

Differential scanning calorimetric (DSC) studies were carried out on a DuPont DSC (910) from -100 to $+100^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$. A sample weight of 5 mg was used.

Thermogravimetric analysis were carried out using a TGA (DuPont Model 951). The heating rate was $10^\circ\text{C}/\text{min}$. The sample weight was 10 mg and the analysis was carried out in nitrogen atmosphere.

Dynamic mechanical spectra were recorded using a dynamic mechanical analyzer (DuPont DMA

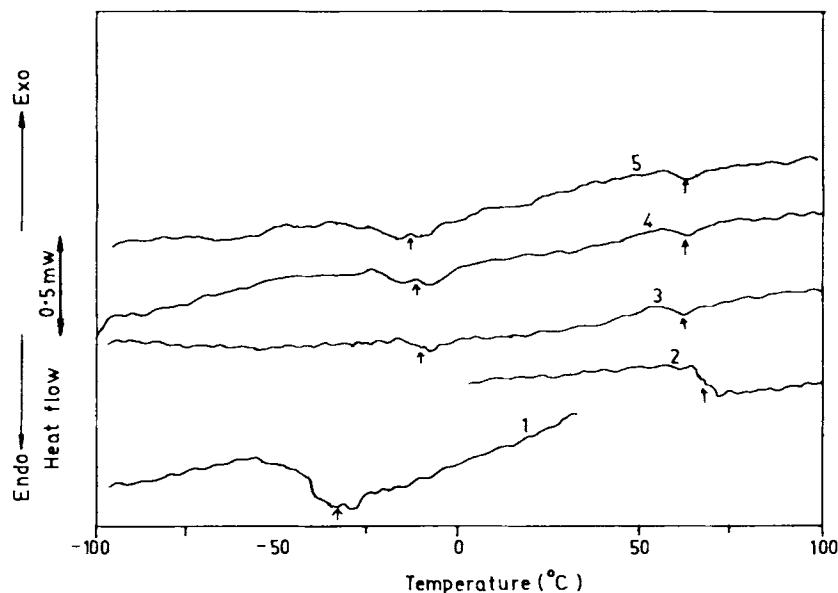


Figure 1 DSC thermograms of polymers and semi-IPNs: (1) cross-linked PBA; (2) PVC-VA; (3) unfilled PBA20 PVC-VA80; (4) unfilled PBA50 PVC-VA50; (5) filled PBA50 PVC-VA50.

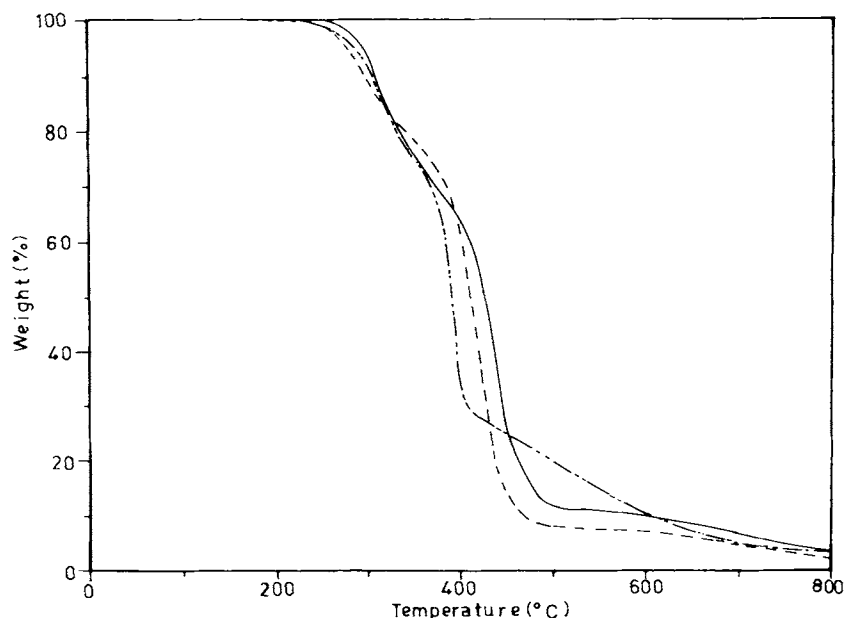


Figure 2 TGA thermograms of semi-IPNs: (—) unfilled PBA50 PVC-VA50; (---) unfilled PBA70 PVC-VA30; (- · - ·) filled PBA55 PVC-VA45.

Model 983) at temperatures between -80 to $+120^{\circ}\text{C}$. The measurements were carried out at a heating rate of $5^{\circ}\text{C}/\text{min}$ by using the resonance mode.

Mechanical Properties

The tensile strength and elongation at break of the IPNs were determined on an Instron testing machine (Model 1123) according to ASTM D 638-77 specification at room temperature at a crosshead speed of $20\text{ mm}/\text{min}$ using dumbbell-shaped specimens. In the case of PVC-VA, parallel strips of $1.5 \times 10 \times 100\text{ mm}^3$ was used since it was difficult to cut dumbbell-shaped specimens.

RESULTS AND DISCUSSION

Differential Scanning Calorimetric Studies

The glass transition temperatures of PBA, PVC-VA, and the various IPNs were measured using a DSC, and a few representative spectra are produced in Figure 1. For the cross-linked PBA, the glass transition temperature is -35°C . The PVC-VA resin exhibited a T_g around 69°C . Two distinct transitions were observed on the DSC thermogram of semi-IPNs. The first transition, T_{g1} , is around $-10 \pm 1.5^{\circ}\text{C}$ for various IPNs and corresponds to

Table 1 Dynamic Mechanical Properties of Semi-IPNs

Composition % by Weight		E' (MPa) at 20°C	$\tan \delta_{1\text{max}}$	$\tan \delta_{2\text{max}}$	$T_{1\text{max}}$ ($^{\circ}\text{C}$)	$T_{2\text{max}}$ ($^{\circ}\text{C}$)
PBA	PVC-VA					
100	0	—	1.79	—	-13	—
70	30	858	0.42	0.19	-5	95
60	40	930	0.32	0.29	-6	96
50	50	1919	0.22	0.72	-2	98
75 ^a	25	110	0.68	0.15	-5	96
65 ^a	35	897	0.45	0.24	0	95
55 ^a	45	1293	0.22	0.42	0	98
0	100	2500	—	1.6	—	102

^a Contains 7.5 phr carbon black.

the cross-linked PBA; the transition is broad due to the cross-linking and the midpoint is taken as the glass transition temperature. The second transition, T_{g2} , is observed at $62 \pm 1^\circ\text{C}$ and is related to the glass transition temperature of linear PVC-VA. With change in composition, the T_g 's were not found to vary; the variation was only $2\text{--}3^\circ\text{C}$, which is within the experimental error ($\pm 1.5^\circ\text{C}$). However,

the T_g 's were shifted in the IPN when compared to that of the starting polymers. Thus, the presence of PVC-VA in the IPN raised the T_g of PBA from -35 to -10°C . The T_g of PVC-VA was decreased from 69 to 62°C . Thus, the two components appear to have some mutual solubility. The effect of PVC-VA raising the T_g of PBA is more pronounced than that of PBA, lowering the T_g of PVC-VA. The carbon

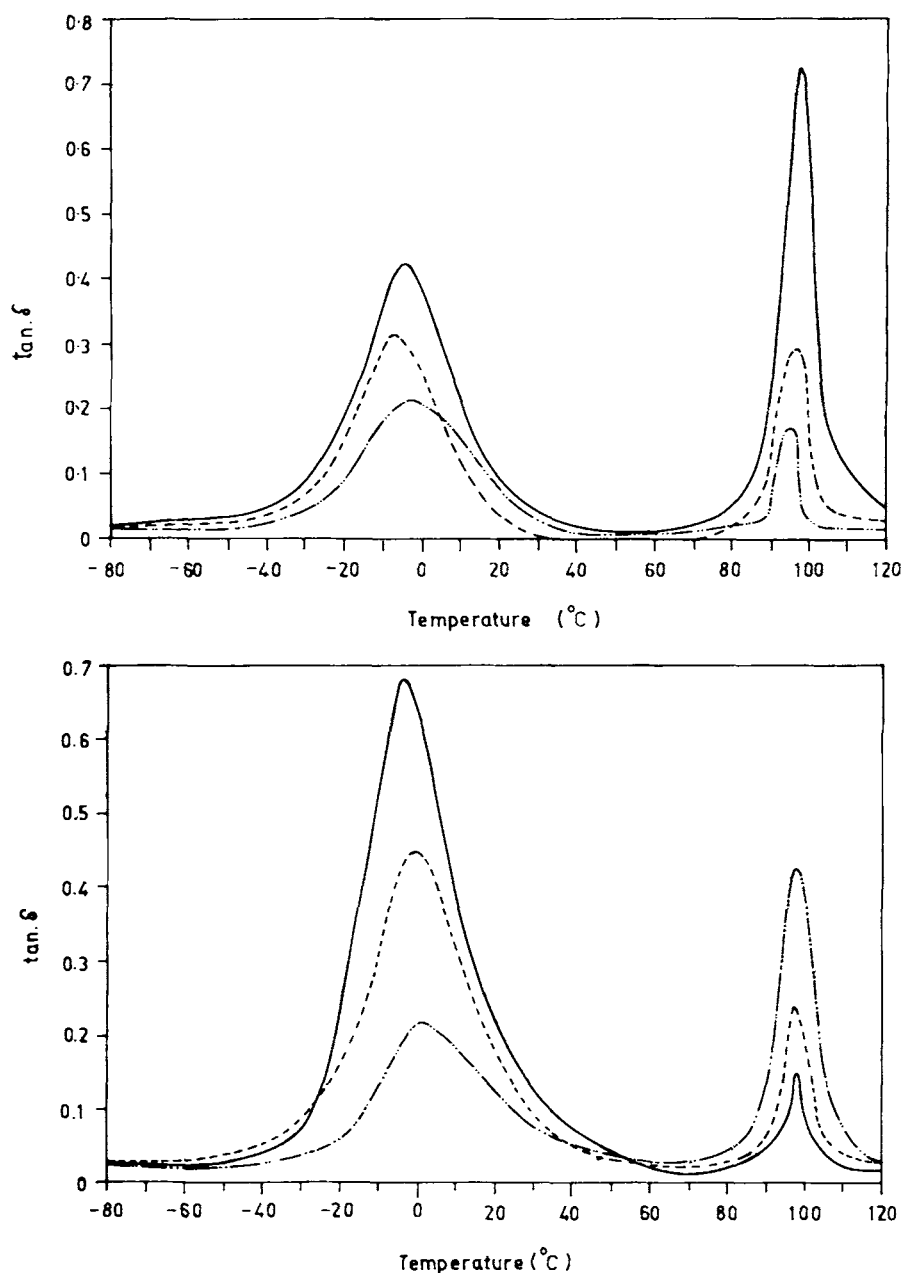


Figure 3 (a) $\tan \delta$ vs. temperature plots of unfilled IPNs: (—) PBA70 PVC-VA30; (---) PBA60 PVC-VA40; (- · - ·) PBA50 PVC-VA50. (b) $\tan \delta$ vs. temperature plots for filled IPNs: (—) PBA75 PVC-VA25; (---) PBA65 PVC-VA35; (- · · · ·) PBA55 PVC-VA45.

black-filled IPNs also showed two T_g 's at similar temperatures as in the case of the unfilled ones (Fig. 1). Studies on semi-IPNs by other workers also have shown that the semi-IPNs exhibit two different T_g 's.¹²⁻¹⁴

Thermogravimetric Studies

The thermogravimetric analysis of the semi-IPNs was carried out and a few typical curves are given in Figure 2. The semi-IPNs were found to be stable up to 300°C. The degradation occurs mainly in three steps. In the case of carbon black-filled IPNs, the second step ends at 30% weight loss, whereas for unfilled IPNs, it ends at 15% weight loss. About 5% char was obtained in all cases.

Dynamic Mechanical Analysis

Dynamic mechanical analysis of PVC-VA and various semi-IPNs were carried out from -80 to +120°C and the results are summarized in Table I. The $\tan \delta$ vs. temperature plots of the IPNs are given in Figure 3 (a) and (b) and a few representative traces of E' vs. temperature plots are given in Figure 4. PBA with a 4% cross-linker level shows a $\tan \delta_{\max}$ at -13°C, and the value is found to be 1.79 as reported by Chang et al.³ The DMA of PVC-VA shows a $\tan \delta_{\max}$ value of 1.6 at 102°C. The semi-IPNs show two $\tan \delta$ peaks. The $\tan \delta_1$ peak corresponding PBA is around $-3 \pm 3^\circ\text{C}$ and is broad, the half-width being

$35 \pm 5^\circ\text{C}$. The $\tan \delta_2$ peak is comparatively narrow (half-peak width $9 \pm 2^\circ\text{C}$) and is observed at $96 \pm 2^\circ\text{C}$ in all cases. Temperatures corresponding to $\tan \delta_{1\max}$ ($T_{1\max}$) and $\tan \delta_{2\max}$ ($T_{2\max}$) did not vary with change in composition. This is in agreement with the results obtained in DSC. However, $T_{1\max}$ and $T_{2\max}$ were found to be around 10°C and 30°C higher than T_{g1} and T_{g2} , respectively. The same observation has also been made in the case of starting polymers (Table I).

The $\tan \delta_{1\max}$ and $\tan \delta_{2\max}$ values were found to vary significantly with change in composition. For example, as the butyl acrylate content is increased from 50 to 70%, $\tan \delta_1$ increases from 0.22 to 0.42 and $\tan \delta_2$ decreases from 0.72 to 0.19. The carbon black-filled IPNs also showed an increase from 0.22 to 0.68 for $\tan \delta_1$ and a decrease from 0.42 to 0.15 for $\tan \delta_2$ when the PBA was increased by 20%. Thus, the study shows that the presence of a second phase reduces the $\tan \delta$ value of each polymer and that the higher the percentage incorporated the lower the $\tan \delta$ value.

The storage modulus values given in Table I show that it decreases with increase in the concentration of PBA, which may be because the modulus of PVC-VA is higher than that of PBA.

Tensile Properties

The tensile properties of the PVC-VA and semi-IPNs of various compositions were studied. The an-

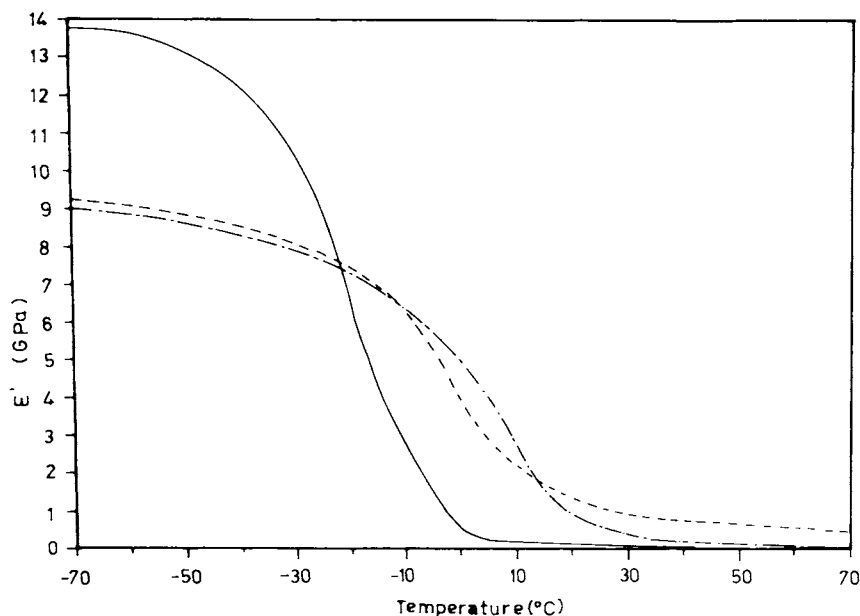


Figure 4 E' vs. temperature plots for filled semi-IPNs: (—) PBA75 PVC-VA25; (---) PBA65 PVC-VA35; (- · - ·) PBA55 PVC-VA45.

Table II Tensile Properties of Semi-IPNs

Composition % by Weight		Tensile strength (kgf/cm ²)	Elongation at break (%)
PBA	PVC-VA		
70	30	70	170
60	40	84	150
50	50	120	160
40	60	115	125
20	80	131	150
75 ^a	25	16	90
70 ^a	30	25	100
65 ^a	35	37	112
60 ^a	40	56	125
55 ^a	45	75	130
0	100	475	35

^a Contains 7.5 phr carbon black.

alytical data are reported in Table II and a few stress-strain curves are reproduced in Figure 5. PVC-VA is a tough material, having a tensile strength of 475 kgf/cm² and elongation 35% at break. Cross-PBA is a soft material having practically no strength. Semi-IPNs from these two materials showed interesting tensile properties. The tensile strength of the IPNs decrease considerably with increase in butyl acrylate content. Thus, by changing the PBA from 20 to 70%, the tensile

strength decreases from 130 to 70 kgf/cm². However, variation in elongation of these IPNs were found to have no direct relation with the PBA/PVC-VA contents. The figure shows that as the butyl acrylate content is increased the elastic region decreases, and above 60% PBA, the IPN behaves as rubber.

The carbon black-loaded IPNs showed lower strength and elongation at break compared to the unloaded ones. For example, the semi-IPN containing 60% PBA and 40% PVC-VA showed a tensile strength of 84.0 kgf/cm² at break, whereas the same composition containing 7.5 phr carbon black showed a small strength of only 56.0 kgf/cm² at break; the elongation was 150% in the former case and 125% in the latter case. It may be possible that the carbon black is incompatible with these polymers and microregions of incompatible phases appear in the filled IPNs, leading to poor tensile strength.

CONCLUSION

Studies on semi-IPNs based on PBA, an elastomer, and PVC-VA, a thermoplastic, have shown interesting properties. The semi-IPNs, however, exhibited two separate T_g 's; they were shifted by the presence of the second polymer. The $\tan \delta$ values were also found to vary considerably in the IPNs. Tensile

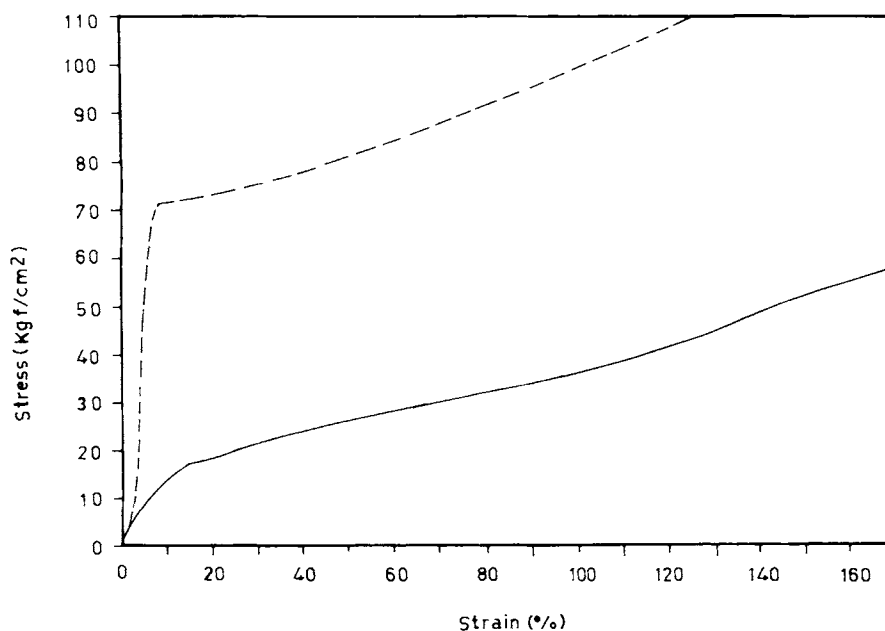


Figure 5 Stress-strain curves for unfilled IPNs: (----) PBA70 PVC-VA30; (—) PBA40 PVC-VA60.

studies showed that the IPNs change from thermoplastic to rubbery by changing the composition.

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