

The Effects of Functional Azo Initiator on PMMA and Polyurethane IPN Systems. II. The Influence of the Interface and the Matrix Structure on the Mechanical Properties

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SYNOPSIS

The mechanical properties of materials prepared by a new method for modifying the structure of polyurethane/poly(methyl methacrylate) (PU/PMMA) interpenetrating polymer networks (IPNs) by using a reactive azo initiator were investigated by means of tensile test, tear test, and dynamic mechanical thermal analysis (DMTA) measurement. The structures of these IPNs were similar to the particulate filled elastomers. It was found that the reactive initiator, which could form blocks of PMMA within the PU matrix (rubber), changed both the filler-matrix interface and the matrix structure. The mechanical properties of these IPNs were dominated by the matrix structure and the interface.

INTRODUCTION

A method for obtaining high-impact materials by the interstitial polymerization of vinyl monomers within a polyurethane elastomer gel has been reported by Allen and co-workers.¹⁻⁵ These products possess semi-interpenetrating polymer networks. The process was shown schematically below:

Elastomer precursors + vinyl monomer
↓ purethane catalyst
Gel swollen with vinyl monomer
↓ vinyl initiator
IPN composite

As the vinyl polymerization proceeded, phase separation occurred between the vinyl polymer and the polyurethane to form a two-phase system. Although the final phase morphology was quite distinct from that of standard toughened plastics (HIPS and ABS, for example), the level of impact resistance obtained was very similar. Morphological studies² on these materials showed that they consisted of

glassy domains of vinyl polymer phase embedded in a continuous polyurethane elastomer matrix, which was similar to the structures of particulate-reinforced elastomers.^{6,7}

Roha and Kim⁸ have studied a new method for modifying the structure of polymer blends by using a reactive initiator that could form chemical bonds between the two phases in the polymer blends. The reactive initiator, 4,4-azo-bis (cyanovaleic acid) (ABC), contained carboxylic functions, which would react with MDI to become part of PU elastomer network. Azo-bis-*iso*-butyronitrile (AIBN) was used as the comparison nonfunctional azo initiator. Their studies showed that the reactive initiator had a significant influence on the morphologies and mechanical properties of the blends.

The mechanical properties of heterogenous IPN systems depend on a number of variables such as preparation methods, reaction parameters, and morphologies.⁹ The effect of interpenetration on mechanical properties of these IPNs may relate to the reduction of the domain size and the increase in the physical entanglement crosslinks and adhesion between the two phases. When the rubber became the continuous phase and the glassy polymer was the dispersed phase, the mechanical properties were determined mostly by filler-reinforcement effect along with the interpenetration effect.¹⁰

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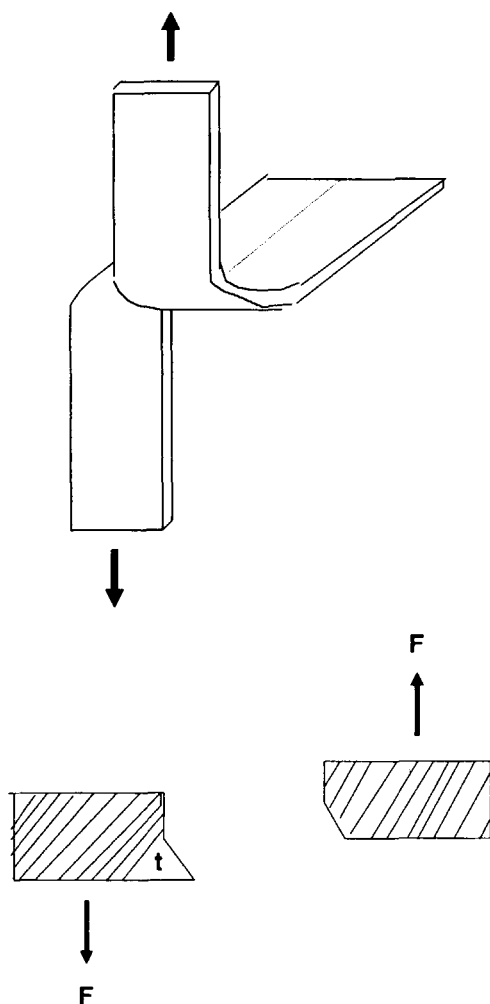


Figure 1 (A) Trouser tear test; (B) effect of shearing on the tear path.

This paper reports studies on the reinforcement behavior of these composites, the mechanism of their reinforcement, and how their properties were influenced by the interactions between the dispersed and the matrix polymers.

EXPERIMENTAL

Paper I of this series¹¹ had described the preparations, morphologies, and mechanical properties of the two-phase polymeric composites made by the interstitial polymerization of methyl methacrylate (MMA) using standard and reactive initiators in a polyurethane (PU) elastomer made from methylene bis 4,4'-(isocyanato phenyl) (MDI), trimethanol propane (TMP), and 1,2-polybutadiene diol

[PBD(1,2)]. These composites, possessing an interpenetrating polymer network (IPN) structure, were prepared by the procedure described previously by Allen and co-workers¹ for the formation, *in situ* at room temperature, of a PU gel swollen by MMA followed by polymerization of the monomer. The blends compositions reported here were: PU/PMMA 0/100, 20/80, 50/50, and 100/0 by weight. Adipic acid (AA) was added to AIBN in the standard initiator blend to provide an equivalent amount of carboxyl functions with AIBN to that provided by the functional ABC systems.

TEST PROCEDURES AND CALCULATIONS

Tensile Tests

Tensile tests were carried out using dumbbell-shaped specimens (ASTM D1708) about 1 mm thick and 4.75 mm wide on an Instron Model 1123. True stress and strain were calculated based on the assumption that the Poisson's ratio of the composites was 0.5. All tensile measurements were carried out at a crosshead speed of about 1 mm/min, corresponding to a strain rate of 4.4%/min.

Other measurements were carried out to determine the dissipation of mechanical energy during stretching. The test piece was stretched repeatedly to different elongations and then allowed to retract at the same rate back to the unstrained state. The hysteresis ratio H , defined as the energy dissipated relative to energy supplied in stretching the specimen, was determined from the area A_1 and A_2 under the loading and unloading force-displacement curves when specimens were stretched to various extensions at a cross-head speed of about 1 mm/min. The hysteresis ratio H was then calculated as follows:

$$H = (A_1 - A_2)/A_1 \quad (1)$$

When the specimens were stretched to near their breaking points and then retracted at the same rate back to unstrained state at the first strain cycle, the hysteresis ratio was called¹² high strain hysteresis ratio H_b . The correlation of H_b and energy input to break (U_b) was given by

$$U_b = K^3 H_b^2 \quad (2)$$

This relationship had been found¹³⁻¹⁵ to hold for a number of amorphous rubbers over a temperature

Table I The Mechanical Properties and Density of PU/PMMA (50%) IPNs

IPNs	Standard IPN	Reactive IPN
Young's modulus (MPa)	146 ± 7	80 ± 12
True tensile stress at break (MPa)	23	18
Elongation at break (%)	59	74
Strain energy density at break (MPa)	7200	7500
Hysteresis ratio at break (H_b %)	87.7 ± 0.2	86.1 ± 0.2
Tear energy at trouser test (kJ/m ²)	9 ± 3	15 ± 3
Density (g/cm ³)	1.045 ± 0.002	1.040 ± 0.002

range of -40 to 140°C . The value of the constant K^3 had been found to vary slightly between different rubbers. Harwood and Payne¹⁶ have suggested that K^3 was the value of energy input to break at the glass transition temperature of the rubber and was thought to reflect the cohesive energy density of the rubber.

Tear Tests

Tear tests were carried out as shown in Figure 1 (a) using strips about 1.5 mm thick. The dimensions of the specimens were: (1) total length 70 mm; (2) leg length 50 mm; (3) total width 15 mm. The samples were also scored with a sharp knife along the center

line to a depth of about one half the original thickness in order to guide the tear path, so that only about 0.7 mm of the thickness remained to be torn through. The rate of tear was about 0.2 mm/min. The tear strength T was given^{17,18} by

$$T = 2F/t \quad (3)$$

where F is the tear force and t is the width of the tear path. The tear path was often about 50% greater than the specimen thickness because the tear plane was not accurately perpendicular to the two surfaces of the specimen but lies at an angle of about 45° to them under the shearing action of the tear force F ¹⁹ [Fig. 1(b)].

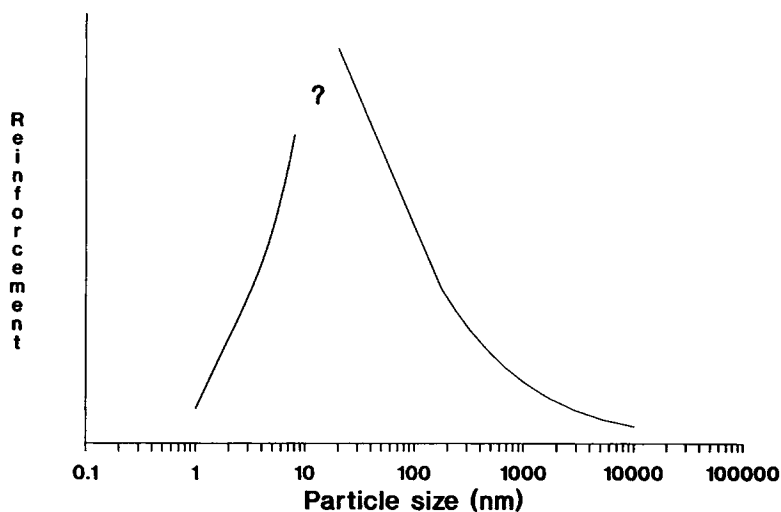


Figure 2 Schematic illustration of the effect of particle size on the rubber reinforcement.

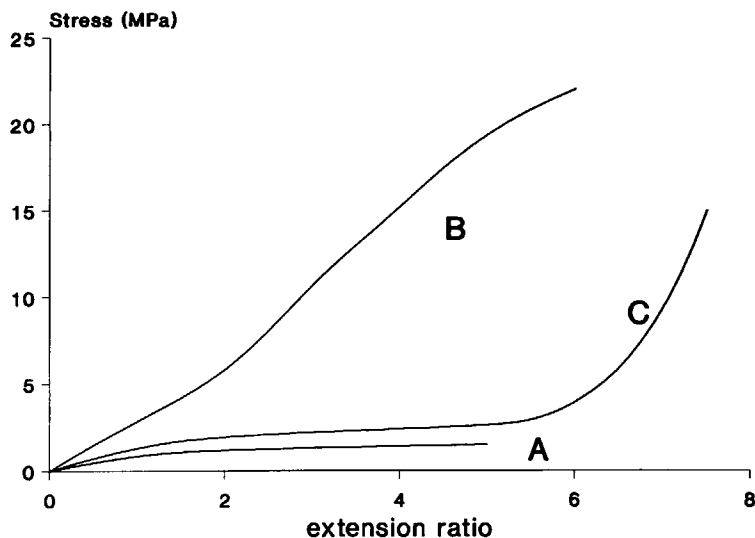


Figure 3 Stress-strain curves (schematic) of vulcanized rubber: (A) pure rubber; (B) reinforced with carbon black (chemical bonding); (C) reinforced with graphitized carbon black (no chemical bonding).

Dynamic Mechanical Thermal Analysis (DMTA)

The specimens for DMTA measurements were cut into approximate dimension of $20 \times 5 \times 1$ mm. The equipment used here was DMTA MK II, made by Polymer Laboratories. The sample was enclosed in an N_2 environmental chamber, which was thermostatically controlled to $\pm 1^\circ C$ over the temperature range from -30 to $+150^\circ C$. The measurements were made in tensile mode at frequencies of 0.3, 1, 3, 10, and 30 Hz, and heating rate $1^\circ C/min$.

RESULTS AND DISCUSSIONS

Reinforcement

The previous morphological studies¹¹ showed that the PMMA domain size was independent of the initiator system. Therefore, the differences in mechanical properties of the blends in this study cannot be caused by differences in the size of PMMA particles themselves, but must arise from the different PU/PMMA interface and by the composition of the matrix.

Table II Effects of Graphitization of Carbon Black on Rubber Reinforcement^a

	Carbon Black A		Carbon Black B	
	Original	Graphitized	Original	Graphitized
Bound rubber (%)	34.4	5.6	30.6	5.8
Stress at break (MPa)	26.2	23.4	27.6	22.7
Stress at elongation of 300% (MPa)	14.4	3.5	10.3	2.9
Elongation at break (%)	450	730	630	750
Hysteresis ^b	0.204	0.297	0.238	0.315
Relative abrasion resistance ^c	100	34	100	47

^a SBR 1500.

^b Method not specified in Brennan et al., *J. Appl. Polym. Sci.*, **8**, 2687 (1964).

^c Laboratory test.

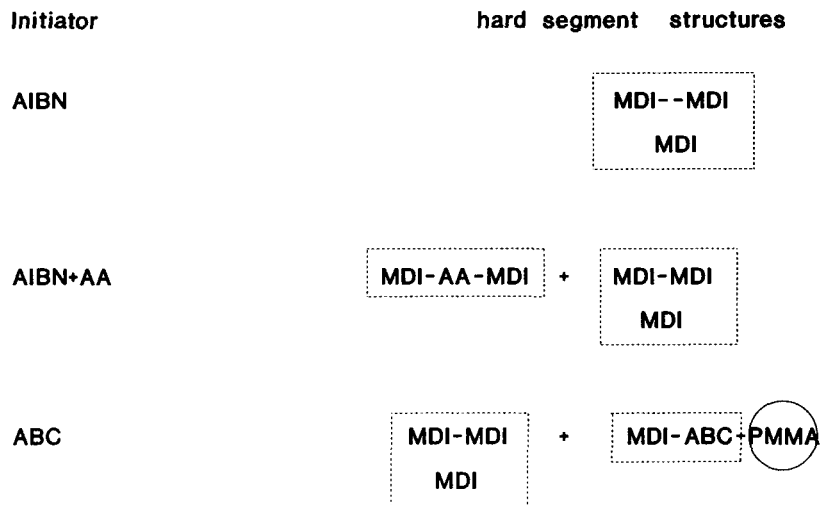


Figure 4 The structure of the hard segment in the polyurethane phase of PU/PMMA semi-IPNs.

The use of ABC, the functional azo initiator produced blocks of PMMA bonded to the PU chain. This was expected to provide additional chemical bonding beyond the imidization reaction, as well as physical bonding, between the dispersed PMMA-rich phase (filler) and the polyurethane-rich matrix (rubber) whereas AIBN, without producing these blocks, would normally provide only the imide bonding along with the physical bonding. It had been found earlier that both systems also reacted to produce bonding between the PU and the PMMA when heated at elevated temperatures. The mechanical properties of the ABC and the AIBN catalyzed blends are summarized in Table I. These data show that the reactive initiator gave blends with lower Young's moduli, tensile strengths, and higher tear strengths and higher elongations at break than did the standard initiator.

In similar heterogeneous IPN systems, it is generally believed¹⁰ that the filler-reinforcing effect (when the rubbery component assumes the continuous phase) play a major role in determining the engineering properties in addition to the interpenetration effect. The increased physical entanglement due to interpenetration did not contribute directly to increasing tensile strength in these IPN systems, but was due mostly to the filler-reinforcing effect of the dispersed glassy PMMA phase.¹⁰ However, the interpenetration at the phase boundaries apparently does enhance the filler-reinforcing effect by reduce the domain size and increasing the adhesive between the phases.^{20,21} The degree of reinforcement provided by a filler depends on a number of variables.²² The two most important features were the size of filler particle and the filler-rubber interaction. In primary size range of 10 to 100 nm (Fig. 2), there was a high

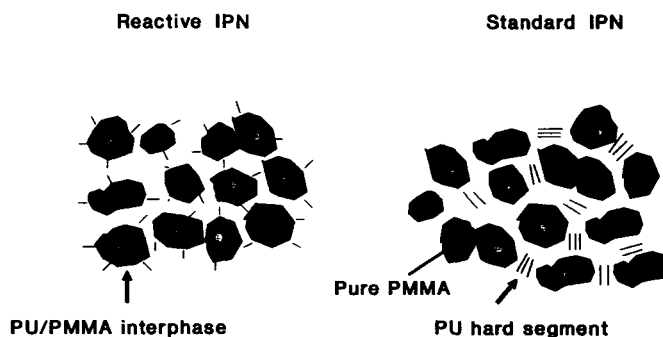


Figure 5 The model of microstructure of PU/PMMA semi-IPNs.

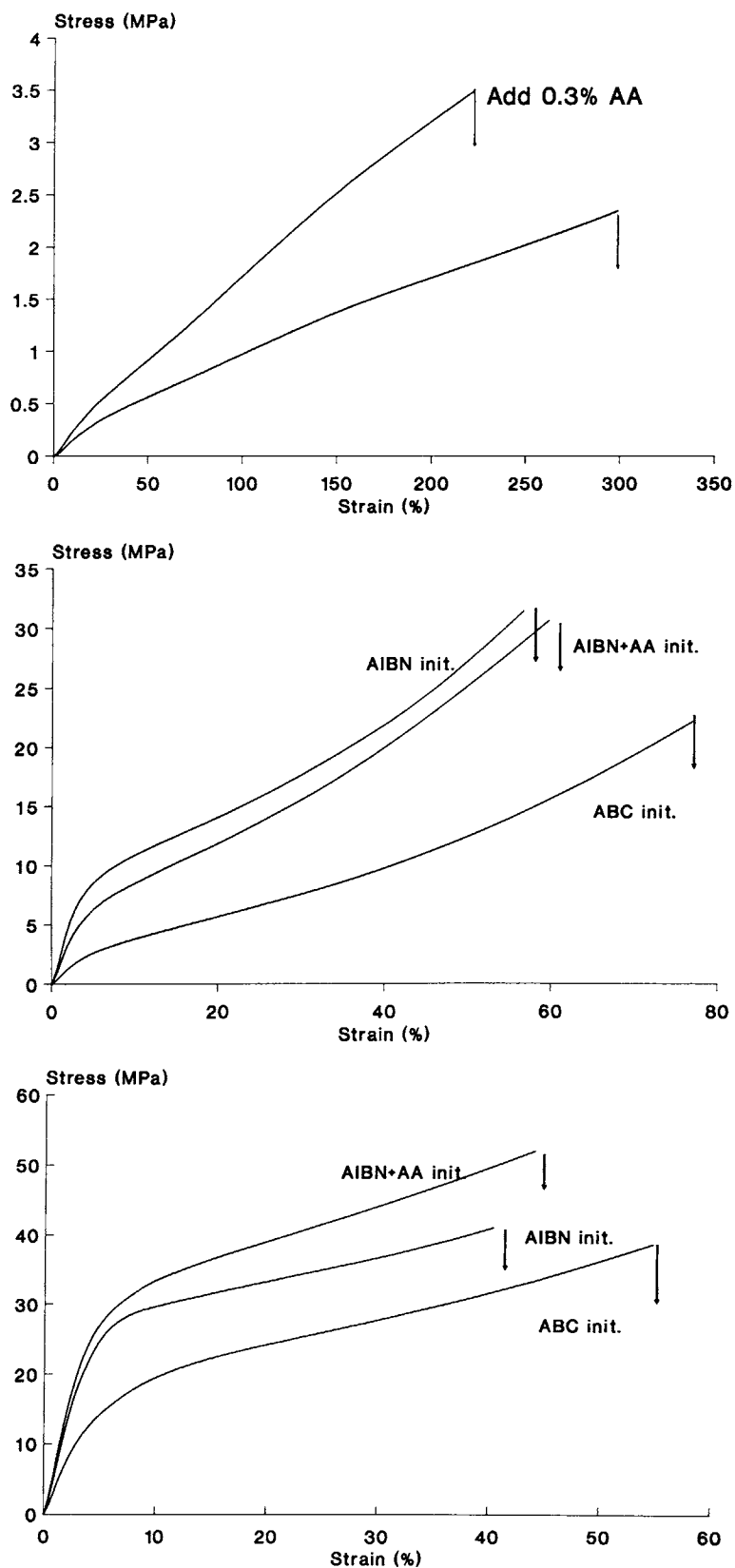


Figure 6 Effect of adipic acid (AA) and reactive initiator on the stress-strain behavior of PU/PMMA IPNs. (A) pure polyurethane; (B) PU/PMMA (50/50) IPNs; (C) PU/PMMA (20/80) IPNs.

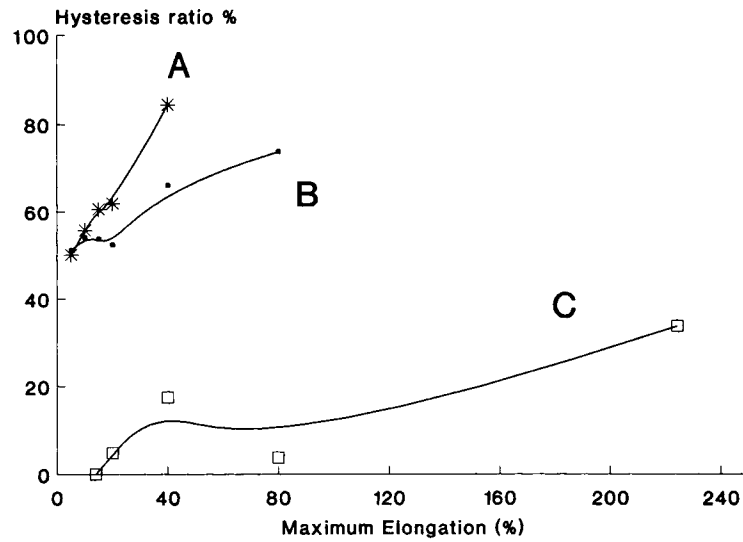


Figure 7 Mechanical hysteresis ratio H vs. maximum elongation of PU/PMMA IPNs in tensile test.

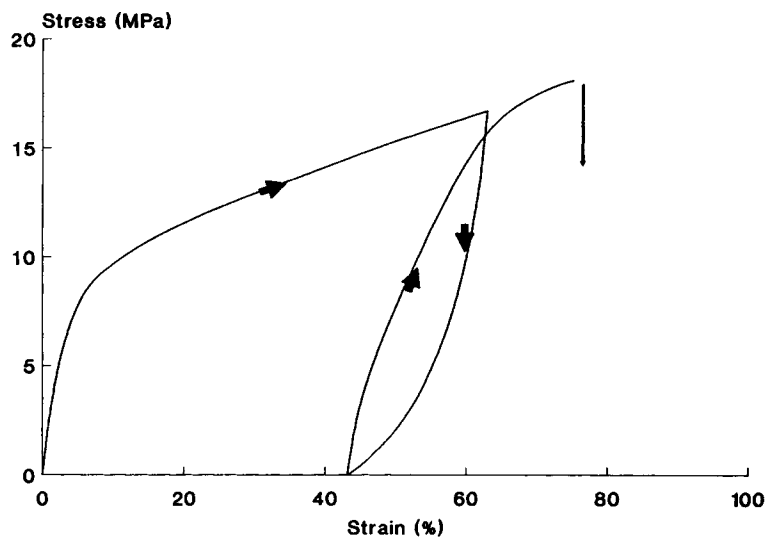
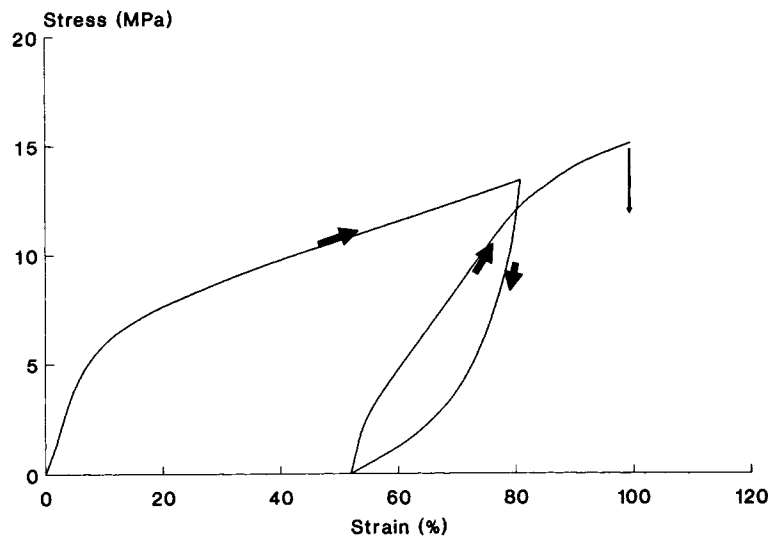


Figure 8 High strain hysteresis in tensile test for (A) reactive PU/PMMA (50%) IPN and (B) standard PU/PMMA (50%) IPN.

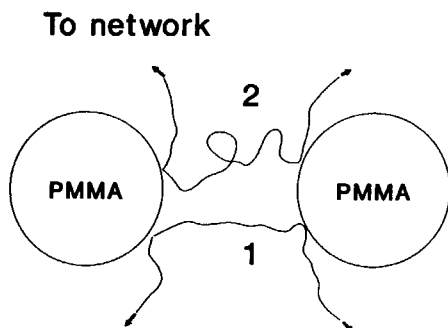


Figure 9 Schematic representation of the PU rubber chains attached to PMMA particles.

degree of reinforcement, which was very dependent on the particle size.

The usual filler-rubber interactions involve both chemical and physical bonding. For example, there was strong evidence²³ for the existence of chemical

linkages between carbon black and the typical rubbers. Carbon black surfaces contained functional groups capable of chemically reacting with polymer molecules during processing and vulcanization. However, heating carbon black to 2700°C or higher in an inert atmosphere removed all surface functional groups that served as highly energetic sites for physical adsorption. This graphitized black produced filled rubbers without filler-rubber interaction (Fig. 3 and Table II). It had been concluded^{7,24-26} that chemical bonding at the rubber-filler interface was not necessary for reinforcement, but did enhance the reinforcement process and contributed to the many excellent mechanical properties associated with carbon black-reinforced rubbers. Schmidt²⁷ concluded that in SBR systems, "small particle size of pigment is of prime importance in elastomer reinforcement, whereas the chemical nature of pigment appears to be of secondary importance."

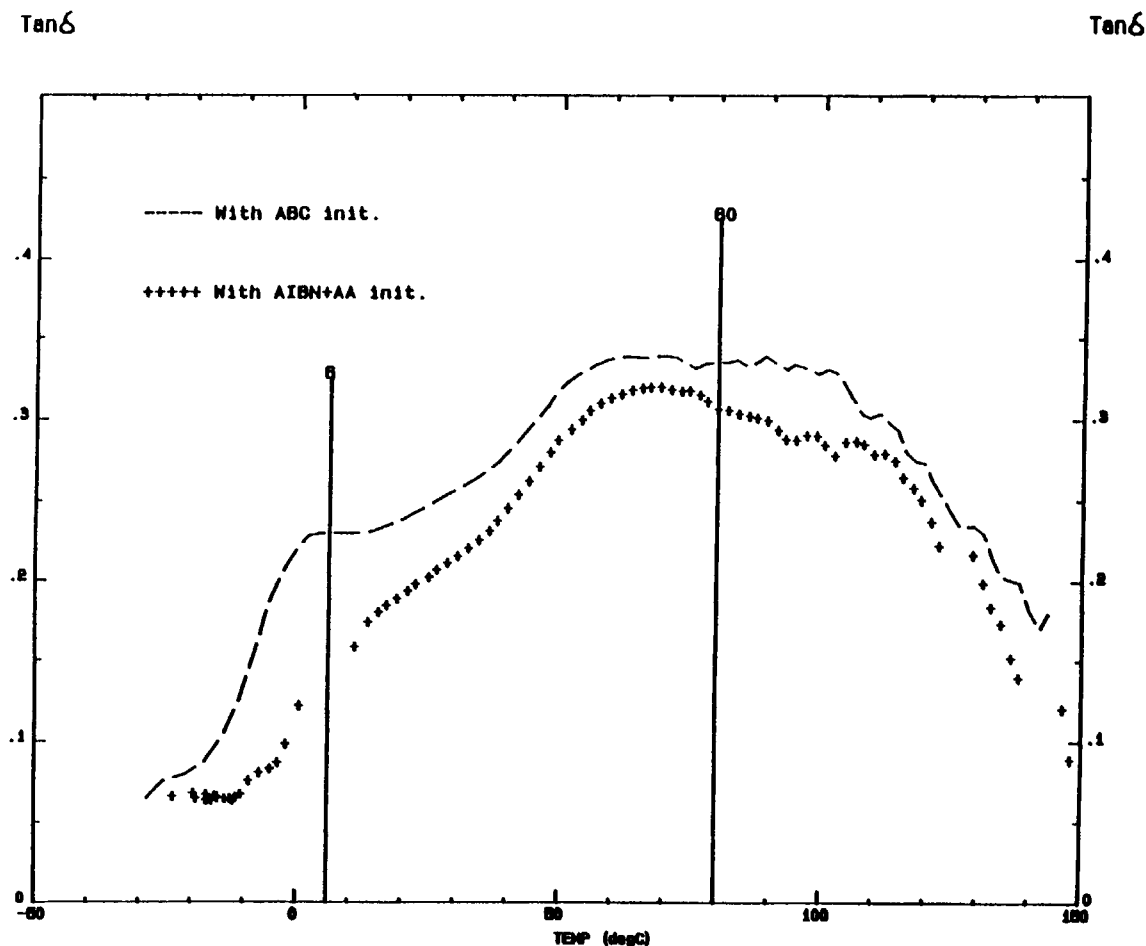


Figure 10a Influence of reactive initiator on the dynamic mechanical properties of 50/50 PU/PMMA IPNs: $\tan \delta$ vs. temperature curves.

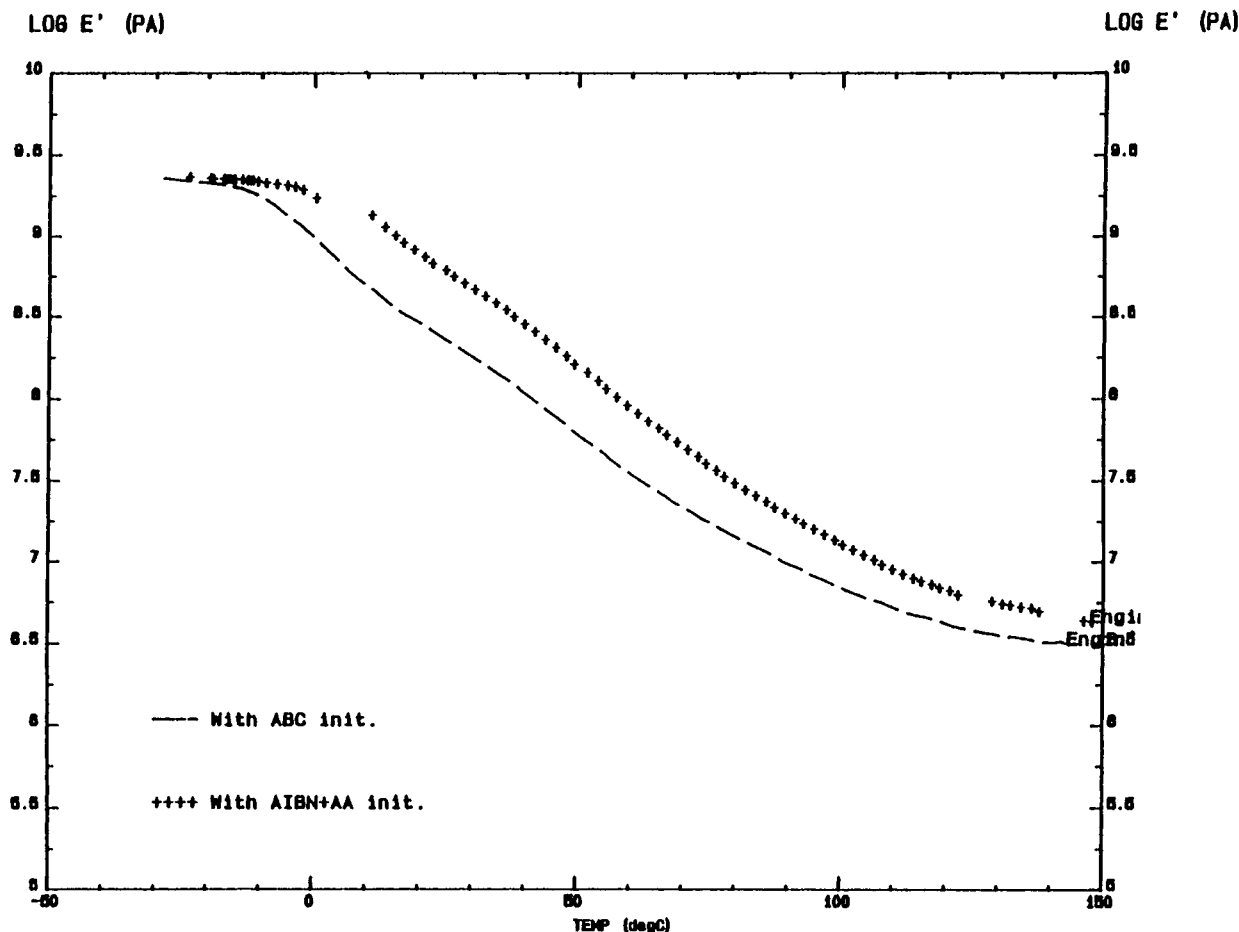


Figure 10b Storage modulus vs. temperature curves.

Tables I and II show that PMMA/PU IPN systems were opposite from those observed in a normal carbon black-reinforced elastomer. This indicated that there must be other factors which control these mechanical properties.

To help answer these questions, PBD(1,2)/PU-PMMA blends have been prepared with ABC, the reactive initiator system, with AIBN alone, and with AIBN with adipic acid (AA), which added carboxyl functions equivalent to those of the ABC. The structure of these IPN systems is shown in Figures 4 and 5. In the ABC blend, the PU-rich rubber matrix was chemically bound to the PMMA particles. Figure 5 shows that the structure of PU rubber matrix was altered by the choice of the initiator systems. Figure 6(a) also shows that the addition of AA increased the moduli of the polyurethane rubber made from MDI and PBD(1,2). In AIBN + AA systems, the AA (adipic acid) acted as chain extender in the polyurethane and increased the amount

of hard segments (MDI-AA-MDI) (Fig. 4). These aggregated hard segments, which act as reinforcement or cross-linking point (Fig. 5), increased the modulus and strength and decreased the elongation at break as is shown in Table I and Figure 6. However, in the ABC-catalyzed blends, the ABC initiator formed a new, low hardness block PMMA segment which decreased the modulus and strengths at break. In Figures 6(b) and 6(c), ABC also produced blends with lower moduli than AIBN + AA or AIBN alone. The absence of the hard blocks formed from AA could not be the only reason for the more elastic properties of ABC products. It was likely that the chemical binding of the PMMA blocks to the polyurethane chains disrupted the normal hydrogen bonding of the urethane groups, thus producing a softer matrix. The higher moduli of the AIBN + AA products were more evident in the 20/80 composition than in the 50/50 composition. This was most likely the result of the higher ratios of AA to poly-

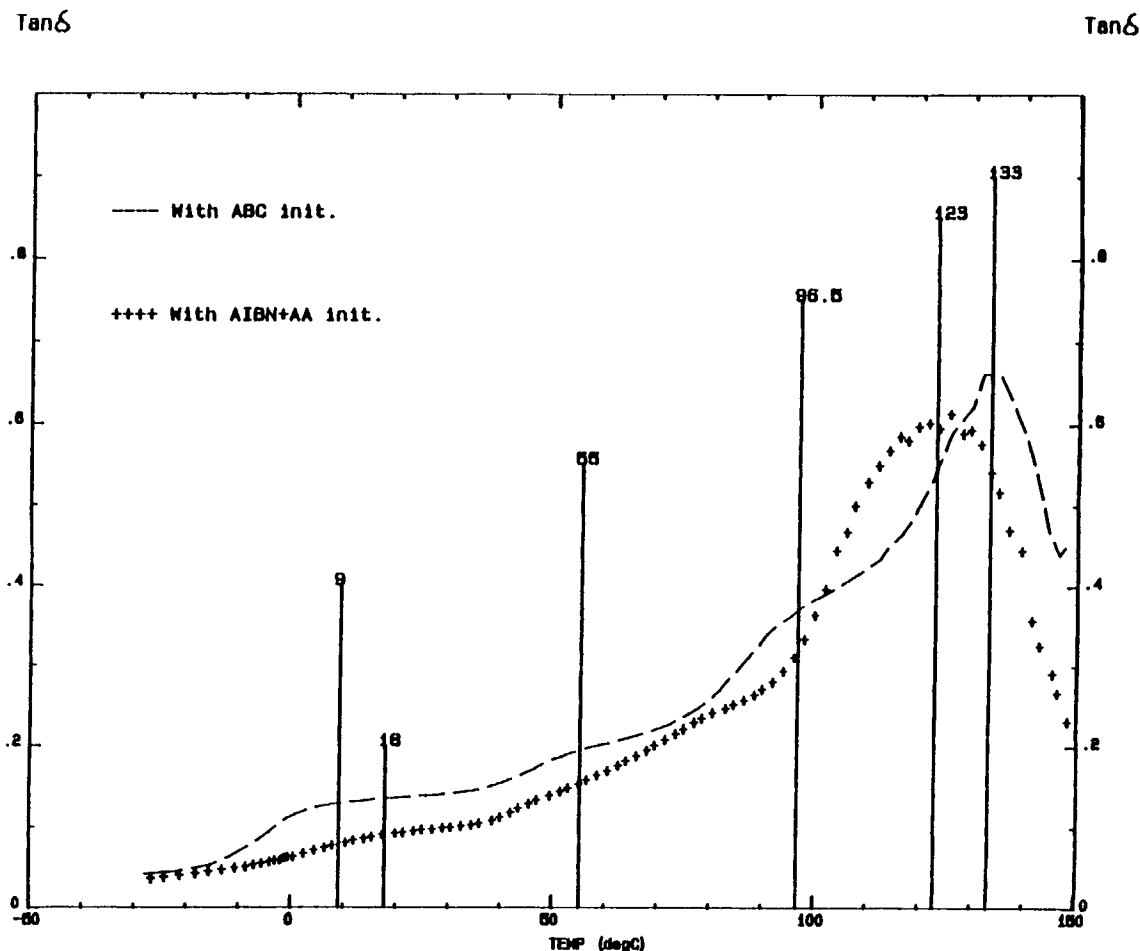


Figure 11a Influence of reactive initiator on the dynamic mechanical properties of 20/80 PU/PMMA IPNs: $\tan \delta$ vs. temperature curves.

urethane in 20/80 compositions, where azo initiator levels were held constant with the MMA monomer. Therefore, ABC produced lower Young's moduli and lower tensile strengths in this reactive blend. It appeared that the higher tear strength in the reactive blend as compared with the standard blend resulted from the chemical bonding between the phases.^{6,7} The blocks of PMMA attached to the PU chains enhanced this chemical bonding.

Hysteresis

Figures 7 and 8 show the hysteresis of these IPN systems. The higher hysteresis ratio in standard blends relative to reactive blend may have resulted from the large amount of PU chains slippage from those chains only physically attached to the PMMA

particles in a manner pictured in Figure 9 by Kraus.⁶ At large deformations, the two PMMA particles moved apart as the network was strained, and chain 1 became highly extended and reached its limits of finite extensibility long before chain 2 contributed to the retractile force of the network. Eventually the chain broke (either at the surface or internally), thus providing a mechanism of stress relaxation. When the chains which were most strained were also given a chance of slipping, they continued to carry the load by stretching to the very moment of rupture. Thus more chains effectively carried the load, resulting in a higher strength. The data in Table I and Figures 7 and 8 show that there was a lower hysteresis ratio in the reactive ABC blend than in the standard AIBN + AA blend. This also indicated that there were higher *physical* bonding between the

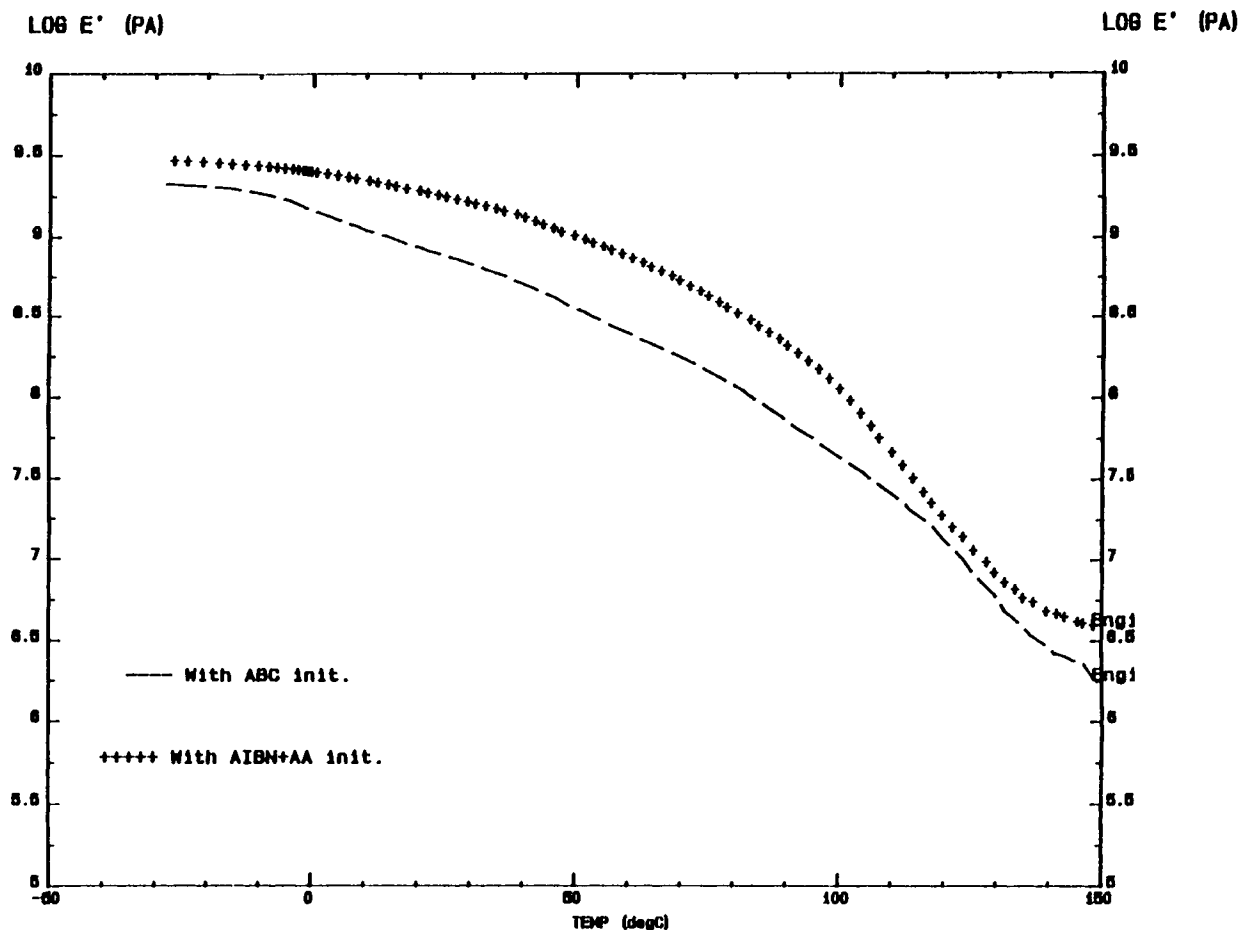


Figure 11b Storage modulus vs. temperature curves.

filler and the rubber matrix in ABC blends than in standard blends.

Repeated elongations gave a more rapid stress increase [Figs. 8(a) and 8(b)] than in the first cycle since the energy of slippage did not have to be provided as it was originally.

Dynamic Mechanical properties

The DMTA data reported in Paper I, along with that shown in Figures 10, 11, and 12, support the conclusions that the reactive initiator had little effect on the interfacial composition of these blends. The higher $\tan \delta$ value and lower modulus with ABC was more significant at the rubber transition region (about 10°C) and indicated that the rubber phase was more elastic in the ABC-blend systems. The rubber phase in these ABC blends appeared to contain fewer hard segments than that existed in the AIBN + AA blends. The small shoulder peak at about 50°C in Figure 12 may have indicated the

higher aggregation of hard segments (or crystallinity) in the AIBN + AA blend.

Densities

Similar differences between ABC and AIBN + AA are also noted in the density measurements¹¹ shown in Table I. The higher density of AIBN + AA products parallels the higher concentration of hard segments. The reactive initiator (ABC) appears to contribute fewer hard segments and reduces the contribution of those present to the properties by forcing them to be attached to the amorphous PMMA particles.

CONCLUSIONS

1. Both standard and reactive initiators contributed to the enhancement of reinforcement of the composites.

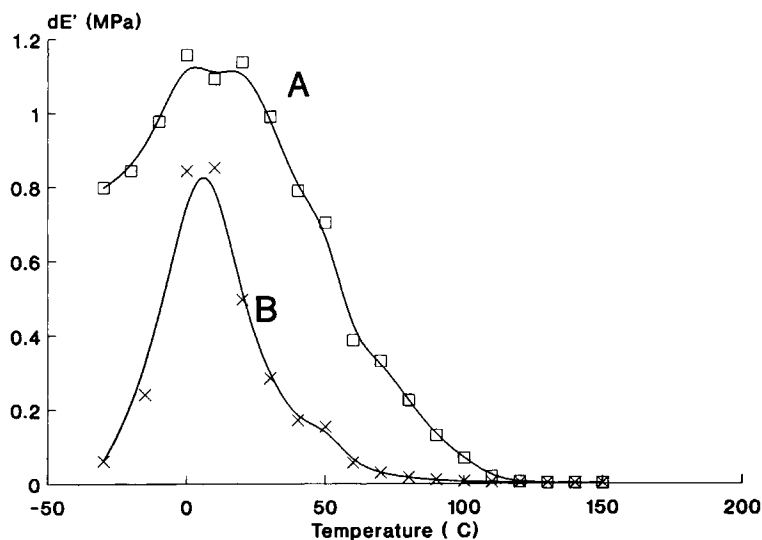


Figure 12 The effect of reactive initiator on the storage modulus of PU/PMMA IPNs: the storage modulus of standard IPN minus the storage modulus of reactive IPN vs. temperature curves: (A) 20/80 PU/PMMA; (B) 50/50 PU/PMMA.

2. The reactive initiator not only enhanced the filler–rubber interaction, but also changed the rubber matrix structure.
3. Chemical bonding between the filler–rubber composite decreased the slippage process and mechanical energy dissipation.
4. Higher concentration of aggregated hard segment in PU matrix of the standard blend relative to the reactive blend gave a higher Young's modulus, higher tensile strength, and higher density.

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REFERENCES

1. G. Allen, M. J. Bowden, D. J. Blundell, F. G. Hutchinson, G. M. Jeffs, and J. Vyvoda, *Polymer*, **14**, 597–603 (1973).
2. G. Allen, M. J. Bowden, D. J. Blundell, G. M. Jeffs, J. Vyvoda, and T. White, *Polymer*, **14**, 604–616 (1973).
3. G. Allen, M. J. Bowden, G. Lewis, D. J. Blundell, and G. M. Jeffs, *Polymer*, **15**, 13–18 (1974).
4. G. Allen, M. J. Bowden, S. M. Todd, D. J. Blundell, G. M. Jeffs, and W. E. A. Davies, *Polymer*, **15**, 28–32 (1974).
5. D. J. Blundell, G. W. Longman, G. D. Wignall, and M. J. Bowden, *Polymer*, **15**, 33–36 (1974).
6. Gerard Kraus, in *Science and Technology of Rubber*, Frederick R. Eirich, Ed., 1978, Chap. 8.
7. B. B. Boonstra, in *Rubber Technology and Manufacture*, C. M. Blow, Ed., 1971, Chap. 7.
8. Max Roha, EP 398490, November 22, 1990; *Chem. Abs.*, **114**(14), 123906e (1991); Y. Kim, Ph.D. Thesis, Case Western Reserve University, 1989.
9. L. H. Sperling, *Interpenetrating Polymer Network and Related Materials*, Plenum, New York, 1981.
10. S. C. Kim, D. Klempner, K. C. Frisch, and H. L. Frisch, *J. Appl. Polym. Sci.*, **21**, 1289 (1977).
11. M. Roha and B. Wang, *J. Appl. Polym. Sci.*, **45**, 1367 (1992).
12. A. I. Medalia, *Rubber Chem. Technol.*, **60**, 45 (1987).
13. L. Mullins and N. R. Tobin, *J. Appl. Polym. Sci.*, **9**, 2993 (1965).
14. E. Guth and O. Gold, *Phys. Rev.*, **53**, 322 (1938).
15. A. R. Payne and R. E. Whittaker, *J. Appl. Polym. Sci.*, **15**, 1941 (1971).
16. J. A. C. Harwood and A. R. Payne, *J. Appl. Polym. Sci.*, **12**, 889 (1968).
17. R. S. Rivlin and A. G. Thomas, *J. Polym. Sci.*, **10**, 291 (1953).
18. H. W. Greensmith and A. G. Thomas, *J. Polym. Sci.*, **18**, 189 (1955).

19. D. Mangis, M. Barquins, and R. Courtel, *Met. Corros. Ind.*, **51**, 1 (1976).
20. M. Morton, J. C. Healy, and R. L. Denecon, in *Proceedings of International Rubber Conference, 1967*, Maclaren, London, 1968, p. 175.
21. M. Morton and J. C. Healy, *Polym. Prepr.*, **8**, 1569 (1967).
22. D. C. Edwards, *J. Mater. Sci.*, **25**, 4175 (1990).
23. D. Rivin, *Rubber Chem. Technol.*, **36**, 729 (1963); **44**, 307 (1971).
24. Gerard Kraus, *Rubber Chem. Technol.*, **51**, 297 (1978).
25. P. Dreyfuss, A. N. Gent, and J. R. Williams, *Rubber Chem. Technol.*, **54**, 1003 (1981).
26. J. Le Bras, *Rubber Chem. Technol.*, **52**, 43 (1979).
27. Ernst Schmidt, *Ind. Eng. Chem.*, **43**, 679 (1951).

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