

Poly(vinyl chloride)/Styrene-Butadiene Rubber Blends Prepared by Dynamic Vulcanization with Nitrile Rubber as the Compatibilizer

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SYNOPSIS

A new kind of thermoplastic elastomer is obtained by dynamic curing of PVC/SBR blends. A compatibilizer is necessary, and of three tested—NBR and two ABSs—NBR-18 is the best. Sulfur and Dicumyl peroxide were chosen as the two different curing agents for the blends. The curing agent and its concentration have a dramatic effect on the mechanical properties. Di(2-ethyl hexyl)phthalate was used as the plasticizer for PVC. Variations in the PVC and di(2-ethyl hexyl)phthalate concentrations can produce materials having a wide range of hardness and strength to meet the needs of different applications. The effects of processing parameters such as blending time and processing temperature and the effect of filler in the blend on the mechanical properties were also investigated. The material, after processing five times, showed no significant changes in physical properties. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic elastomers (TPEs) are a new class of thermoplastics of which the properties can be more easily tailored—more so than block copolymers—by simply changing the ratio of the rubber to plastic in the blend.^{1–10} These materials are phase-separated systems in which one phase is rubbery at room temperature and the other is hard and solid. They possess the elasticity of a rubber and the thermoplasticity of a plastic, yet retain unique features of its components such as better ultraviolet and ozone resistance, solvent resistance, and high deformation temperature compared to elastomers. As a result, many commercial TPEs have been developed for various applications. Generally, it is easy to combine a rubber and a plastic of similar polarities and solubility parameters to produce a useful thermoplastic elastomer such as polypropylene (PP)/ethylene-propylene-diene copolymer (EPDM),

epoxidized natural rubber and poly(vinyl chloride),¹⁰ poly(vinyl chloride) (PVC)/acrylonitrile-butadiene rubber (NBR),^{11,12} and nylon/NBR.¹³ On the other hand, it is difficult to produce a TPE using a plastic and an elastomer having different polarities and solubility parameters because of the high interfacial tension. This problem can be resolved by the use of a compatibilizer to improve the interfacial adhesion between the two phases.^{14,15}

One of the well-known miscible polymer blends is PVC/NBR. PVC/NBR blends have been used since 1940 in applications such as sealants, gaskets, valve disks, coatings for electric wires and cables, soles, hoses, footwear, and artificial leather, due to low cost and desirable properties such as ultraviolet and ozone resistance, tear resistance, thermal aging, and solvent resistance.

Modifications of 70/30 (weight ratio) PVC/NBR blends using natural rubber (NR) and styrene-butadiene rubber (SBR) have been attempted by George et al.¹⁶ Their results show that replacement of NBR by NR up to 15% (by weight) improves mechanical properties and decreases the cost of the blend. If SBR is used, NBR up to 30% can be re-

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placed without any deterioration in mechanical performance. Because SBR is more flexible and cheaper than NBR, it is desirable to replace NBR with SBR. However, to produce a useful PVC/SBR blend, a compatibilizer is necessary to improve the interfacial adhesion between these two phases.

The choice of a compatibilizer is the key to obtaining a useful PVC/SBR blend because SBR and PVC are incompatible. Without coupling between the SBR and the PVC phases, the blends are of no practical use. A compatibilizer is necessary to reduce the interfacial tension between the SBR and PVC phases. The ideal compatibilizer has two components—one compatible with the PVC phase, and the other compatible with the SBR phase. NBR is known to be compatible with PVC. Blends of NBR and PVC have been reported to have a single broad glass transition temperature over a temperature range between the glass transition temperatures of the individual components.¹⁷⁻¹⁹ Wang and Cooper showed that PVC/NBR blends are compatible at 31% acrylonitrile (AN) content by DSC and the infrared dichromism method.²¹ In a study by Matsuo,²¹ an increase in the acrylonitrile content of NBR shows increased compatibility with PVC, indicating that the acrylonitrile component of NBR is compatible with PVC. Manoj et al.²² reported that crosslinking can occur between NBR and PVC through the allylic chlorine sites in PVC and the $-C\equiv N$ groups in NBR without a crosslinking agent and that DCP can crosslink PVC and NBR.²³ The

Table II Compositions of the Curing Systems

Curing system Ingredient	C1	C2	C3
	Parts by Weight		
Compatibilizer	10	10	10
SBR	40	40	40
PVC	50	50	50
DOP	50	50	50
Sulfur	1.5	—	1.5
MBT	1.5	—	1.5
DCP	—	1.5	1.5
TAIC	3.0	3.0	3.0
ZnO	3.0	3.0	3.0
Zinc stearate	1.5	1.5	1.5
Barium stearate	1.5	1.5	1.5

nonpolar component of NBR should be compatible with SBR. Covulcanization of SBR and NBR can further strengthen the coupling between these two rubbers. ABS is chosen as another compatibilizer for the same reason.

Various plasticizers that have been used to improve processability and flexibility of the PVC include low molecule weight aromatic esters, oligomers, and linear polymers. Because the addition of a plasticizer to PVC affects its mechanical properties, the effects of plasticizer concentration on the mechanical properties of PVC/SBR blends will be investigated.

Table I Summary of the Materials Used

Blend Component	Material	Abbr.	Source
Compatibilizer	Poly(vinyl chloride)	PVC	Jiling Chemicals Co.
	Styrene-butadiene rubber	SBR	Nanzhou Chemicals Co.
	Nitrile rubber	NBR	Nanzhou Chemicals Co.
	Acrylonitrile-butadiene-styrene	ABS-1	Gaoqiao Chemicals Co., Shanghai
Curing agent for the rubber	Acrylonitrile-butadiene-styrene	ABS-2	Bayer Co., Germany
	Sulfur		
Accelerator	Dicumyl peroxide	DCP	
	2-mercaptobenzothiazole	MBT	
Plasticizer	N-triallyl-triisocyanate	TAIC	Kasei Co., Japan
	Di(2-ethyl hexyl) phthalate	DOP	
Filler	Silicon dioxide		
Stabilizer	Carbon black		
	Zinc stearate		
	Barium stearate		

Table III Effects of the Curing System and Compatibilizer on the Physical Properties of the Blends

Curing system Compatibilizer	C-1				C-2				C-3					
	NBR-18	NBR-26	NBR-40	ABS-1	ABS-2	NBR	ABS-1	ABS-2	NBR	ABS-1	ABS-2	NBR	ABS-1	ABS-2
Properties														
Hardness, shore A	60	60	62	76	72	66	66	66	64	72	70	64	72	70
Elongation, %	100	220	180	100	100	230	130	130	380	140	110	380	140	110
Tensile strength, MPa	1.7	3.2	2.8	3.9	5.4	6.7	3.6	3.8	8.0	4.4	4.2	8.0	4.4	4.2
Strength 100% elongation, MPa	—	1.7	1.6	—	—	3.1	—	—	8.0	4.4	4.2	8.0	4.4	4.2
Tear strength, kN/m	8	20	15	18	17	26	15	15	31	20	15	31	20	15
Tensile set, %	3	7	3	7	7	7	3	3	13	7	3	13	7	3

* These blends do not contain compatibilizer and have 50 parts by weight of SBR.

The objective of this work is to develop a compatibilized and dynamically vulcanized low-cost PVC/SBR blend. The characterization of these blends by DSC, SEM, and Rheometrics mechanical analyzer will be presented in a subsequent articles.²⁴

EXPERIMENT

A summary of the materials used in this work is given in Table I. The basic formulation contains 50 parts PVC and 50 parts rubber (SBR + compatibilizer) by weight. The total resin content is 100 parts. In addition to the polymers, 3.0 parts of stabilizer and 50 parts of DOP were added per 50 parts of PVC, and 1.5 parts of curing agent (sulfur or DCP) was added per 50 parts of rubber. When sulfur

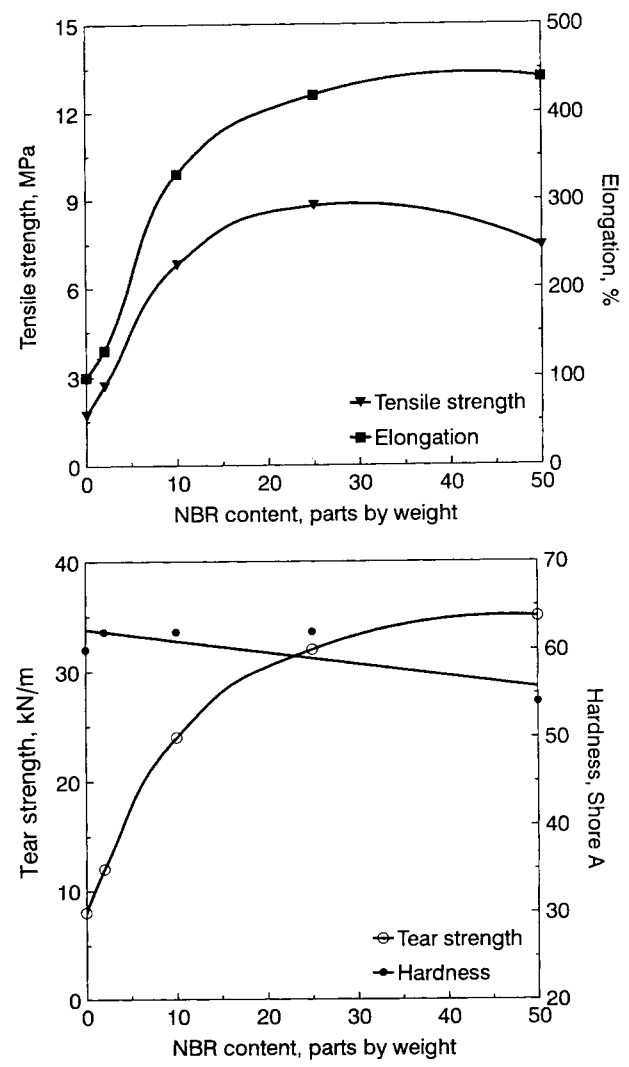


Figure 1 Mechanical properties as a function of NBR content.

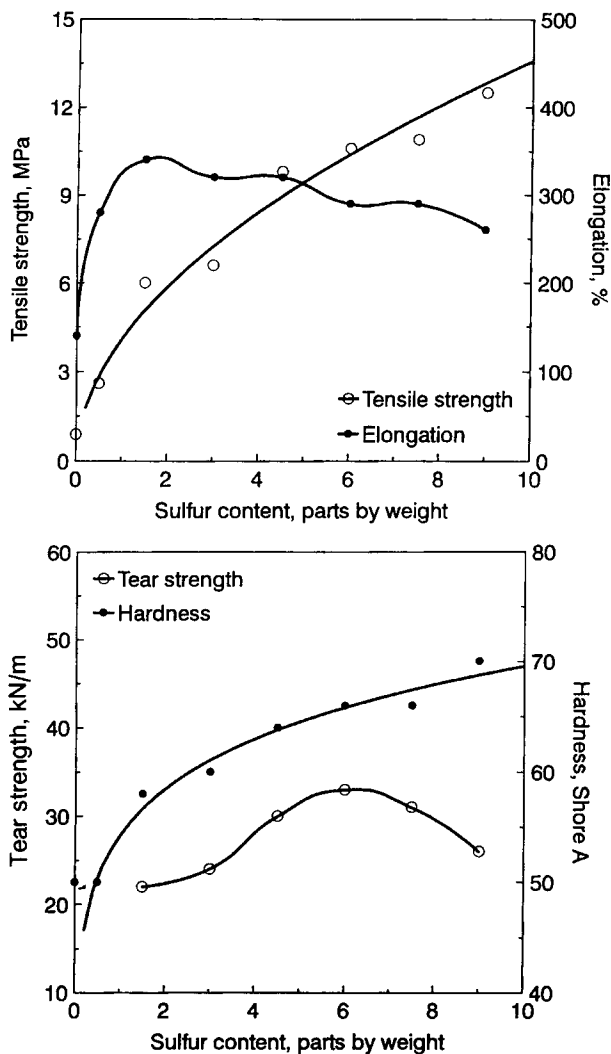


Figure 2 Mechanical properties as a function of sulfur content.

was used as the curing agent, 1.5 parts of MBT was added to the formulation. When the DCP system was used, 1.5 parts of TAIC and 3.0 parts of ZnO per 50 parts of rubber were also added to the formulation. Our objective in choosing sulfur, DCP, and their combination, as shown in Table II, is to compare the efficiency of the two crosslinking agents—sulfur and DCP. In addition, vulcanizates prepared by different curing systems have different crosslink densities that affect the mechanical properties of the blends.

The PVC with a stabilizer and the DOP were first melted on a two-roll mill at 160°C, then the SBR and a compatibilizer were added and blended for about 5 min. Blending times were measured after a curing agent had been added. Then, the vulcanizate was milled into a sheet for molding.

The milled sheet was press molded in a 10 × 10 × 0.2 cm mold at 160°C for 10 min in a 45-ton press, then was removed to a cold press. After cooling down for 5 min, the sample was taken out for dicing.

Tensile properties were measured according to the ASTM method D638-90, and elastic recovery of the blends was determined by measuring the tensile set of the samples according to ASTM D412-87. The tensile set values were calculated according to the following equation:

$$\text{tensile set} = \frac{L_2 - L_0}{L_1 - L_0} \times 100\% \quad (1)$$

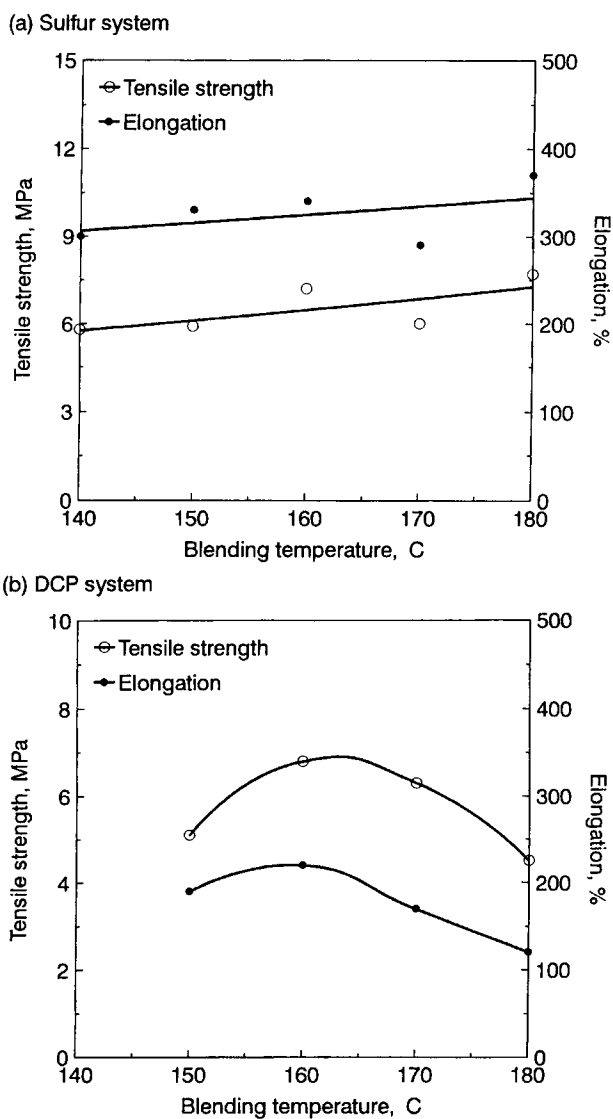


Figure 3 Mechanical properties as a function of blending temperature.

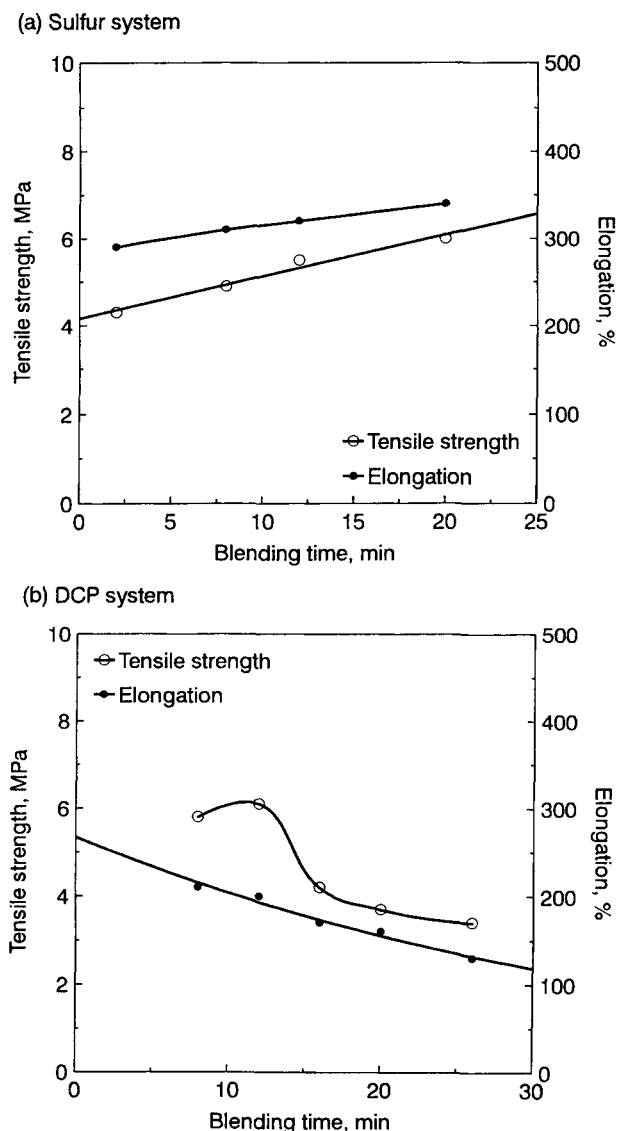


Figure 4 Mechanical properties as a function of blending time.

where L_0 is the length of the gauge marks, L_1 is the distance between the gauge marks at full extension, and L_2 is the final distance between gauge marks after 3 min of recovery. Tear resistance of the blends was measured according ASTM D624-86. The hardness of the samples was measured and expressed in Shore A units.

RESULTS AND DISCUSSION

Effects of Compatibilizer and Curing System

Table III summarizes the mechanical properties of the blends with different compatibilizers and differ-

ent curing agents. Clearly, the blends with compatibilizer are better than those without. These results confirm that a compatibilizer is, indeed, necessary to enhance the adhesion between the SBR and PVC phases. The results shown in Table III reveal that NBR is the best compatibilizer among the candidates tested. Although the compatibility of NBR with PVC increases with an increase in the AN content as indicated by an inverse gas chromatography study,²⁵ the mechanical property data shows that the blend with NBR of AN content of 18% has the best performance among the blends prepared, with NBRs having an AN content up to 40%. This is probably due to the fact that an increase in AN content will reduce the compatibility of NBR with SRB.

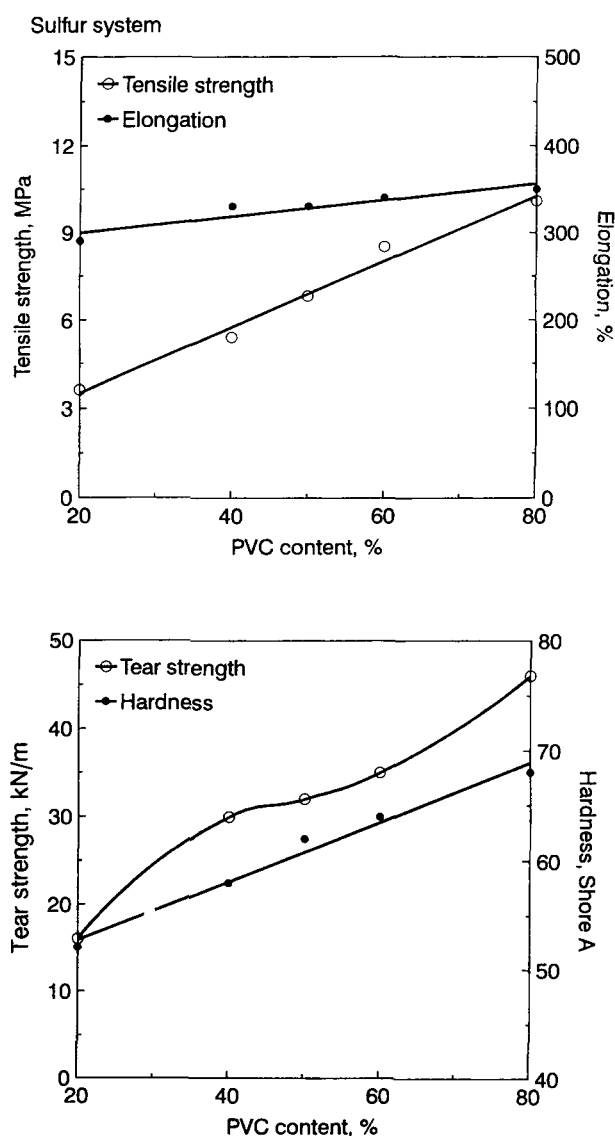


Figure 5 Mechanical properties as a function of PVC : rubber ratio for the sulfur system.

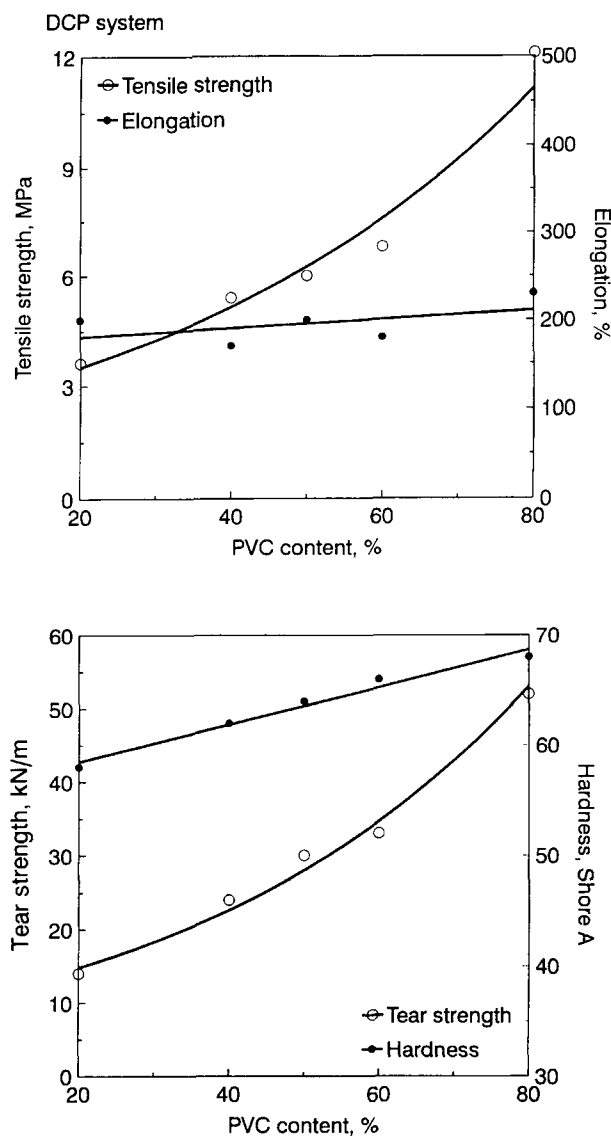


Figure 6 Mechanical properties as a function of PVC : rubber ratio for the DCP system.

We notice that NBR increases the tensile strength, elongation, and tear strength by 3 ~ 5, 2 ~ 3, and 1.5 ~ 3 times, respectively, and the improvements from the other two compatibilizers are not as good. Hence, we chose NBR-18 as the compatibilizer for the latter experiments.

Besides the chemical nature of the compatibilizer, its concentration also plays an important role in determining the physical properties of the blends. In each blend, the optimal concentration has to be determined experimentally. Figure 1 shows the effects of the concentration of NBR on the mechanical properties of the blends. The improvement in tensile strength, elongation, and tear strength tends to level off at about 10 to 20 parts by weight. The hardness

does not change significantly with the concentration of the NBR as expected because the total amount of rubber is kept constant. Considering the balance between the cost of the materials and improvement in the mechanical properties, a concentration of 10 parts of NBR (40 parts of SBR) has the most commercial potential.

Curing systems C-1 and C-2 produced comparable PVC/SBR blends, whereas C-3 produced the best material. Vulcanization produces crosslinking, which hinders the rubber molecules to slip past each and, thus, minimizes permanent plastic deformation of the rubber phase. However, C-3 also produces the NBR compatibilized PVC/SBR blend with the highest tensile set.

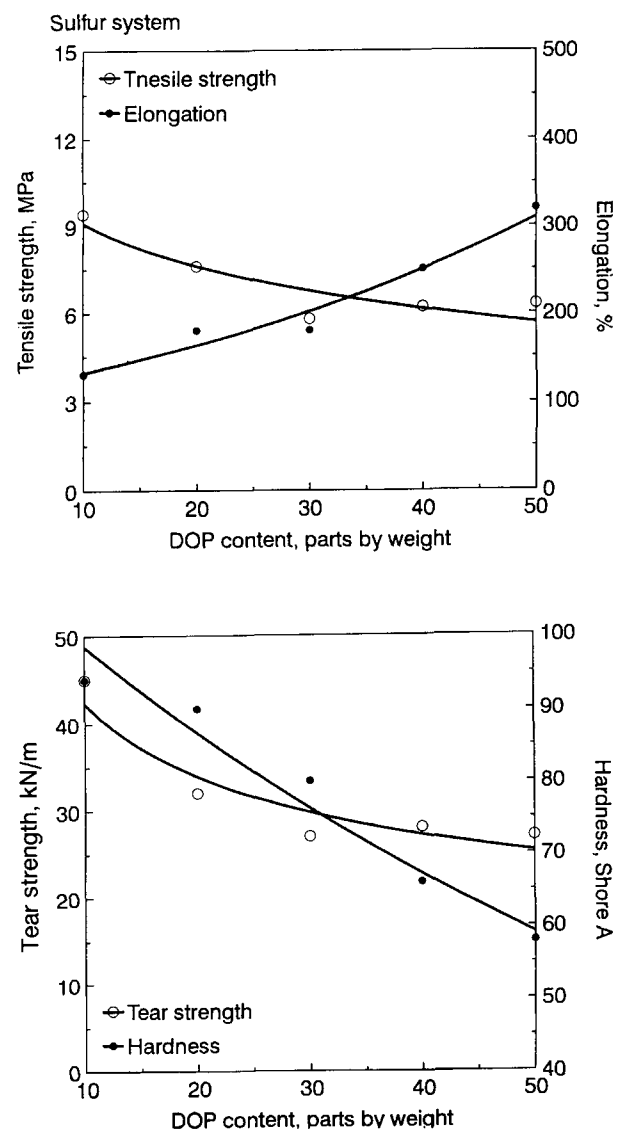


Figure 7 Mechanical properties as a function of DOP content for the sulfur system.

The concentration of the curing agent in the formulation, in general, determines the crosslinking density, which significantly affects the mechanical properties. The results shown in Figure 2 indicate that the tensile strength and hardness increase with the sulfur concentration up to a fairly unusually high amount, and the elongation decreases beyond 2 parts by weight of sulfur and tear strength has a maximum at approximately 6 parts by weight of sulfur. Different sulfur concentrations can be used to produce blends having the required mechanical properties.

Effects of Blending Time and Temperature

The optimal blending time and temperature are those that ensure the complete vulcanization of the rubber but do not decompose the PVC severely. Control experiments were performed with PVC alone and no increase in the torque was observed even after a blending time of 20 min; hence, we conclude that PVC was not crosslinked during blending within that period of time. The DCP system is more sensitive to temperature than the sulfur system and is more likely to cause excessive vulcanization or may burn the batch. The results of tensile strength and elongation tests, as shown in Figure 3, suggest that the optimal processing temperature for the DCP system is about 160°C. In contrast, the sulfur system is not very sensitive to the processing temperature.

The optimal blending time should be chosen according to the curing rate in order to ensure complete vulcanization of the blend. Figure 4 shows that, with the sulfur system, a blending time up to 20 min produces materials with higher strength and elongation. However, for the DCP system a blending time of approximately 12 min produces material with the highest tensile strength and adequate elongation (approximately 200%). The reason for this difference may lie in the fact that DCP is an initiator for the decomposition of PVC and can cause excessive vulcanization because of the higher curing rate.

From the results shown in Figures 3 and 4, it can be concluded that the optimum blending time is around 10 min for the DCP system and 15 to 20 min for the sulfur system, and a processing temperature of 160 to 170°C is acceptable for both systems. Vulcanizates prepared with DCP have high tensile strengths and lower elongations because DCP can crosslink both PVC and SBR and has a higher curing rate.

Effects of PVC : Rubber Ratio

One of the advantages of TPEs is that their chemical and mechanical properties can be tailored to a spe-

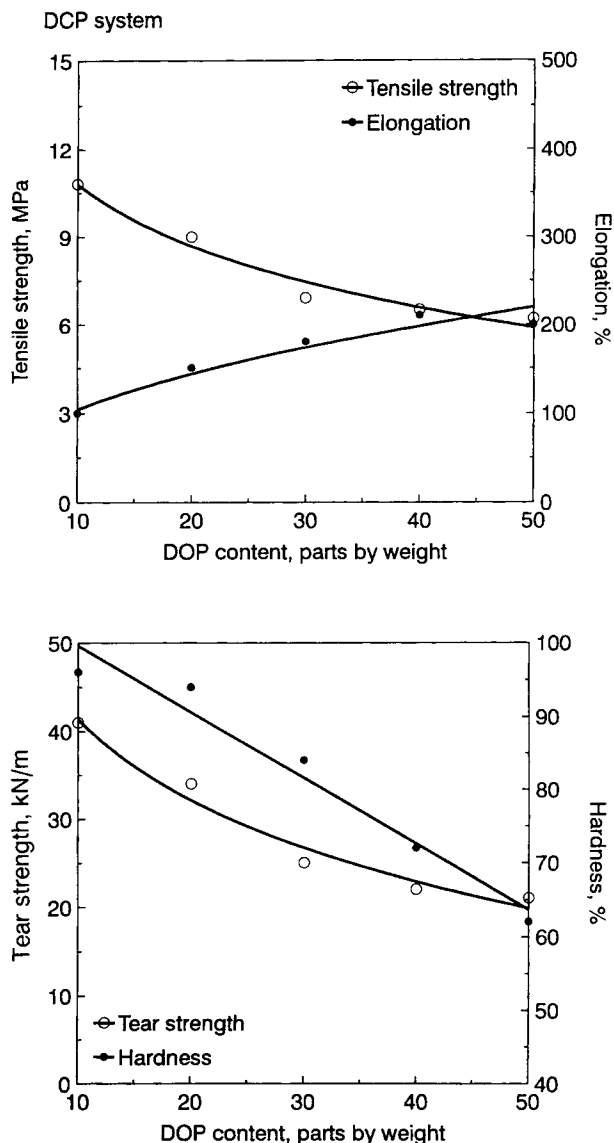


Figure 8 Mechanical properties as a function of DOP content for the DCP system.

cific application by changing the ratio of the components. The effects of the PVC : rubber ratio on mechanical properties is shown in Figures 5 and 6. An increase in the PVC concentration increases the tensile strength, tear strength, and hardness but does not cause any significant changes in the elongation.

Effects of the Plasticizer

The concentration of DOP in the TPEs has strong effects on the properties, as shown in Figures 7 and 8. Changing the concentration of DOP from 10 to 50 parts can bring about a change of tensile strength from 9.4 to 6.3 MPa, elongation from 130 to 320%,

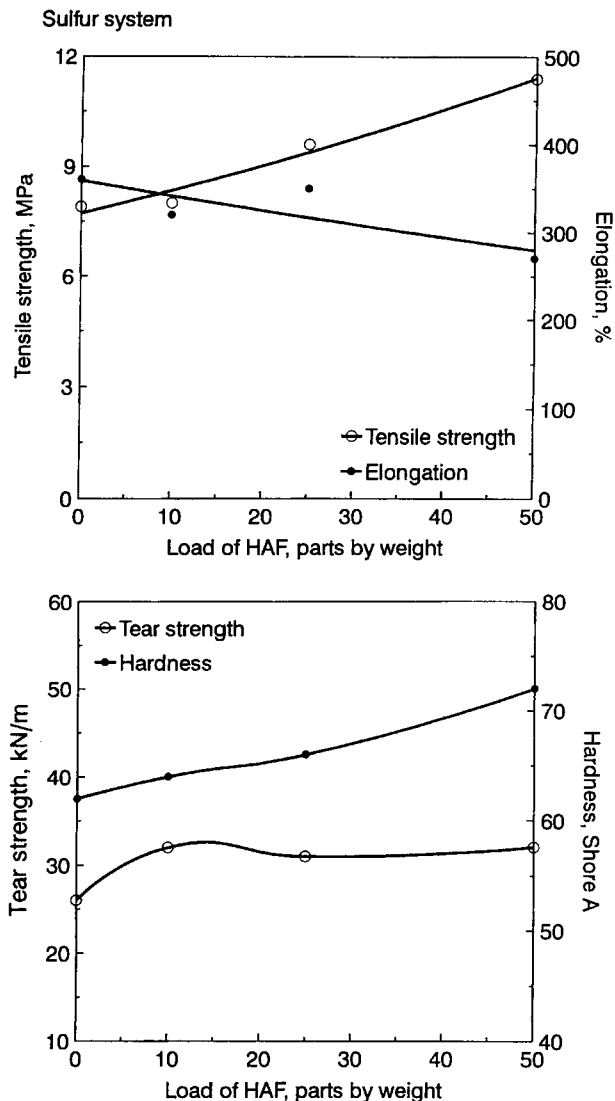


Figure 9 Mechanical properties as a function of load of HAF for the sulfur system.

tear strength from 45 to 27 kN/m, and hardness from 96 to 58 Shore A for the sulfur curing system. Similar results were obtained for the DCP curing systems. Therefore, DOP could be used to tailor the properties according to the application.

The Effect of Filler

Fillers are usually used in rubbers for reinforcement and cost reduction. Reinforced elastomers generally show an increase in modulus, hardness, tensile strength, abrasion, and tear resistance as well as resistance to fatigue and cracking. In some noncompatible polymer blend systems, compatibilization can be achieved by the addition of a large amount of filler.²⁶ The most commonly used fillers in rubbers

are silica and carbon black. In this study, a fumed silica and a high abrasion furnace carbon black were selected as the fillers. The reason for this choice is that carbon black is generally known as a reinforcing filler for elastomers, whereas the adhesion between silica and SBR is minimum without the use of a coupling agent. Furthermore, the study by Voet et al. showed the importance of the curing system for the adhesion between silica and SBR.²⁶ Their results show that strong adhesion can be achieved with a radical sulfur-vulcanization system but not with an ionic sulfur-vulcanization system. The objective of these experiments is to determine the effects of filler and curing system on the mechanical properties of the blend.

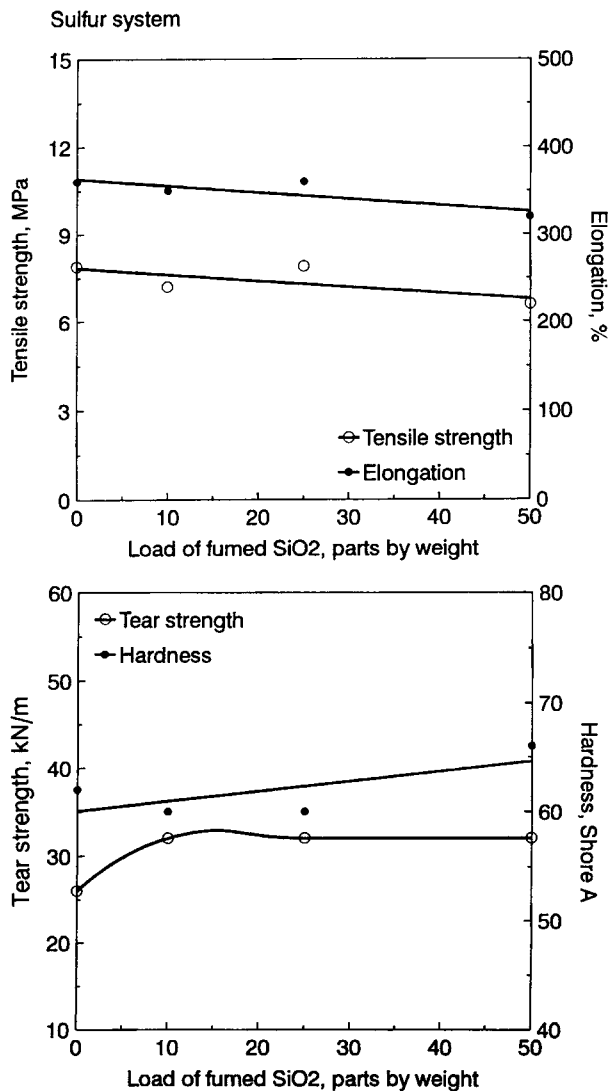


Figure 10 Mechanical properties as a function of load of fumed silica for the sulfur system.

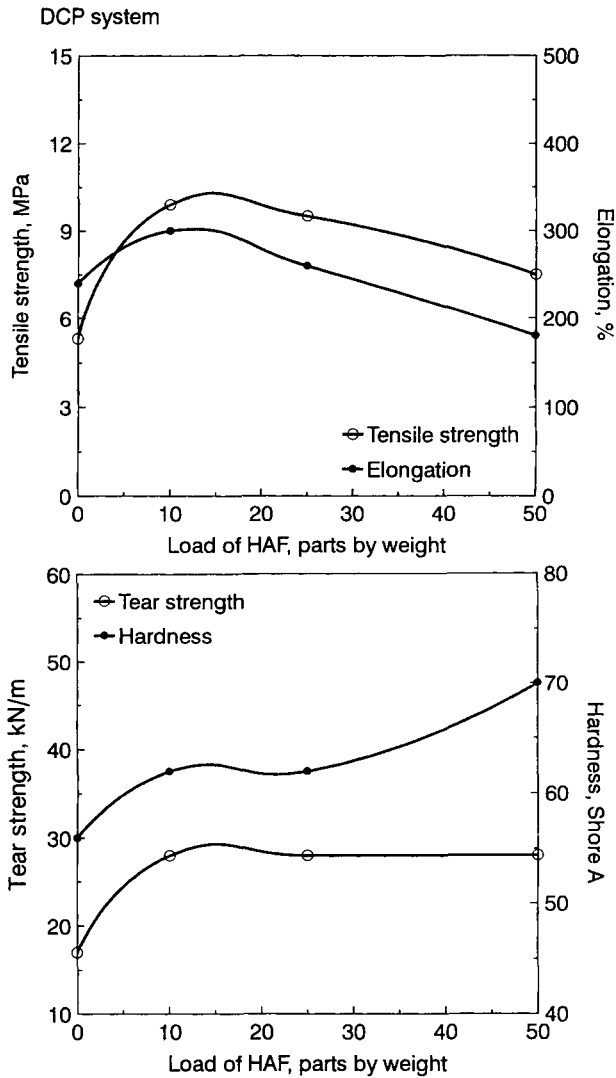


Figure 11 Mechanical properties as a function of load of HAF for the DCP system.

From the results for the sulfur system shown in Figures 9 and 10, it is apparent that the tensile strength increases significantly as the concentration of carbon black increases, whereas the addition of silica has no positive effects on the mechanical properties—both tensile and elongation decrease when the concentration of silica reaches 50 parts by weight. The effects observed with the addition of silica can be explained by the fact that silica is not a reinforcing filler and the dispersion of silica in SBR is known to be difficult.²⁷ For the DCP system, the results as shown in Figures 11 and 12 indicate that an optimal filler concentration is about 10 to 25 parts by weight of carbon black and about 10 parts by weight of silica. The difference in the performance of carbon black in the same blend reflects the importance of the curing system because the

curing rate may affect the dispersion of the filler in the thermoplastic and elastomer phases and the chemical nature of the curing system can also affect the interaction between the filler and the polymers. These effects will be investigated in a subsequent article.²⁴

Retention of Physical Properties after Repeated Processing

One of the advantages of TPEs is that they can be processed like thermoplastics—the scrapes are recyclable. The usefulness of this blend after repeated processing was determined by measuring its mechanical properties after it had been diced, press

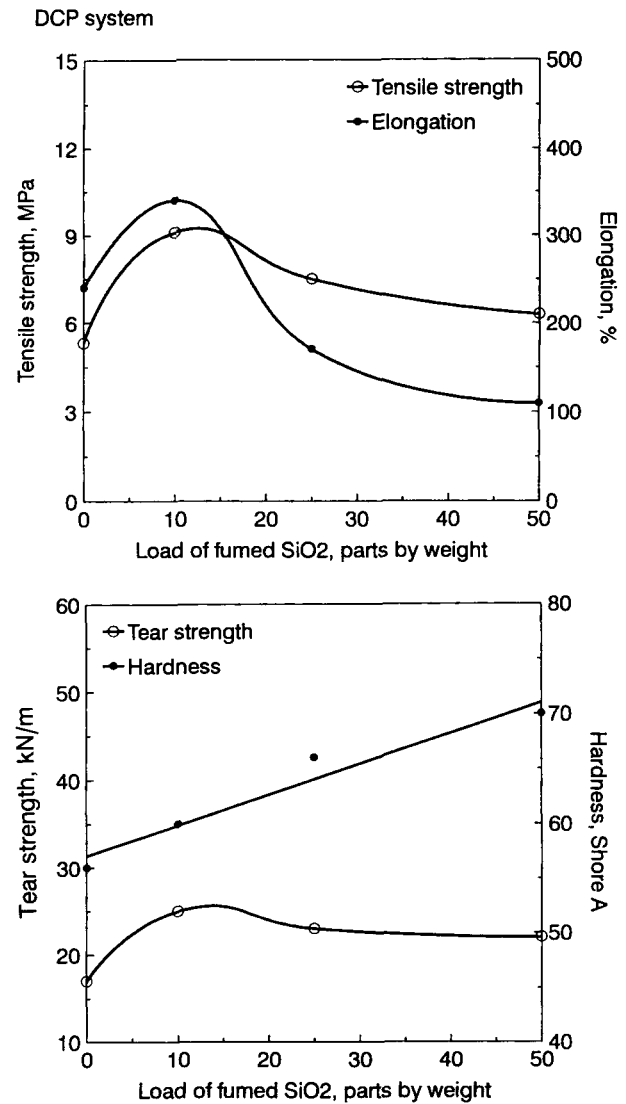


Figure 12 Mechanical properties as a function of load of fumed silica for the DCP system.

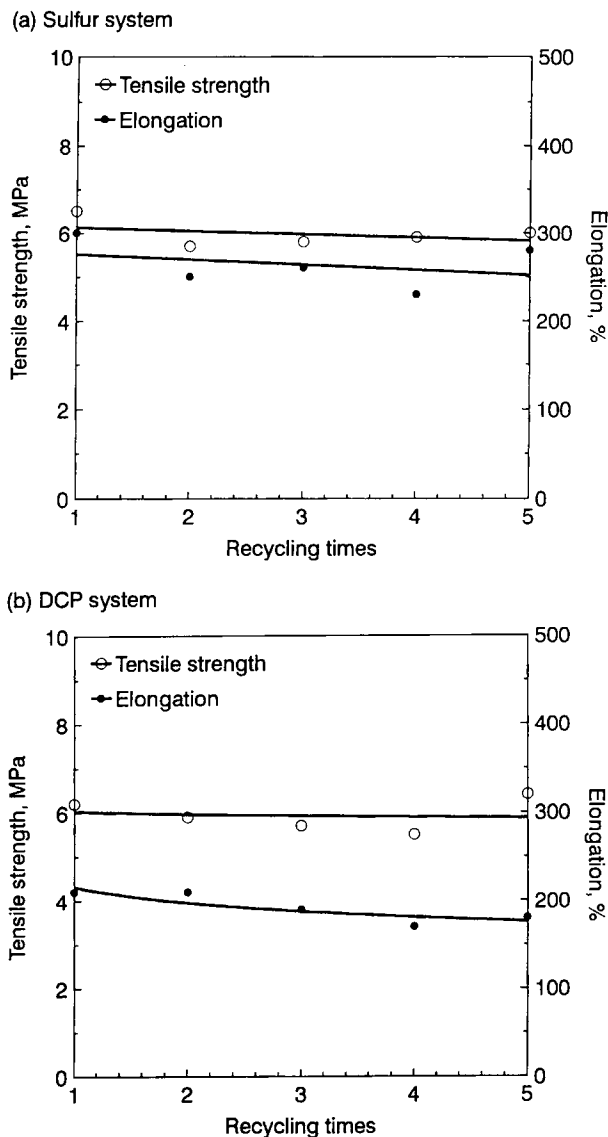


Figure 13 Mechanical properties as a function of the number of processing cycle.

molded, and processed in the two-roll mill five times. The processing temperature and blending time for each run were 160°C and 20 min, respectively. No discoloration was observed. The results shown in Figure 13 indicate that the samples retain tensile strength and elongation for both curing systems. Based on these results, we can conclude that this blend is recyclable and can be used with a high degree of regrind.

CONCLUSIONS

1. PVC/SBR is a new kind of TPE with desirable properties at an economical cost of pro-

duction. The optimum blending time is around 10 min for the DCP system and 20 min for the sulfur system; and the optimum processing temperature is approximately 160–170°C. By varying the PVC/SBR ratio and the concentration of the DOP and curing agent, we can obtain TPEs with a wide range such as hardness from 50 to 90 Shore A and tensile strength from 5.0–14 MPa. High loading of filler can be used for reinforcement as well as cost reduction for the sulfur system and for cost reduction alone for the DCP system.

2. NBR is a good compatibilizer for PVC/SBR blends. The compatibilization is achieved by the combination of the compatibility of PVC with NBR and covulcanization of the rubbers.
3. The blend is recyclable and can be used at high regrind ratios.

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