Dynamic Vulcanization of Acrylic Rubber-Blended PVC

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ABSTARCT: Poly(vinyl chloride) was blended with an acrylic rubber at a variety of blending ratio using a twin-screw extruder. The acrylic rubber was compounded with sulfur and sodium stearate in a two-roll mill prior to the blending. Dynamic vulcanization was performed in a compression mould at 170°C. Mechanical properties of the blends were determined by using a tensile testing machine. Scanning electron microscope was used to examine morphology of these blends. Degree of crosslinking of acrylic rubber in the blends was evaluated by using a differential scanning calorimeter. It was found that the normal blends are miscible regardless of the blending variables. By performing dynamic vulcanization, however, the blends became immisicible, showing a typical dispersed particle morphology, which was accompanied by a remarkable improvement of tensile properties. The screw-rotating speed was an important parameter affecting particle size and crosslink density of the rubber phase, which in turn controlled the tensile toughness of the blends. On the one hand, tensile toughness increased with the speed because of the decreasing particle size. On the other hand, the toughness decreased with the speed because of the decreasing crosslink density of the rubber. As a result, there was an optimum speed for each blend ratio, which corresponded to the maximum toughness. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2657–2663, 2003

Key words: dynamic vulcanization; polymer blend; acrylic rubber; poly(vinyl chloride)

INTRODUCTION

Dynamic vulcanization is basically a process of vulcanization of a rubber during its melt mixing with a thermoplastic, which results in polymer blends with some advantage properties. For example, dynamic vulcanized polypropylene–styrene–butadiene–styrene triblock copolymer (SBS) blends had higher impact strength, yield stress, and percentage elongation than those of the corresponding normal blends.[1] Similarly, dynamic vulcanization of polyamide–nitrile rubber (NBR) blends led to significant improvements in tensile properties, hardness, swelling in oil, and high-performance temperature of the material.[2] It was also found that the use of dicumyl peroxide as a curing agent induced a thermal degradation of polyamide, whereas the use of a phenolic curing agent resulted in better tensile properties of the blends.

In addition, it is possible to obtain a thermoplastic elastomer from the dynamic vulcanization. Mousa et al.[3] investigated the rheological behaviors of a dynamic vulcanized poly(vinyl chloride)-epoxidized natural rubber blends and found that the apparent viscosity decreased with increase in apparent shear rate following a pseudoplastic behavior. The result indicated that the dynamic vulcanized blends could be processed as thermoplastic materials. Similarly, Jain et al.[4] studied on polypropylene–ethylene–propylene–diene copolymer (EPDM) blends and found that the dynamically vulcanized blends display a highly pseudoplastic behavior, which can be processed by injection molding or extrusion. Bhowmick and Jha[5] demonstrated that the interaction between epoxy group of an acrylic rubber and amine or carboxylated groups of nylon 6 enhanced mechanical properties and performance of the resulted blends. Coran and Patel[6] also reported the properties of thermoplastic elastomers from polyamide–chlorinated polyethylene reactive blends.

This research concerns toughening of PVC by using an acrylic rubber. In our earlier study,[7] it was found that the two polymers are compatible and tended to be miscible if the blending time was sufficiently long. In this work, the dynamic vulcanization of PVC–acrylic rubber blend was carried out in a twin-screw extruder. The aim of this work is to investigate the effect of screw-rotating speed and the dynamic vulcanization on morphology and mechanical properties of the acrylic rubber-blended PVC.

EXPERIMENTAL

Materials

PVC compound (B0303 CLA) was supplied by the Thai Plastic and Chemicals Public (Thailand). Acrylic

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rubber (AR-71) was supplied by the Zeon Advanced Polymix (Thailand). The major component of the acrylic rubber is poly(ethyl acrylate), which contained a minor amount ($\sim$ 5%) of chlorine cure-site monomer. Curing agents used in this work are sulfur and sodium stearate, which were obtained from the Zeon Advanced Polymix.

Blending

Acrylic rubber was first compounded with sulfur (1 phr) and sodium stearate (10 phr) in a two-roll mill. After that, the compound was blended with PVC in a twin-screw extruder (HAAKE Polylab rheomex CTW 100P) at various ratios (80/20, 70/30, and 60/40 PVC/AR % w/w). The temperature profile along the barrel from zone 1 (near feed hopper) to zone 4 (near die) was 160, 165, 170, and 175°C, respectively. Three levels of screw-rotating speed were used: 10, 40, and 80 rpm. The extrudate was solidified by passing through a water bath before undergoing pelletization. After that, the pellet blend was passed through the extruder again to produce a more homogeneous blend.

Compression molding

The extrudate pellet was converted into a sheet sample by further mixing in a two-roll mill (Lab Tech Engineering) at 170°C for 3 min. After that, the sheet was turned into a standard tensile test piece (1 mm thick, in accordance with ASTM D638 type IV) by using a hydraulic hot press (Lab Tech Engineering) at 12 ton and 170°C. After performing the compression molding for 5 min, the sample was cool for 5 min before opening the mould. Tensile properties of the blends were determined by using a tensile testing machine (Monsanto, Tensometer 2000). The test was carried out at the cross-head speed of 100 mm min^{-1}. The initial gauge length was 25 mm and the load cell was 5,000 N. Five specimens were tested for each blend and the average value was reported. Tensile toughness of the blend was determined by integration of the area under the obtained force–displacement traces.

Scanning electron microscopy

Morphology of various blends was examined by using a JEOL (JSM 6301 F) scanning electron microscope in conjunction with a back-scattering electron detector. The tensile specimen was fractured in its glassy state using liquid nitrogen. After that, the sample was coated with carbon using a vacuum evaporator (JEOL, JEE-400). Finally, the specimen was mounted onto aluminum stub and put into the SEM specimen stage.
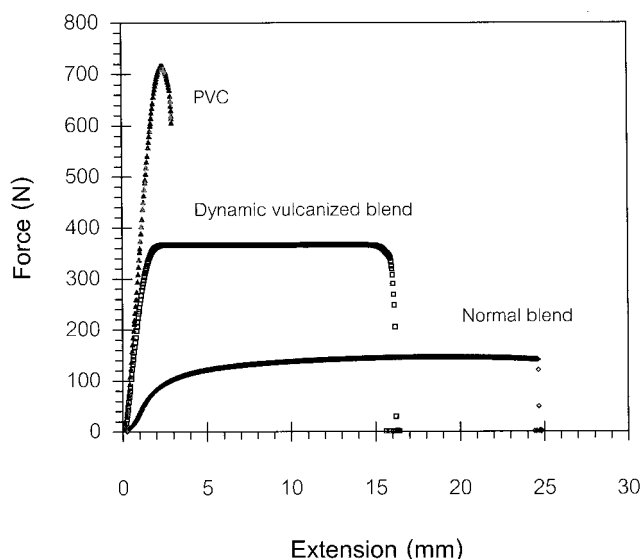

Figure 1 Force–extension traces of PVC, a normal blend, and a dynamic vulcanized blend.

Thermal analysis

To evaluate the degree of crosslinking of an acrylic rubber phase in the blends, DSC experiments were carried out by using a Perkin Elmer (series 7) machine. About 30 mg of the sample was used and the experiment was performed under nitrogen atmosphere at a scanning rate of 20°C min^{-1}. The DSC experiment for each sample was repeated by using the same sample weight to verify the calculated enthalpy of curing.

RESULTS AND DISCUSSION

First, it is worth mentioning that the dynamic vulcanization was initially carried out by adding all of the blend components (PVC, acrylic rubber, sulfur, and sodium stearate) into the twin-screw extruder. As a result, the extrudate was a characteristically brittle, porous, and yellow material, which was accompanied by a dehydrochlorination. Such effect was more pronounced if a higher rubber content was used. It was believed that PVC degraded under that blending condition. Consideration of the curing mechanism of an acrylic rubber, which contained chlorine cure sites,[8] suggested that the curing agents (sulfur and sodium stearate) may induce the dehydrochlorination of PVC. This is due to the fact that the curing agents function by reacting with alpha protons and chlorine atoms, which are also present in the PVC molecules. To avoid such effect, an acrylic rubber was compounded with the curing agents in a two-roll mill, prior to blending with PVC. Interestingly, the extrudate became smoother and stronger regardless of the blending parameters. These results suggested that mechanical properties of a dynamic vulcanized PVC–acrylic rubber blend are sensitive to the blending method and the
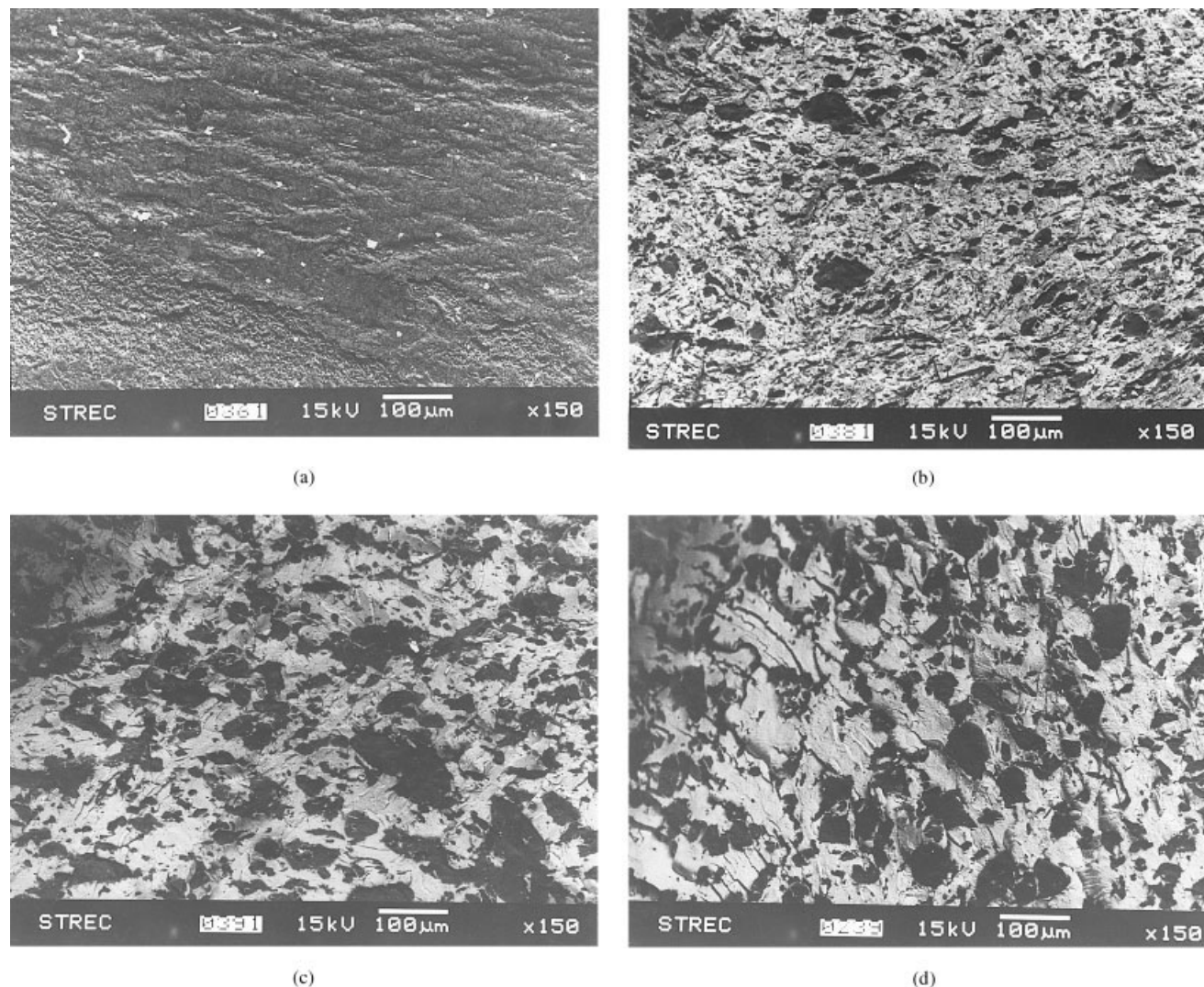
Figure 2 Scanning electron micrographs of various PVC–acrylic rubber blends (70/30% w/w; 40 rpm): (a) a normal blend without vulcanization; (b) the blend vulcanized with 0.25 phr of sulfur; (c) the blend vulcanized with 0.5 phr of sulfur; (d) the blend vulcanized with 1 phr of sulfur.

interaction between PVC and the curing agent should be controlled.

Figure 1 illustrates force–displacement behaviors of three different materials, PVC, a PVC–AR blend (70/30% w/w) without crosslinking in the rubber phase (normal blend), and a dynamic vulcanized blend (30 wt % of rubber and 1 phr of sulfur). It can be seen that, by performing the vulcanization, tensile strength, modulus, and toughness of a normal blend increased at the expense of its elongation. Similar aspects were observed for the blends with different rubber content. Scanning electron micrographs revealed that the normal blends are miscible regardless of blending ratio [Fig. 2(a)]. On the other hand, the dynamic vulcanized blends are immiscible [Fig. 2(d)], showing a phase separation. It seems that the dynamic vulcanization induced a dispersed particle morphology, which led to better tensile properties.

Changes in tensile toughness of the blends (30 wt % of acrylic rubber) as a function of sulfur content can be seen in the Table I. By decreasing the sulfur content from 1 to 0.5 phr, the toughness decreased from 5.8 to 3.4 J. Scanning electron micrographs [Fig. 2(c,d)] revealed that the particle size of the rubber did not remarkably decreased, which suggested that the lower the crosslink density, the lower the toughness. By further decreasing the sulfur content to 0.25 phr, tensile toughness decreased to 2.5 J and the particle size obviously decreased.

Table I also shows changes in tensile toughness of various blends as a function of screw-rotating speed. For the normal blends (40 wt % of acrylic rubber), it seems that the toughness rarely changed with the speed, taking into account the standard deviations, whereas toughness of the dynamic vulcanized blends (40 wt % of the rubber) initially increased with the

TABLE I
Tensile Toughness Values of Various Blends

| Rubber content (%)	Sulfur content (phr)	Speed (rpm)	Toughness (J)
40	0	10	2.03 ± 0.26
	0	40	2.06 ± 0.26
	0	80	1.92 ± 0.19
	1.0	10	2.54 ± 0.18
	1.0	40	3.69 ± 0.32
	1.0	80	2.35 ± 0.25
30	0	10	2.22 ± 0.38
	0	40	2.96 ± 0.17
	0	80	2.34 ± 0.28
	0.25	40	2.51 ± 0.30
	0.5	40	3.44 ± 0.28
	1.0	10	3.36 ± 0.29
	1.0	40	5.81 ± 0.35
	1.0	80	4.85 ± 0.37
20	0	10	1.84 ± 0.48
	0	40	2.48 ± 0.49
	0	80	2.63 ± 0.59
	1.0	10	3.07 ± 0.18
	1.0	40	3.38 ± 0.40
	1.0	80	6.61 ± 0.36

speed up to the maximum value at 40 rpm. Beyond that speed, the toughness decreased again. Figure 3 shows that particle size of the acrylic rubber phase decreased with the speed. Generally, the higher the speed, the higher the shear rate. Therefore, the decrease in particle size with the speed may be attributed to changes in shear rate and viscosity of an acrylic rubber, which was predicted by the modified Taylor's equation.[9] Furthermore, as a consequence of the particle size reduction, ligament thickness decreased with the speed. These factors contributed to a higher toughness by promoting more crazing and shear yielding in the PVC matrix.[10,11]

On the other hand, data from DSC thermograms (Fig. 4 and Table II) revealed that an exothermic enthalpy (per gram of the rubber phase) increased with the speed. The enthalpy can be related to crosslink density of the acrylic rubber, i.e., the higher the enthalpy, the lower the crosslink density. In other words, crosslink density of the acrylic rubber phase decreased with the speed, which is due to the fact that the higher the speed, the shorter the residence time in the extrusion. In regard to toughness, it should be reminded that toughness decrease with decreasing crosslink density (Table I and Fig. 2). Therefore, changes in particle size and crosslink density of the acrylic rubber with the speed contributed to the toughness in the opposite direction. Hence, the optimum speed corresponding to the maximum toughness was at 40 rpm.
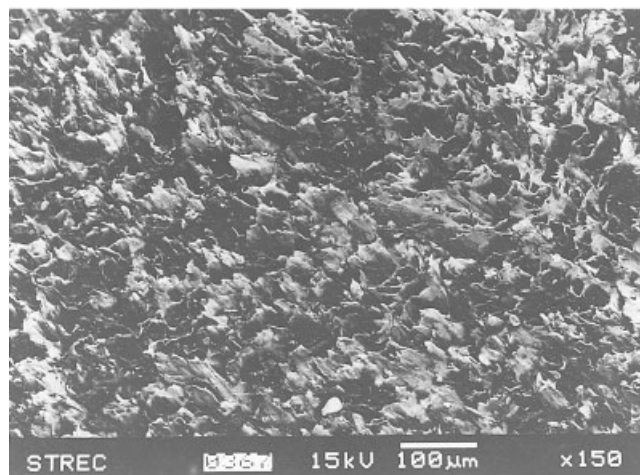
It is worth mentioning that cross-comparison of the exothermic enthalpy curing of the blends with different composition is not recommended because of two main reasons. First, for the blends with different PVC
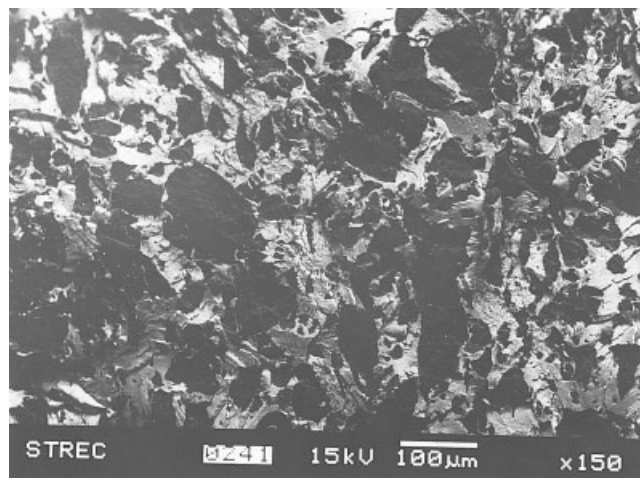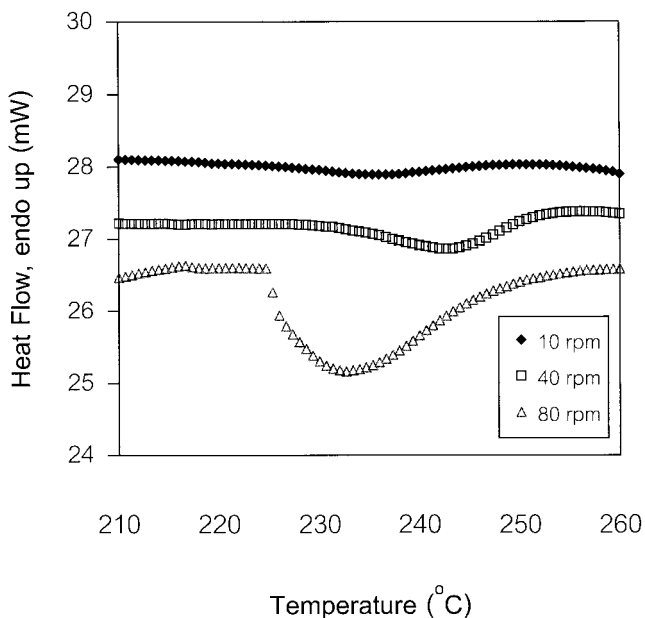
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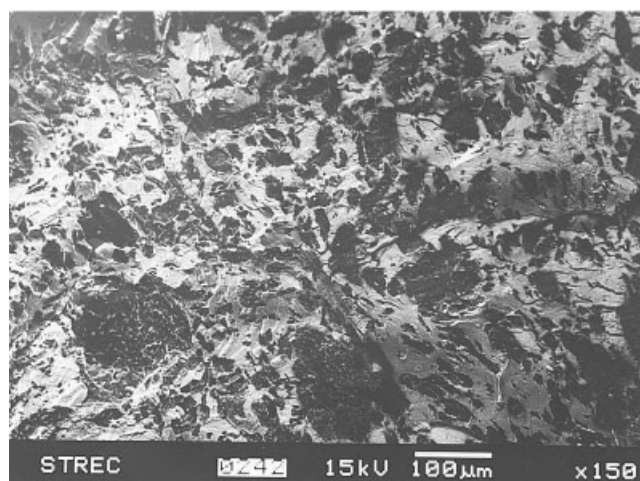
(b)

(c)

Figure 3 Scanning electron micrographs of PVC–acrylic rubber blends (60/40% w/w) at various screw rotating speeds: (a) 10 rpm; (b) 40 rpm; (c) 80 rpm.
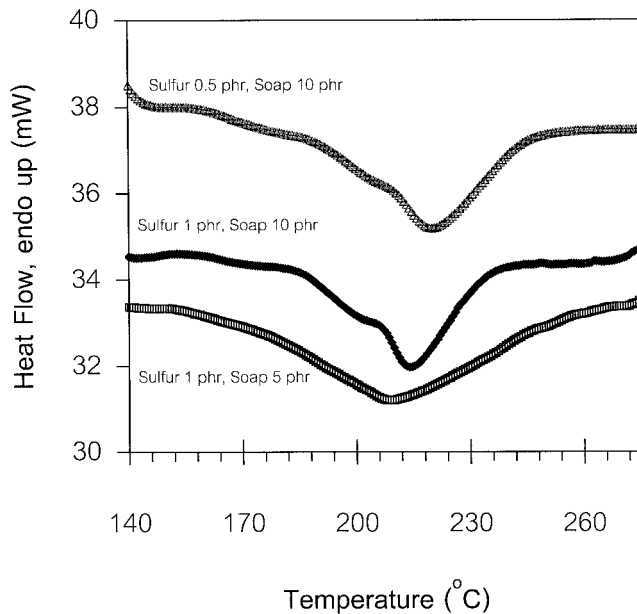
Figure 4 DSC thermograms showing curing peaks of the acrylic rubber in PVC–acrylic rubber blends (60/40% w/w) as a function of screw speed.
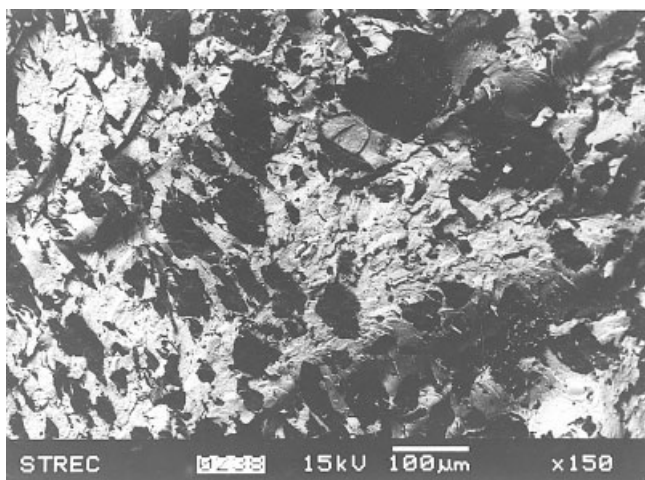

Figure 5 DSC thermograms showing the curing peaks of an acrylic rubber as a function of sulfur-to-sodium stearate ratio.

content, the actual residence time in the extruder (at a fixed screw-rotating speed) was different owing to a different melt viscosity. Therefore, these blends experienced different degree of crosslinking. Secondly, the enthalpy of acrylic rubber phase in the blends should not be directly correlated with that of a pure acrylic rubber. It may be possible that the curing agents (sulfur and sodium stearate) diffuse into the PVC phase, which is also characteristically polar molecule. As a result, the sulfur-to-sodium stearate ratio in the acrylic rubber phase changed and a profile of the curing peak in a DSC thermogram may be changed. This statement was confirmed by our control experiments, which showed that the enthalpy of curing increased with the sulfur-to-sodium stearate ratio (Fig. 5). These results implied that the vulcanization kinetic and crosslinking characteristics of an acrylic rubber are sensitive to the sulfur-to-sodium stearate ratio. Therefore, compari-
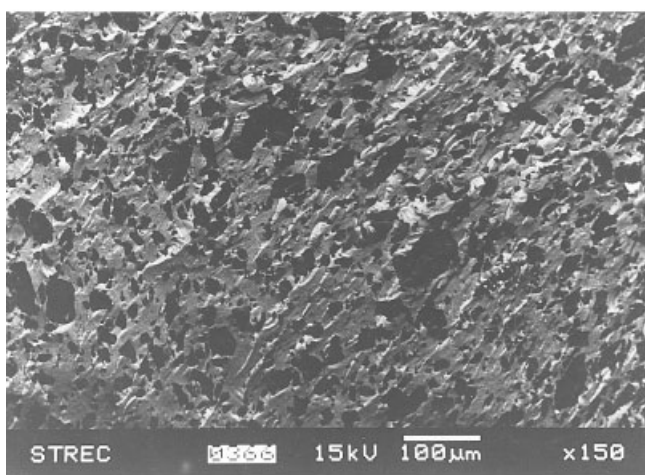
sons of curing enthalpy of the rubber phase in blends to that of the pure acrylic rubber can be misled. In other words, the enthalpy (per weight of rubber) should not be converted to percentage of crosslinking by using the enthalpy of a pure acrylic rubber. However, for PVC–acrylic rubber blends with the same composition, the enthalpy can be qualitatively compared.

Similarly, for the dynamic vulcanized blends containing 30 wt % of the rubber, toughness initially increased with the speed. By further increasing the speed from 40 to 80 rpm, toughness did not increase but tended to decrease. Again, scanning electron micrographs [Figs. 2(d) and 6] revealed that the particle size decreased with the speed, whereas data from DSC thermograms (Table II) suggested that crosslink density of the acrylic rubber decreased with the speed.

Finally, for the dynamic vulcanized blends with 20 wt % of the rubber, toughness at 10 and 40 rpm were not significantly different. However, as the speed was increased from 40 to 80 rpm, the toughness increased by 100%. This was in a good agreement with the scanning electron micrographs (Fig. 7) showing that particle size of the acrylic rubber phase rarely decreased as the speed was increased from 10 to 40 rpm. However, as the speed was further increased from 40 to 80 rpm, the particle size remarkably decreased. Table II showed that the crosslink density continuously decreased with the speed. It seems that, at a low rubber content (20 wt %), the effect of crosslink density on toughness became less important and the overall toughness was dominated by the effect of particle size.

TABLE II
Enthalpies of Curing of Acrylic Rubber Phase in Blends as a Function of Speed

| Acrylic rubber content (wt %)	Screw speed (rpm)	Enthalpy (J/g)
40	10	0.5
	40	1.4
	80	5.6
30	10	2.3
	40	3.0
	80	4.8
20	10	5.0
	40	9.9
	80	12.3

(a)

(b)

Figure 6 Scanning electron micrographs of PVC–acrylic rubber blends (70/30% w/w) at various screw rotating speeds: (a) 10 rpm; (b) 80 rpm.

CONCLUSIONS

The dynamic vulcanization of PVC–acrylic rubber blends in a twin-screw extruder was studied. According to morphological study, the vulcanization induced a phase separation of the blends, which led to higher tensile toughness. Screw-rotating speed in the extrusion process was an important parameter controlling crosslink density and particle size of the acrylic rubber. Increasing the speed decreased the particle size and the crosslink density. These factors attributed to toughness of the blends in the opposite directions. Toughness increased with decreasing particle size and with increasing crosslink density and thus there was an optimum speed corresponding to the maximum toughness of each blend ratio. For the blends that contained 30–40 wt % of the rubber, the optimum speed was 40 rpm, whereas that containing less amount of the rubber (20 wt %) was 80 rpm. In the latter case, the effect of crosslink density was
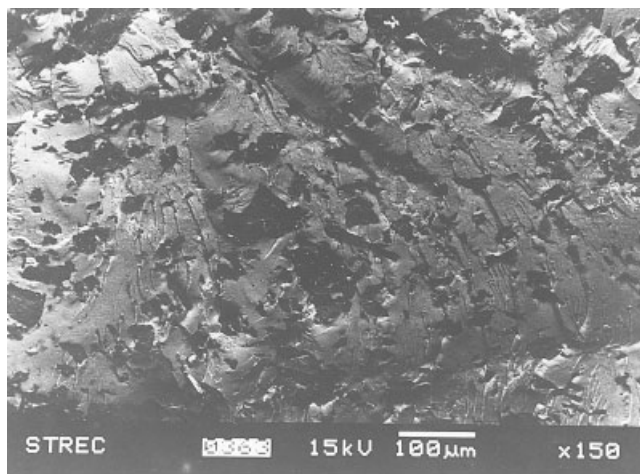
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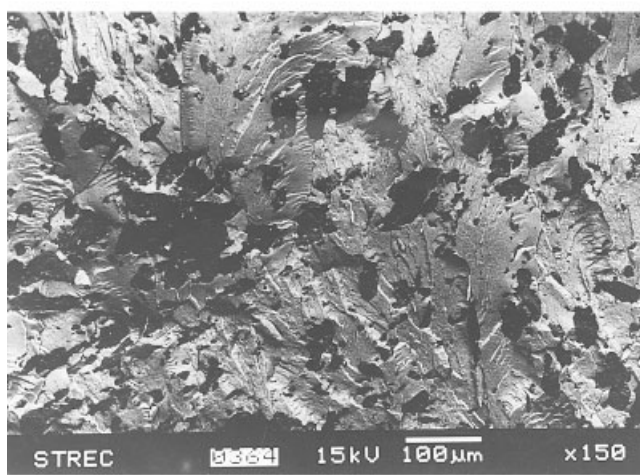
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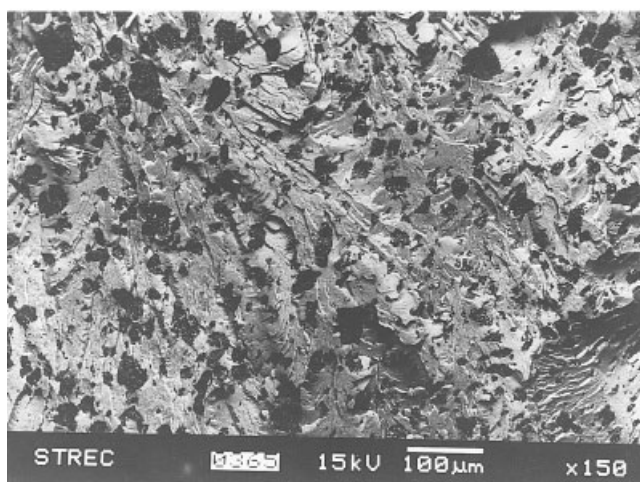
(c)

Figure 7 Scanning electron micrographs of PVC–acrylic rubber blends (80/20% w/w) at various screw rotating speeds: (a) 10 rpm; (b) 40 rpm; (c) 80 rpm.

insufficiently strong to control the toughness, which was dominated by the effect of particle size.

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