# Study of Compatibility, Morphology Structure and Mechanical Properties of CPVC/ABS Blends

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**ABSTRACT:** Compatibility, morphology structure, and mechanical properties of CPVC/ABS (Chlorinated polyvinyl chloride/acrylonitrile-butadiene-styrene) blends were studied. The core-shell ratios of ABS were set at 40/60 and 70/30. The interface interactions between ABS and CPVC were changed by modifying the acrylonitrile (AN) content of the shell. The compatibility of CPVC with the shell of ABS was studied by the blends of CPVC/SAN with different AN content in SAN. Dynamic mechanical analysis results of CPVC/SAN were in accordance with the morphological properties of CPVC/ABS. The mechanical properties of CPVC/ABS blends in which the polybutadiene content was set to 15 wt % were studied. Results showed, with the change of AN content, the impact strength followed different way for CPVC/ABS blends with different core-shell ratios of ABS because of the influence of the compatibility. When the core-shell ratio was 40/60, the CPVC/ABS blends were much ductile in more widely AN range than the blends, whereas the core-shell ratio of ABS was 70/30. The differences also showed in the SEM micrographs by the investigation of toughening mechanism. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3448–3454, 2010

**Key words:** CPVC; ABS; toughen; compatibility; morphology; core-shell polymers

## INTRODUCTION

Chlorinated polyvinyl chloride (CPVC) is known for its excellent high temperature performance, along with other desirable physical properties. Because of its high glass transition temperature, high heat deflection temperature, outstanding flame and smoke properties, and chemical inertness, CPVC has become a valuable engineer thermoplastic. However, the poor impact strength and difficulties in processing limited the use of CPVC, and mostly used in pipe.[1]

The core-shell impact modifiers such as ABS, MBS (methacrylate-butadiene-styrene) can be used to toughen glassy polymers. Compatibility and dispersion of minor phase in the matrix determine the morphology and mechanical properties.[2,3] The optimum size of dispersed rubber particle in rubber-toughened polymers depends on the chain structure of the matrix.[4] It is well known that larger rubber particles are more effective in initiating the crazing and small ones are more effective in initiating the yielding. To achieve a suitable particle size or design the mechanical properties successfully of the polymer blends, the compatibility and the morphology of the blends need to be regulated.[5,6]

CPVC modification was first announced by Dionissia et al.[7] But in recent years, there were few papers in the CPVC modification. Perhaps it was restricted by patents,[8,9] no explicit explications were given about the relationship between structure and properties in the modification of CPVC by modifiers. Miscibility of CPVC with other polymers was little reported. However, chlorinated PVC (CPVC) that contains a higher content of chlorinate and a higher α-hydrogen content than PVC, may have a wider miscibility window than PVC when blending with other polymers.[10–12] As for the blends of CPVC/SAN, Marvin[13] found that the blends exhibited preferably a single homogenous phase when the chloride content in CPVC was between 60 and 65%, and the AN content in SAN was between 15 and 25%. The study of PVC/SAN blends by Moon et al. showed that they were immiscible.[14]

In this article, ABS copolymers were synthesized to core-shell ratio of 40/60 and 70/30. The AN content in the shell were changed. The compatibility, morphology structure, mechanical properties

**TABLE I**
**Characteristics of ABS Used in CPVC/ABS Blends**

| Designation | Rubber content (wt %) | AN content in the shell (wt %) | $M_w$ of SAN grafted on the PB rubber (g/mol) | Molecular weight polydispersity of the SAN | ABS particle size (nm) | ABS grafting degree (%) |
|---|---|---|---|---|---|---|
| ABS40-5 | 40 | 5 | 70045 | 2.142 | 410.4 | 25.31 |
| ABS40-15 | 40 | 15 | – | – | 407.5 | 66.44 |
| ABS40-20 | 40 | 20 | – | – | 388.7 | 100.90 |
| ABS40-25 | 40 | 25 | 63224 | 2.248 | 415.4 | 88.82 |
| ABS40-30 | 40 | 30 | – | – | 404.5 | 80.54 |
| ABS40-35 | 40 | 35 | – | – | 410.3 | 81.40 |
| ABS40-45 | 40 | 45 | 76525 | 2.322 | 432.5 | 102.20 |
| ABS70-5 | 70 | 5 | 54367 | 1.743 | 346.6 | 21.93 |
| ABS70-15 | 70 | 15 | – | – | 371.6 | 34.17 |
| ABS70-20 | 70 | 20 | – | – | 357.7 | 34.52 |
| ABS70-25 | 70 | 25 | 68391 | 1.913 | 349.6 | 34.34 |
| ABS70-30 | 70 | 30 | – | – | 359.8 | 34.85 |
| ABS70-35 | 70 | 35 | – | – | 365.2 | 35.36 |
| ABS70-45 | 70 | 45 | 44944 | 1.966 | 358.6 | 37.62 |

together with toughening mechanism of CPVC/ABS blends were studied in detail.

## EXPERIMENTAL

### Materials

The CPVC with procession aids used in this work was a commercial product (TempRite 88,628) of Lubrizol Corporation. The Cl content of CPVC was 65% (provided by the Lubrizol Corporation). The weight-average molecular weight (Mw) of CPVC was 237,663 and the polydispersity was 2.892 (GPC, Water-410). The Izod impact strength was 130.2 J/m (ASTM D256), and $T_g$ was 136.9 (DMA).

### Preparation of ABS and SAN copolymers

Polybutadiene (PB) latex with 300 nm of the average latex particle size and gel content of 70% was supplied by Jilin Chemical Company, China. PB-g-SAN impact modifiers were synthesized by grafting styrene and acrylonitrile monomers onto PB latex rubber particles. The emulsion polymerization was performed in a 2 L glass reactor under nitrogen at 60°C. The redox initiator system consisted of cumene hydroperoxide (CHP), sodium pyrophosphate (SPP), dextrose (DX), and iron (II) sulfate (FeSO4). Sodium abietate aqueous solution was used as surfactant. First, the water, PB, initiator and KOH were added to the glass reactor and stirred 5 min under nitrogen, then the mixture of styrene, acrylonitrile monomers, and chain transfer agent, TDDM, were added in a continuous feeding way to the glass reactor. The polymers were isolated from the emulsion by coagulation and dried in a vacuum oven at 60°C for 24 h before being used. ABS

with different core-shell ratios (40/60 and 70/30) and the AN content were prepared.

The SAN was synthesized in which the AN content was also changed with the same composition as the shell of ABS. They were synthesized by emulsion polymerization, and the characteristics were listed in the Tables I and II.

### Characterization of ABS modifier

The grafting degree and grafting efficiency were determined by extracting the ungrafted SAN by acetone (a solvent for SAN but not for PB). After the acetone solutions of the dried ABS impact modifiers were shaken for 8 h at room temperature, the solutions were centrifuged at 15,000 rpm in a GL-21M ultracentrifuge for 30 min. The grafting degree and the grafting efficiency were calculated from the following equation:

$$\text{Grafting degree (\%)} = 100 \times \frac{\text{gel\%} - \text{PB\%}}{\text{PB\%}}$$

where gel% is the weight fraction of the acetone insoluble part in the sample and PB% is the weight fraction of polybutadiene in the ABS sample.

Particle size of the ABS core-shell copolymer was measured by Brookhaven 90 Plus Laser Particle analyzer.

The molecular weight of pure SAN and the SAN which grafted on to the PB rubber were estimated by the gel permeation chromatography (GPC, Waters-410). The analysis was calibrated with polystyrene standards. The measurements were performed in THF at 35°C and a flowing rate of 1 mL/min.

TABLE II
Characteristics of SAN and the Glass Transition Temperature of CPVC/SAN Blends

| Designation | AN content (wt %) | $M_w$ of SAN (g/mol) | Molecular weight polydispersity of the SAN | $T_g$ (°C) | CPVC/SAN blends 1 : 1 (wt/wt) | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | $T_g1$ (san) (°C) | $T_g2$ (CPVC) (°C) | $\Delta T_g{}^a$ (°C) |
| SAN-50 | 50 | 122416 | 2.523 | 117.3 | 119.1 | – | 1.8 |
| SAN-45 | 45 | – | – | 117.7 | 119.3 | – | 1.6 |
| SAN-35 | 35 | – | – | 116.9 | 118.8 | – | 1.9 |
| SAN-30 | 30 | – | – | 114.3 | 117.8 | – | 3.5 |
| SAN-25 | 25 | 103115 | 2.329 | 108.8 | 115.4 | – | 6.6 |
| SAN-20 | 20 | – | – | 109.9 | 114.5 | – | 4.6 |
| SAN-15 | 15 | – | – | 107.2 | 112.3 | – | 5.1 |
| SAN-5 | 5 | 108789 | 2.416 | 109.3 | 109.9 | – | 0.6 |

$^a$ $\Delta T_g = T_g1_{(san)} - T_g$.

## Preparation of CPVC/ABS and CPVC/SAN blends

CPVC/ABS blends were prepared by melt-blending using a laboratory two-roll mill at 180°C for 5 min, and blends sheets were about 1.0 mm thickness. The PB content was set at 15 wt % in all the blends. Blends of CPVC/SAN were prepared using the same way. The sheets were molded at 190°C for about 5 min, and then cut to the notched Izod impact strength testing bars and DMA testing samples.

## Dynamic mechanical analyses

Compatibility of CPVC/ABS was studied by using the CPVC/SAN (1 : 1) blends, which was a simplified model for the CPVC/ABS system. DMA (Diamond-DMA) were used to test the $T_g$ of each phase. The scans were carried out in the tensile mode, at 1 Hz frequency and a heating rate of 3°C/mm in the temperature range from 50 to 160°C. All samples were sized $30 \times 10 \times 1 \text{ mm}^3$.

## Mechanical properties

Notched Izod impact tests of CPVC/ABS blends were performed under the ASTM D256 standard at 23°C on a XJU-22 apparatus. The impact strength data represented average values of at least five test specimens.

## Morphological properties

SEM (Japan JSM-5600) was used to reveal the dispersed morphology of the modifiers ABS in CPVC matrix. The samples were cut at a low temperature (−100°C) to achieve a smooth surface and etched in $H_2SO_4/CrO_3$ solution for 5 min, then sputtered with gold before observation. The stress-whitened zone of

fractured Izod impact specimens were also viewed by SEM. The specimens were prepared by splitting impact-tested samples, and the cryogenic fracture surface was perpendicular to the impact fracture and passed through the stress-whitened zone.

## RESULTS AND DISCUSSION

### Compatibility

The effect of AN content on compatibility of CPVC/SAN blends was a simplified model for the CPVC/ABS system. The AN content in the SAN were changed from 5 to 50 wt %. The ratio of CPVC and SAN were set at 1 : 1 (wt/wt). It was interesting that the result of all the DMA curves of CPVC/SAN blends showed only one glass transition temperature, which was nearer to the pure SAN glass transition temperature. The selected tested curves were showed in Figure 1. The glass transition temperatures of blends were listed in the Table II. However,
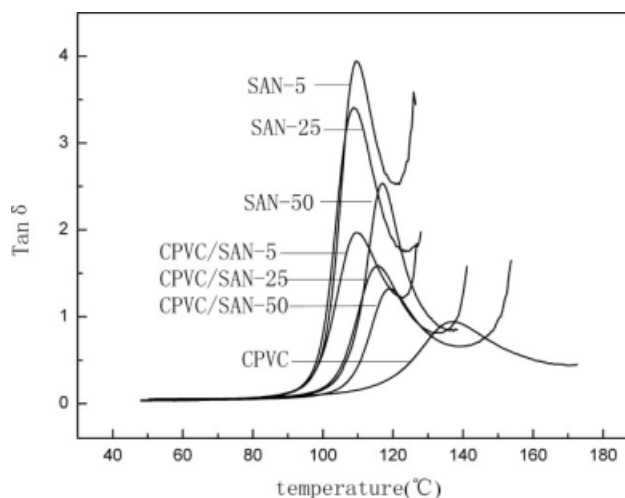


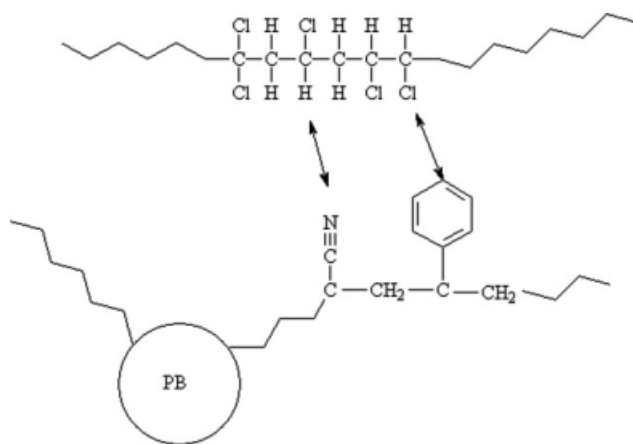**Figure 1** DMA curves of CPVC/SAN blends and SAN.

**Figure 2** Intermolecular interactions between CPVC and ABS.

the single glass transition temperature could not be a direct proof of compatibility in the polymer blends.[15]

## Characteristics of SAN and the glass transition temperature of CPVC/SAN blends

As for the CPVC/SAN blends, the one glass transition temperature might be attributed to the lower $T_g$ but a higher tanδ peak of SAN and the higher $T_g$ but a lower tanδ peak of CPVC. For this reason the magnitude of first peak of SAN in tanδ predominated and hided the second one. However, we could find in the Table II that the AN content between 15 and 30 wt % showed a higher value of $\Delta T_g$ (about 3.5–6.6°C) than the $\Delta T_g$ of other blends (about 0.6–1.9°C). As for $\Delta T_g$, which was the $T_g$ shift of pure SAN with the SAN rich phase in the CPVC/SAN blend, could be a indication of compatibility. The intermolecular interactions could be explained by the equation shown in Figure 2.

When the AN content was between 15 and 30 wt %, the higher $\Delta T_g$ values means the intermolecular interaction might be even more stronger. On the other hand, from Figure 1, we can find in the CPVC/SAN blends, the peak which is nearer to the pure SAN is lower than the peak of the pure SAN. This downward of the peak also means the intermolecular interactions between SAN and CPVC.

When temperature increased above 140°C, the blends became viscous flow. Figure 3 is the dependence of storage modulus of CPVC/ABS blends on temperature. We can find that the storage modulus of the blends all decreased to minimum when temperature increased. This effect makes the blends show only one glass transition temperature. That would be explained by the difference of the thermal resistance between CPVC and SAN.

The morphology properties of CPVC/ABS blends were in accordance with the DMA results of CPVC/SAN blends. Figure 4 showed morphology property of CPVC/ABS blends for ABS with a core-shell ratio of 40/60, and AN content of 5, 25, and 45 wt % in the shell. The holes were because of the removal of the ABS modifiers by etching. Agglomeration of core-shell modifiers took place in all blends. While the AN content was 25 wt % in the shell [Fig. 4(b)], the dispersed morphology of the modifiers improved significantly. The effect might be due to the enhanced compatibility of the blends when AN content was 25 wt %.

## Mechanical properties

In the use of core-shell particle as impact modifiers, the dispersion of the modifiers in matrices is more often encountered. ABS core-shell modifiers have been used to toughen polyvinyl chloride (PVC).[16] The results showed that the chemical composition of the shell, such as the AN content, had a very important influence on the mechanical properties of the PVC/ABS blends.

Figure 5 showed the notched Izod impact strength of CPVC/ABS blends as a function of AN content in ABS shell. The results showed that the ABS with 40/60 core-shell ratio expressed higher toughen efficiency than the ABS with 70/30 core-shell ratio in the AN content range which proved to have good compatibility between CPVC and SAN by the results of DMA. While in the incompatibility zone, which AN content were 5 wt % or 45 wt %, the values of Izod impact strength nearly the same of the two blend series, and fractured in brittle mode. The results indicated that the AN content had an important effect on the mechanical properties of these blends. Also, the mechanical properties as function
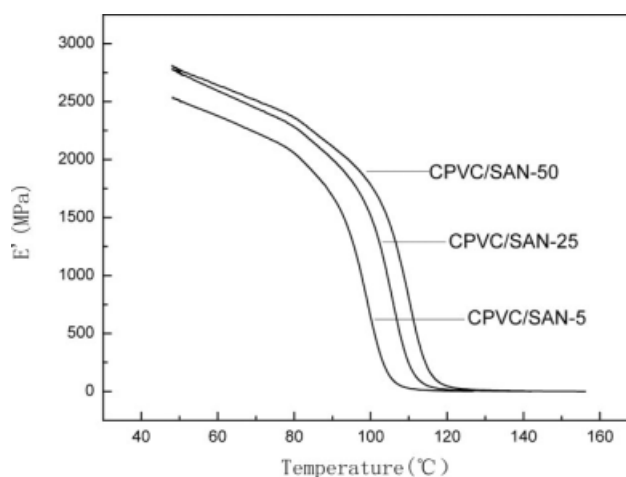


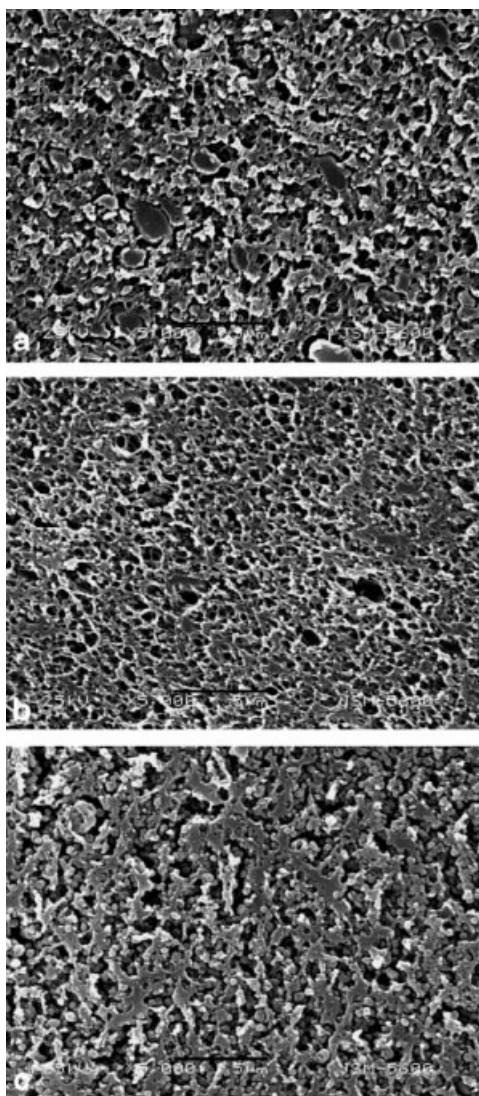**Figure 3** Dependence of storage modulus of CPVC/ABS blends on temperature.

**Figure 4** AN content on the morphology of CPVC/ABS blends. The blends for (a) CPVC/ABS40-5, (b) CPVC/ABS40-25, (c) CPVC/ABS40-45.

of AN content could be illustrated by the SEM morphology properties of CPVC/ABS blends.

The agglomeration of modifiers could induce poor impact strength of the CPVC/ABS blends, while uniform dispersion of impact modifiers in the CPVC matrix could perform great improvement of the impact strength. However, when AN content of the shell was 25 wt %, there was a downward deviation of impact strength from 20 to 30 wt % AN content. That, because the chemical composition of the shell should be chosen to impart compatibility with the matrix and which resulted in improved dispersion of the modifier in the matrix, and a suitable particle size dispersed in the matrix should be considered.

ABS with different core-shell ratio showed different toughening efficiency. The impact strength of CPVC/ABS blends with 40/60 core-shell ratio ABS as modifier showed little downward deviation com-

pared with the blends with 70/30 core-shell ratio ABS as modifier when AN content was 25% on the shell. This may be explained by the lower grafting degree of 70/30 core-shell ratio ABS compared with the 40/60 core-shell ratio ABS. The lower grafting degree resulted in the decrease of molecular weight and grafting chain length of grafted SAN chain, which also can be found in the Table I, and can induce the lower entanglement density between the shell (SAN) and CPVC. So a small change in the SAN composition of lower grafting degree could induce obvious change of intermolecular interactions, and the dispersion of the modifier. While the higher grafting degree of ABS, with a longer grafting chain length, performed a higher entanglement density between the shell (SAN) and CPVC. A small change in the SAN composition of higher grafting degree could not show obvious change of intermolecular interactions; also with a core-shell ratio of 40/60 ABS, the entropic repulsion between neighboring rubber particles becomes stronger, resulting in the uniform dispersion of rubber particles in the matrix. So the core-shell ratio of 40/60 ABS expressed a border range of AN content in the shell induced ductile fracture mode of the blends, and showed higher values of impact strength than the core-shell ratio of 70/30 ABS blends.

## Toughening mechanism analysis

In the study of the toughening mechanism of the PVC/ABS blends, Zhou et al.[17] announced that ABS acted as a stress concentrator in the PVC/ABS blends and induced a large number of crazes during the deformation process, moreover, the termination of the crazes by ABS also was found. Except for the craze mechanism, shear yielding of the matrix and
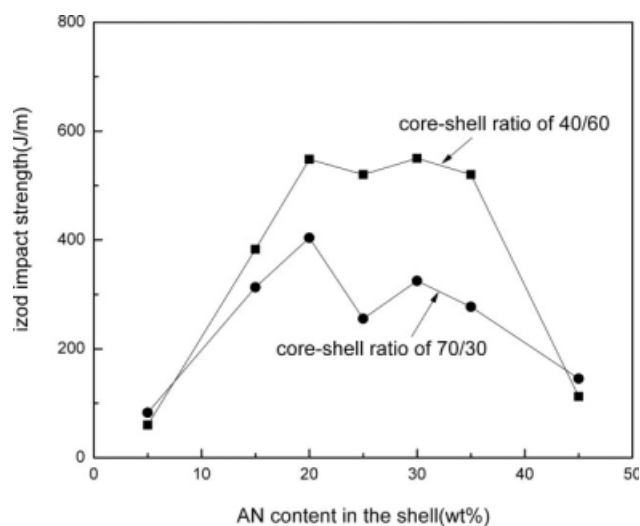


**Figure 5** Effect of AN content in the shell of ABS on impact strength of CPVC/ABS blends.

cavitation of the rubber particles were found by Zhou et al.,[18] which depended on the composition of the PVC/ABS blends.

Toughening mechanism was studied by the observation of the stress-whitened zone and outside the stress-whitened zone through SEM. Figures 6 and 7 showed the SEM photographs of CPVC/ABS40-25 blends which had the maximal Izod impact strength and the CPVC/ABS70-25 blends with a lower Izod impact strength. The AN content of the shell were chosen 25 wt % because of the good compatibility with CPVC matrix. Figures 6(a) and 7(a) were SEM photographs taken inside the stress-whitening zone. Figures 6(b) and 7(b) were taken outside the stress-whitening zone. Compared with the small holes in Figure 6(b), we could see that lots of larger holes existed because of the volume expansion of the rubber particles in Figure 6(a), which was an indication of the cavitation of the rubber. This effect was the same as the finding of Zhou et al. in the study of PVC/ABS blends.[18] On the other hand, we could find out that the extension of the rubber toward one side, which might attributed to the shear yielding or shear band formation.

It is well known that the role of the dispersed rubber modifiers is to cavitate and change the stress states of the matrix in the neighborhood of the cavitated particle,[19,20] consequently enhance the shear deformation of the matrix.[21] Important aspects that
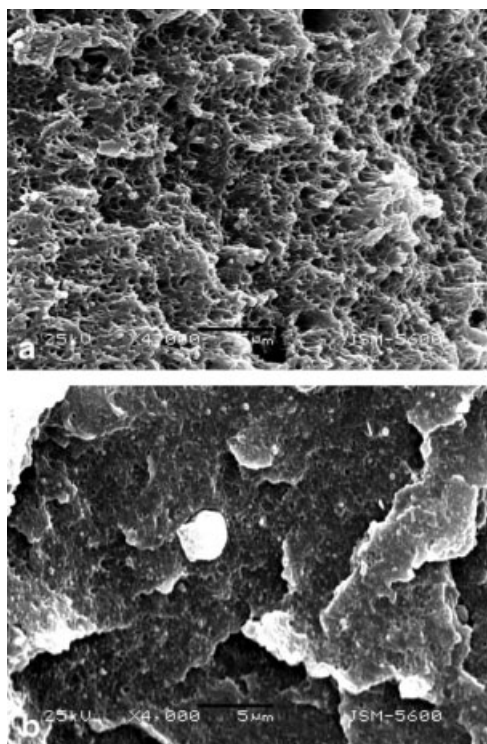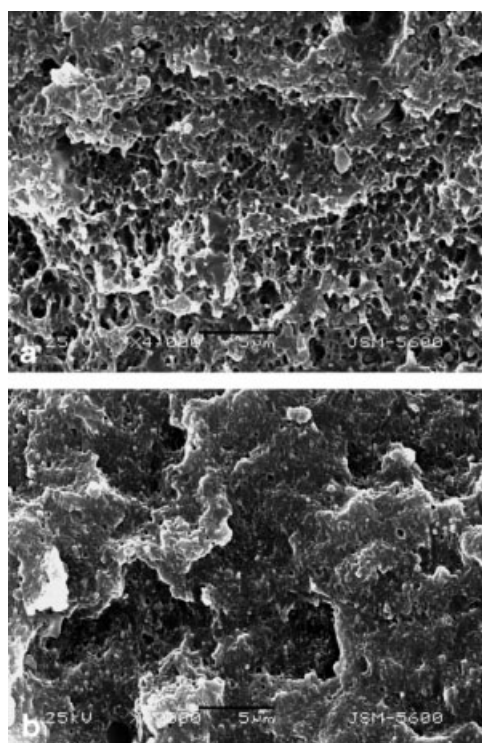


**Figure 7** Deformation in Izod impact strength tested CPVC/ABS70-25 blends. The blends for (a) stress whitening zone, (b) outside the stress whitening zone.

influence cavitation are the size of the rubber particles and the adhesion of these particles to the matrix polymer.

Cavitation of the stress-whitening zone also could be found in the CPVC/ABS70-25 blends. Compared with small holes in Figure 7(b) which were made by the splitted original rubber particles, in Figure 7(a), larger holes existed in the stress-whitening zone. However, inside the holes, round particles which were PB rubbers without volume expanding could be found. That means the holes were mainly produced by the debonding of the dispersed rubber particles with the CPVC matrix, which might be due to the lower interface interaction between the CPVC matrix and the shell. The debonding during the deformation might induce the shear yielding, which was also meaningful in the toughening mechanism.[22]

## CONCLUSIONS

In this article, a series of ABS impact modifiers with different core-shell ratios (40/60 and 70/30) and AN content were prepared by emulsion polymerization. Mechanical property and the morphology structure were studied. SEM morphology gave the proof that the uniform dispersion of modifiers could improve the mechanical property greatly. Meanwhile, compatibility studies between CPVC matrix and SAN



**Figure 6** Deformation in Izod impact strength tested CPVC/ABS40-25 blends. The blends for (a) stress whitening zone, (b) outside the stress whitening zone.

provided the facts that the AN content influenced the interface interaction greatly. The AN range between 15 and 30% of SAN might have good compatibility with CPVC matrix, however, the graphs of the DMA could not prove the compatibility between CPVC and SAN in the full range of the AN content because the blends become viscous flow on higher temperature.

The toughening mechanism results showed that, in the blends of CPVC with 40/60 core-shell ratio ABS, the rubber cavitation was the main toughening mechanism. While in the blends of CPVC with 70/30 core-shell ratio ABS, cavitation was caused by the debonding of the dispersed rubber particles.

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