Damage Zone in PVC and PVC/MBS Blends. I. The Effect of Rubber Content and Temperature

S. BENSASON, A. HILTNER, E. BAER

Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, Ohio 44106

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ABSTRACT: The damage zone development in poly(vinyl chloride) (PVC) and its transparent blends with methyl methacrylate–butadiene–styrene (MBS) core/shell rubber was studied as a function of temperature and rubber content in a triaxial stress state under slow tensile loading. Failure at the semicircular notch occurred by shear yielding followed by stress whitening. In unmodified PVC, the shear yielded plastic zone size was not affected by temperature in the range between −40 and 40°C. In the blends, the plastic zone preceding stress whitening increased in size with temperature and rubber content, shifting the stress-whitened zone further away from the notch root. Below 0°C, stress whitening initiated at the notch root and the stress-whitened zones had a crescent shape similar to those of PVC/CPE blends studied previously. In unmodified PVC, stress whitening initiated from the growth of preexisting microvoids at the tip of the shear yielded zone containing two families of curving slip lines emanating from the notch root. In contrast, stress whitening in the blends was more intense and was initiated by the cavitation of the rubber particles. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 703–713, 1997

Key words: poly(vinyl chloride); MBS; cavitation; stress whitening; failure; impact modification

INTRODUCTION

Poly(vinyl chloride) (PVC), a relatively ductile polymer, is often modified by the incorporation of a rubbery phase for improved impact toughness and reduced notch sensitivity. Methacrylate–butadiene–styrene (MBS), a core/shell rubber, is the modifier of choice in applications that require transparency. The addition of a rubbery phase into PVC is conducive to stress whitening upon deformation, a process that is attributed to cavitation in or at the interface of rubber particles.[1,2] However, even in the absence of a rubbery phase, PVC may exhibit stress whitening depending on formulation, presumably due to microvoiding at insoluble additives.[3,4]

Cavitation of rubber particles and the subsequent profuse shearing are the mechanisms that impart toughness to PVC blends, as in the case of other rubber toughened ductile polymers, such as polycarbonates.[5] Because cavitation is caused by the hydrostatic component of applied stress, the triaxial stress field at a notch is suitable to examine the localized failure processes that precede fracture. The semicircular notch geometry is particularly appropriate for the study of prefracture failure because it imposes a large enough triaxiality condition for cavitation yet a minimal tendency for crack growth. Slow tensile loading of transparent specimens allows *in situ* observation of the onset and interaction of two yielding modes, shearing and dilation, within the macroscopic damage zone that forms at the notch root.

The irreversible deformation modes in PVC and in PVC/CPE (chlorinated polyethylene)

Correspondence to: A. Hiltner.

blends in a triaxial stress state using the semicircular notch geometry were studied previously by Tse et al.[6,7] PVC first exhibited a core-yielding zone with discernible slip lines, similar to the observations with some other polymers.[8,9] A stress-whitened zone (SWZ) subsequently initiated near the tip of the slip-line zone away from the notch root. In contrast to PVC, stress-whitening in PVC/CPE blends initiated at the notch surface with no prior shearing and formed a crescent shaped damage zone at the notch root. The initiation and growth pattern of the zones in the blends were not affected by temperature in the subambient range.

The present study forms an extension to the work by Tse et al. on PVC and PVC/CPE blends. The effect of temperature and rubber content on the damage zone development in PVC blends with MBS are presented. Also included is the effect of temperature on the damage zone evolution in PVC, which was not studied previously. The mechanism of stress whitening in PVC and in the blends is examined and compared. Results of a few new experiments with PVC/CPE blends are also presented for comparison with PVC/MBS blends.

EXPERIMENTAL

Materials and Sample Preparation

PVC (Georgia Gulf 2066, $K = 55$) and its transparent blends with 5, 10, 15, and 20 phr (parts per hundred) MBS (Kanega Texas, B22), a core/shell type rubber, also containing 2.5 phr heat stabilizer (Mark 1900, Argus Chemical), 1.5 phr processing aid (Paraloid K175, Rohm and Haas), 1.5 phr internal lubricant (Loxiol HOB 7111, Henkel Corporation), and 0.3 phr ultraviolet (UV) stabilizer (Tinuvin 328, Ciba-Geigy) were supplied in the form of 1.5 mm thick roll-milled sheets by the Dow Chemical Company, Louisiana Division, Plaquemine, Louisiana. Rectangular pieces that were cut from the sheets were first preheated for 5 min at 175°C, then compressed for 5 min under 10000 lb ram force at the same temperature and cooled down to room temperature in 10 min under pressure. Rectangular tensile bars of dimensions $150 \times 20 \times 2$ mm and ASTM D638 Type I specimens were cut from the molded plaques with a router. A semicircular single edge notch of 1 mm radius was machined by an end mill midway on the tensile bars.

Methods

Tensile testing of both notched and unnotched specimens was carried out at 40, 21, 0, −20, and −40°C in an Instron 1123 testing machine equipped with an environmental chamber. The tensile yield stress was measured from the peak of the stress-strain curves obtained with ASTM D638 Type I specimens pulled at a cross head speed of 10 mm/min. Using the same specimen geometry, the tensile modulus measurements were performed at a crosshead speed of 1 mm/min at strains less than 0.4% using strain gauges on specimens that were annealed for 4 h at 80°C prior to testing.

The notched bars were pulled at a crosshead speed of 0.1 mm/min with an initial grip separation of 110 mm. At this crosshead speed, the strain rate experienced at the notch root is approximately equivalent to the strain rate during unnotched tensile testing at 10 mm/min.[10] The growth of the damage zone ahead of the notch root was monitored by a 35 mm camera equipped with a telescopic lens attachment. During room temperature experiments, a traveling optical microscope was used allowing higher magnifications. Sequential micrographs were taken with the focus at the center plane of the transparent specimens in the thickness direction where the degree of plane strain was highest.

For transmission electron microscopy (TEM), the damage zone region of specimens deformed to 75–80% of the yield stress was cut by a low speed saw and embedded in Hysol epoxy resin, exposing the midplane through the thickness. The blocks were trimmed and stained for two days in 2% OsO_4 solution. Sections of approximately 100 nm thickness were cut by an RMC (MC-6000XL) ultramicrotome using fresh glass knives and were mounted on copper grids. The sections were examined by a JEOL 100B transmission electron microscope operating at 100 kV at various magnifications.

The microtomed surfaces of blocks of unmodified PVC prepared in the same manner as for TEM were examined by a Digital Instruments Nanoscope III atomic force microscope. Prior to examination, the specimens were washed with distilled water to remove any static charge due to microtoming and dried in vacuum for 2 h at room temperature. A digital image analysis system, Olympus CUE-4, was used in the evaluation of the void size distribution from images obtained by AFM. Following a contrast enhancement routine,

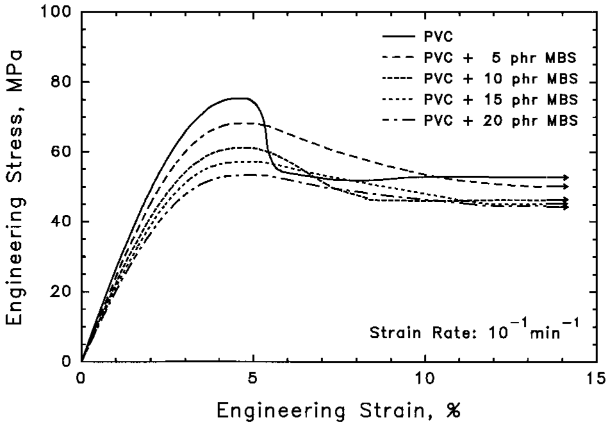

Figure 1 Engineering stress–strain curves for PVC and PVC/MBS blends at 0°C.

the contours of the voids were traced from magnified images and analyzed.

RESULTS AND DISCUSSION

Uniaxial Tensile Properties

The effect of MBS rubber content on the tensile stress-strain behavior is illustrated in Figure 1 with data obtained at 0°C, which was in the middle of the temperature range studied. Addition of MBS to PVC caused a decrease in both tensile modulus and yield stress; however, no significant change in the yield strain was observed. A sharp drop in engineering stress accompanied localized necking of PVC. The addition of 5 phr MBS resulted in pronounced broadening of the strain softening region and more diffuse necking. Increasing the rubber content caused some further broadening of the strain softening region. While necking was accompanied by stress whitening in all cases, stress whitening was much more intense in the blends than in PVC.

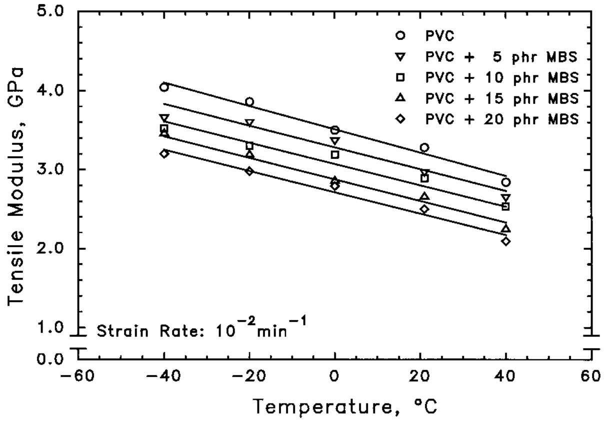

Figure 3 Temperature dependence of the tensile modulus for PVC and PVC/MBS blends.

The effect of temperature on tensile deformation behavior is illustrated in Figure 2 with data for the blend with 10 phr MBS. The elastic modulus and yield stress decreased as the temperature increased. Increasing temperature also resulted in broadening of the strain softening region. The effect of temperature on the modulus and yield stress qualitatively resembled the effect of MBS content; however, the effect on the yield strain was different. The yield strain decreased significantly as the temperature increased, while the yield strain was not significantly affected by addition of MBS.

Both the modulus and the yield stress de-

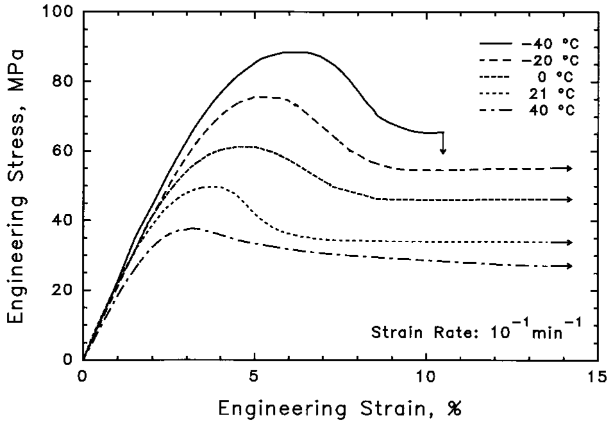

Figure 2 Engineering stress–strain curves for PVC with 10 phr MBS as a function of temperature.

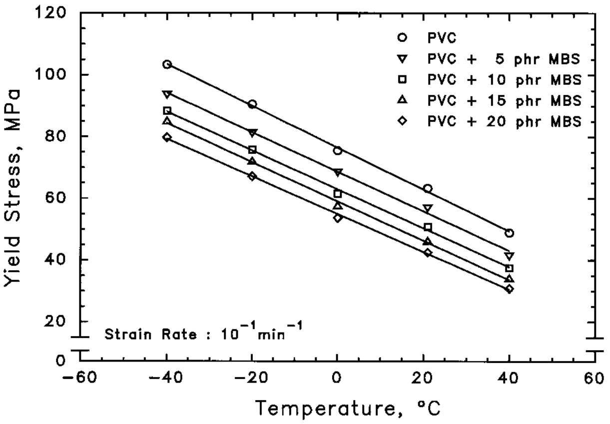

Figure 4 Temperature dependence of the yield stress for PVC and PVC/MBS blends.

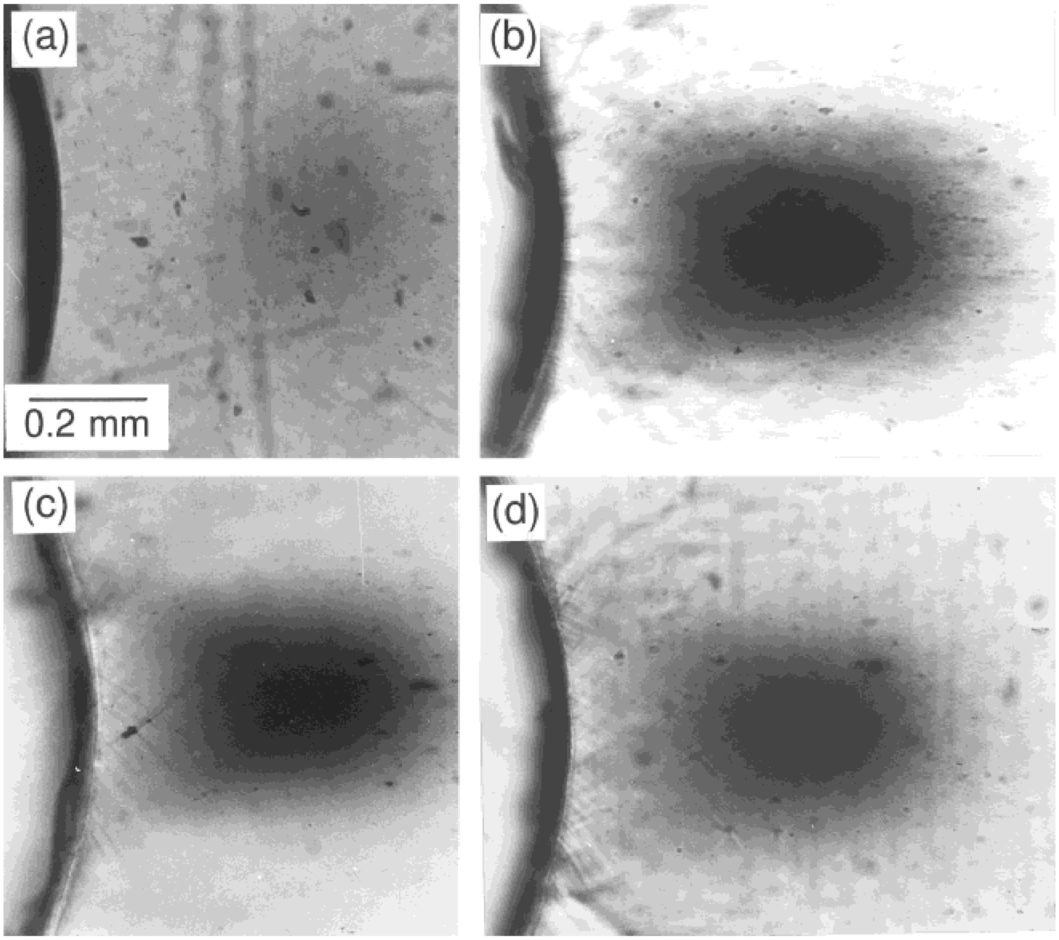

Figure 5 Optical micrographs of the damage zone in unloaded PVC specimens deformed to 80% of the yield stress: (a) 40°C, (b) 21°C, (c) 0°C, and (d) −40°C.

creased linearly with increasing temperature (Figs. 3 and 4). The scatter in the elastic modulus, obtained with strain gauges, was larger than that of the yield stress, taken as the maximum in the stress-strain curve. Although the trend was the same, the temperature dependence of the yield stress was approximately double that of the modulus.

Damage Zone in PVC at a Semicircular Notch

In PVC, the evolution of prefracture failure ahead of a semicircular notch at room temperature was previously described by Tse et al.[6] First, visible damage as PVC was loaded in tension occurred shortly past the linear limit of the stress-displacement curve. The two families of curving slip lines that emanated from the notch surface formed a core yielding zone at the root of the semicircular notch. As the load increased, a diffuse SWZ appeared some distance from the notch root at the tip of the core yielding zone. The stress whitening intensified, and the SWZ increased in size upon further loading. The increase in size was due to growth of the SWZ outward from the notch root; the SWZ did not grow toward the notch root as the load increased. Examples of well-developed damage zones in PVC are shown in Figure 5. Near the maximum in the stress-displacement curve, global yielding in the form of intersecting shear was visible as two dark bands that emanated from the notch root and extended above and below the SWZ.

Increasing or decreasing the temperature in the range −40°C to +40°C did not produce any significant changes in the evolution of the damage zone observed at room temperature. Optical micrographs of unloaded PVC specimens deformed at different temperatures to 75 to 80% of the tensile yield stress are compared in Figure 5. The slip lines of the core yielding zone were clearly

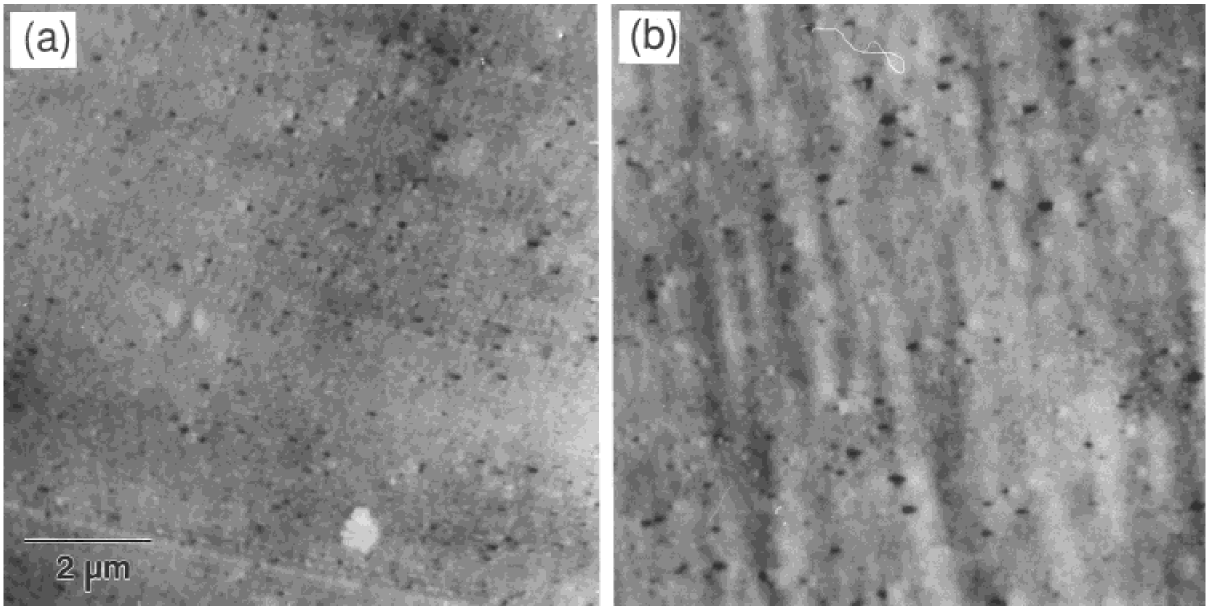

Figure 6 AFM images for (a) undeformed and (b) deformed PVC (SWZ at 80% of the yield stress) from microtomed blocks.

discernible at each temperature, with the exception of 40°C. At 40°C, the slip lines were absent, and stress whitening was diffuse. The position of the near notch boundary of the SWZ, which identified the length of the core yielding zone at the initiation of stress whitening, was not dependent on temperature. The SWZ was always observed to initiate a distance equal to approximately one fifth of the notch radius ahead of the notch root, or approximately 0.20 mm ahead of the 1 mm radius notch.

Stress Whitening of PVC in Microscale

Stress whitening in rigid PVC is generally attributed to the interfacial failure at second-phase constituents, such as stabilizers, lubricants, and other processing additives.[2] In uniaxial tension, the degree of stress whitening observed may vary greatly depending on the formulation of the resin.[1] In a triaxial stress state, the propensity for stress whitening is increased; and in thick notched specimens, internal crazing may follow stress whitening.[11]

In the microscale, Tse et al.[6] examined the stress-whitened zone forming ahead of a semicircular notch by SEM of cryogenically fractured surfaces through the damage zone. A profusely cavitated region was observed. In extension to Tse et al., two other microscopic techniques were used here as an attempt to elucidate the mechanism of dilation in unmodified PVC. The first method, TEM, was carried out in parallel with the blends. Unlike the blends, in PVC, thin sections obtained from the stress-whitened zone did not yield any information on failure in microscale. The images obtained were featureless up to magnifications of ×40,000, and there was no indication of voids or second-phase particles. Furthermore, identical regions from both deformed and undeformed specimens were indistinguishable. Vapor-phase staining of the sections did not improve the results.

The remaining microtomed surfaces of the blocks prepared for TEM were examined by atomic force microscopy (AFM), as a complementary method. AFM revealed fine topographic detail with numerous voids both in deformed and undeformed specimens. Only a limited number of micrographs were obtained by 10×10 μm and 4.3×4.3 μm scans. A comparison of deformed and undeformed specimens is shown in Figure 6 with 10×10 μm scan images. The voids in the deformed specimen clearly appear larger than those in the undeformed specimen. The undulations on the surface are due to microtoming.

Histograms of the void radii obtained by image analysis are shown in Figure 7. The largest population of voids observed in both deformed and undeformed PVC was between 10 and 100 nm in size. The surface density of voids for deformed and undeformed specimens did not show a significant difference. However, the void size distribution for

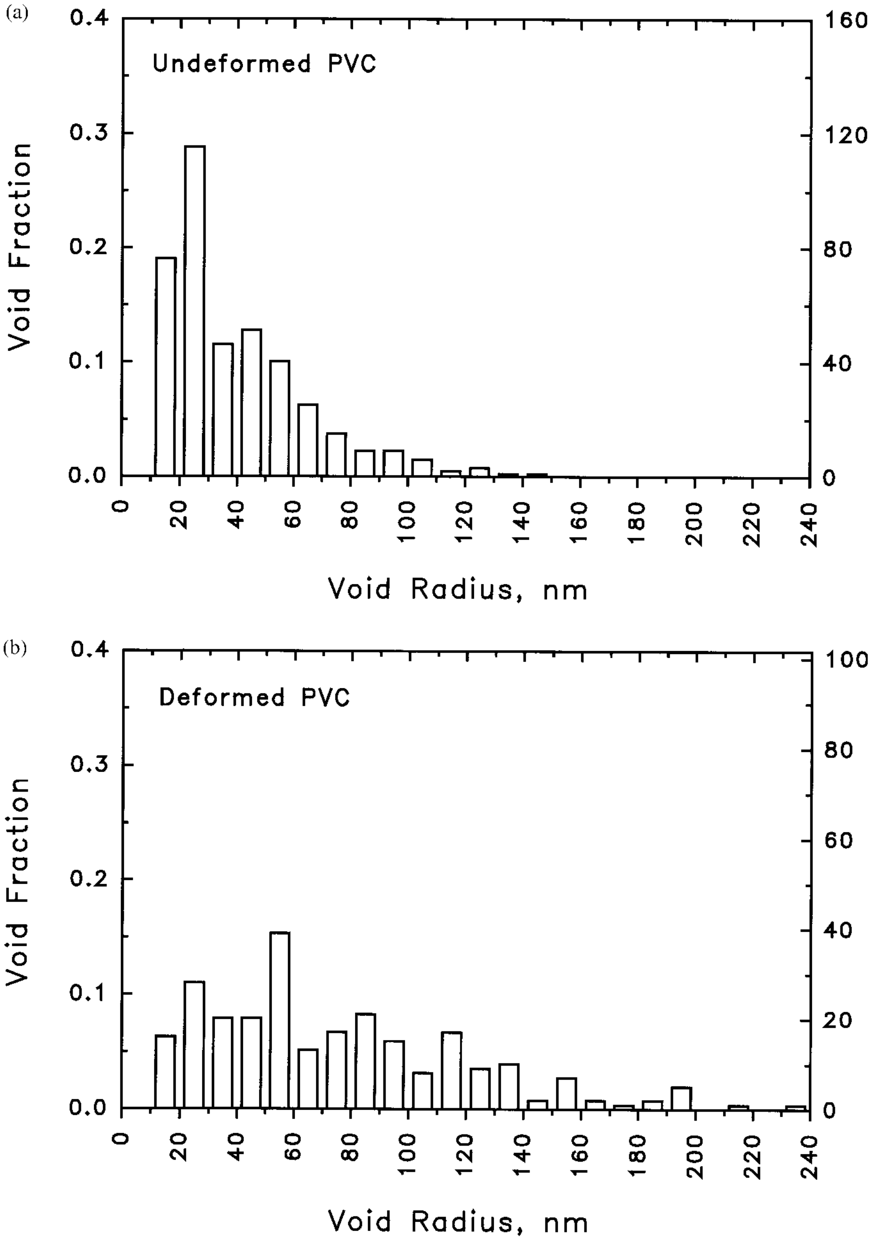

Figure 7 Histograms of void radius obtained by AFM: (a) undeformed PVC; (b) deformed PVC.

the deformed specimen was shifted towards larger values, hinting to the possibility of growth of preexisting voids upon deformation. Because PVC was transparent, the large portion of the voids observed in the undeformed state have to be small enough not to cause significant light scattering. Therefore, it was postulated that stress whitening was caused by the growth of preexisting voids at the upper end of the size distribution. AFM did not reveal any particles in the vicinity or inside the voids in control and deformed PVC. Therefore, the voids may be related to the primary particulate structure encountered in PVC.[12]

Damage Zone in PVC/MBS Blends at a Semicircular Notch

Similar to PVC, a SWZ in the blends initiated at a distance from the notch root and grew outward with increasing load, while the position of the near notch boundary remained constant. A typical stress displacement curve is shown in Figure 8

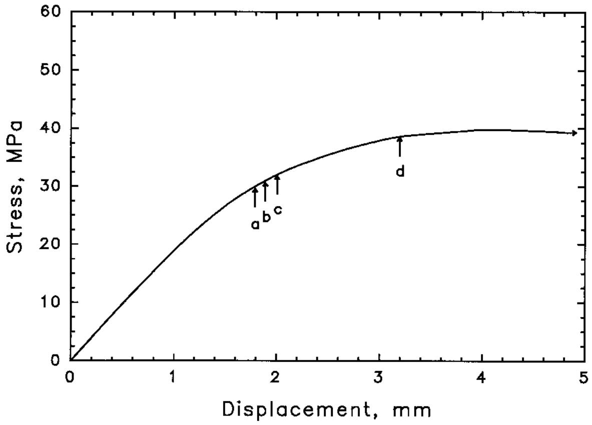

Figure 8 Stress displacement curve for PVC with 10 phr MBS at room temperature.

for PVC with 5 phr MBS deformed at room temperature, together with a corresponding sequence of micrographs illustrating the growth of the damage zone in Figure 9. Unlike PVC, no slip lines were observed in the yielded region between the notch root and the SWZ, which was attributed to delocalization of shear yielding in the blends. Furthermore, stress whitening in the blends was more intense and produced a more opaque zone. The increased intensity was due in part to numerous microshear bands that were visible in and around the SWZ of the blend. Also, the shape of the SWZ in the region furthest from the notch was more elongated, or less rounded, in the blend than in PVC. The distance from the notch root to the boundary of the SWZ at room temperature decreased from 0.20 mm in PVC to 0.09 mm in the blend with 10 phr MBS, and 0.02 mm in the blend with 5 phr MBS.

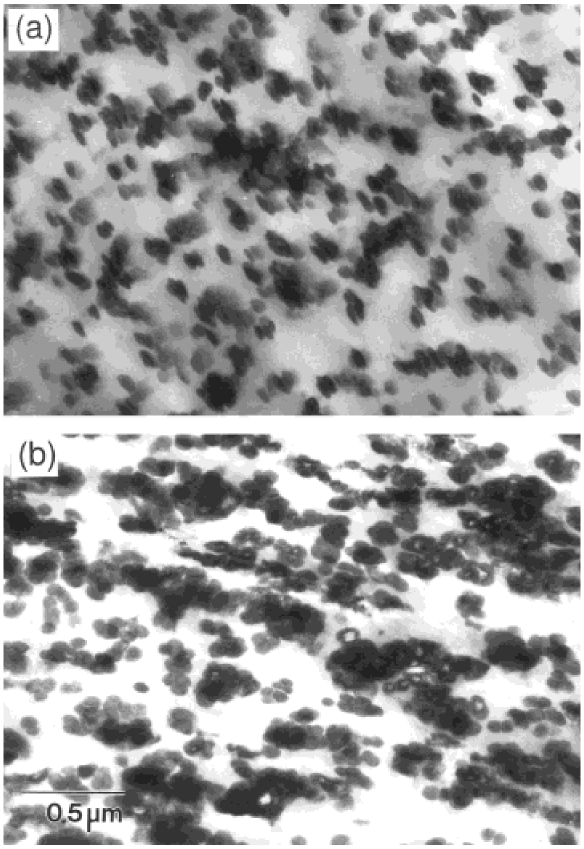

Figure 10 High-magnification TEM micrographs of PVC with 10 phr MBS: (a) undeformed; (b) deformed.

Stress Whitening in PVC/MBS Blends in Microscale

A comparison of the intensities of SWZs in PVC and the blends by optical microscopy suggests a difference in the mechanism of stress whitening in the blends. In contrast with PVC, stress whitening in the blends could be studied by TEM. The micrograph in Figure 10(a) shows a stained section of the undeformed resin with 10 phr MBS, where rubber particles 0.08 μm in size were dispersed in the PVC matrix with occasional agglomeration. For comparison, a stained section microtomed from the center of the stress-whitened zone of the same blend after

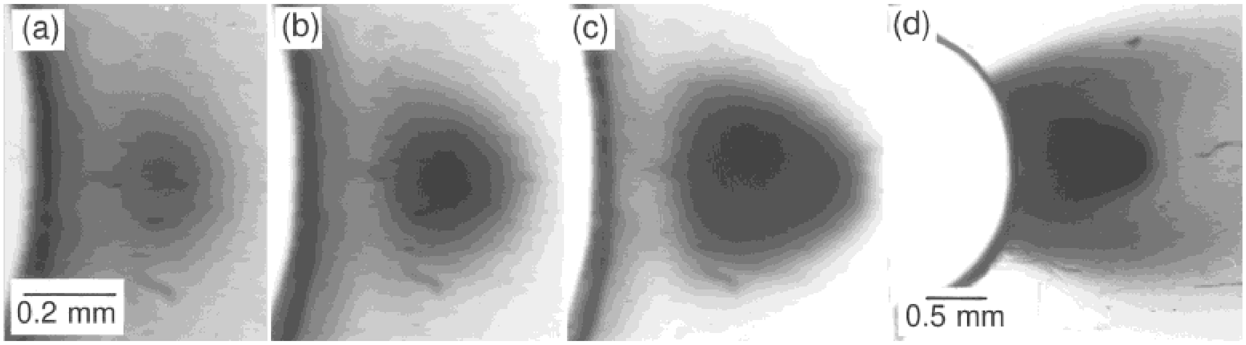

Figure 9 Optical micrographs of the damage zone taken during loading corresponding to the indicated positions in the stress displacement curve in Figure 8.

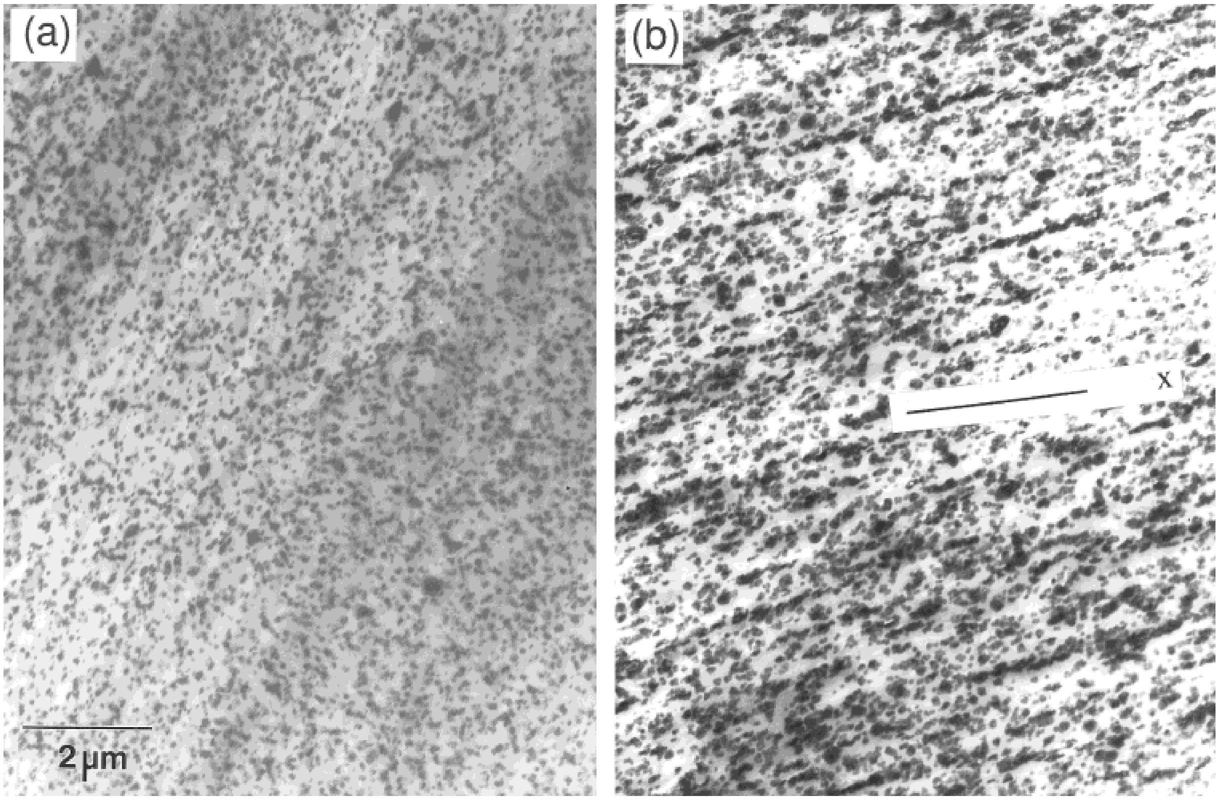

Figure 11 TEM micrographs of PVC with 10 phr MBS: (a) undeformed; (b) deformed. The arrow in (b) is perpendicular to the applied stress and indicates the direction of damage zone growth.

it was deformed to 80% of the yield stress is shown in Figure 10(b). The deformed particles retained their spherical shape but had increased in size and cavitated. Since the thickness of the sections was comparable to the diameter of the particles, cavitation appeared as bright holes surrounded by the dark, stained rubber. Cavitation was predominantly in the particles rather than at the MBS-PVC interface, which implied good interfacial adhesion. Since light scattering from the cavitated rubber particles was the cause of stress whitening, the boundary of the SWZ defined the region where the hydrostatic component of the stress intensification was high enough to cause particle cavitation.

Examination of the deformed sections at lower magnifications (Figure 11) further revealed that cavitated particles were aligned in thin bands perpendicular to the direction of the applied stress, as in the case of polycarbonate/MBS blends reported by Cheng et al.[13,14] The bandlike features are sections of disk-shaped domains of cavitated and deformed particles. They are oriented perpendicular to the applied stress direction and are formed by the cooperative cavitation of the rubber particles. A cooperative cavitation process of similar nature was also observed in other rubber-toughened polymers.[15,16]

The TEM micrographs shown in Figures 10 and 11 reveal a fundamental difference between the cavitation mechanism in the blends and in unmodified PVC. In the former case, cavitation occurred within the rubber particles, and it can be anticipated that material properties of the rubber influenced the cavitation condition. In the latter case, PVC cavitated by the growth of preexisting microvoids. Though the exact mechanism of voiding in PVC is not clear, it can be stated that cavitation in PVC was dominated by the material properties of the matrix.

Effect of Temperature and Composition on the Damage Zone in MBS Blends

The position of the SWZ relative to the notch root was found to depend on the amount of rubber in the blend. Increasing the rubber from 5 phr to 20 phr gradually shifted the near notch boundary of the SWZ outward from the notch root. Figure 12

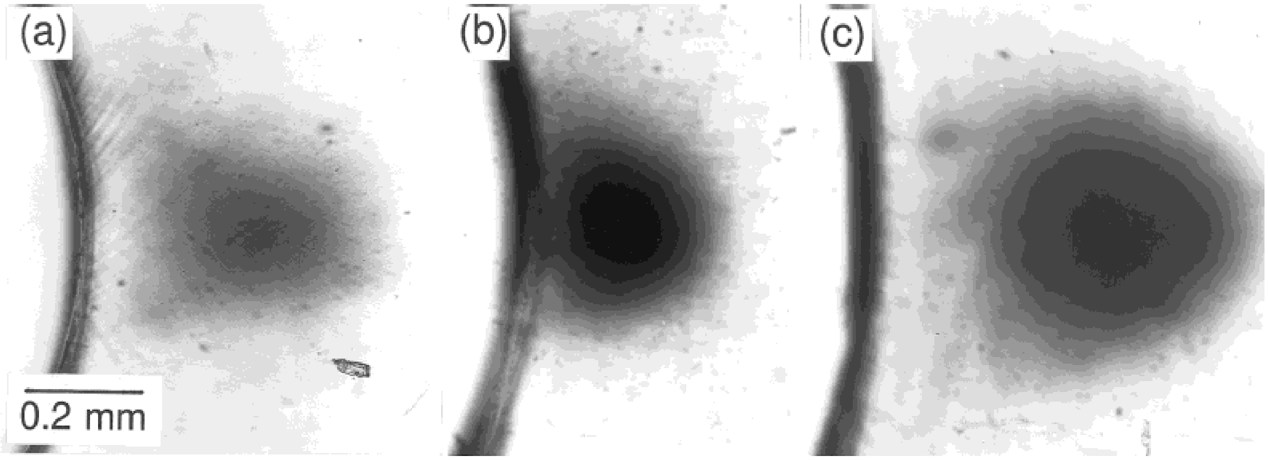

Figure 12 Optical micrographs of the damage zone taken during loading at room temperature in specimens deformed to about 80% of the yield stress: (a) PVC, (b) 5 phr MBS blend, and (c) 20 phr MBS blend.

shows micrographs of the damage zone for PVC, PVC with 5 phr, and 20 phr MBS all deformed to about 80% of the yield stress at room temperature. In the blends, the gradual movement of the near-notch boundary away from the notch root revealed an increase in the cavitation stress relative to the yield stress. Since the yield stress decreased with increasing MBS, this meant that the cavitation stress did not decrease as rapidly as the yield stress when the rubber content was increased.

Stress whitening was observed at all temperatures in the range of −40° to +40°C. The stress whitening was less intense at the highest temperature, an effect that was attributed to the absence of the fine shear bands in and around the SWZ. Temperature also had a significant effect on the position of the SWZ in the blends. Decreasing the temperature shifted the near notch boundary closer to the notch root until stress whitening started at the notch root. When this occurred, the form of the SWZ changed from circular to a crescent-shaped one. Figure 13 illustrates three optical micrographs on the effect of temperature on the SWZ of blends with 15 phr MBS all deformed to about 80% of the yield stress. The near-notch boundary of the SWZ shifted from 0.22 mm from the notch root at 40°C to 0.06 mm at 0°C. At −40°C, stress whitening initiated at the notch

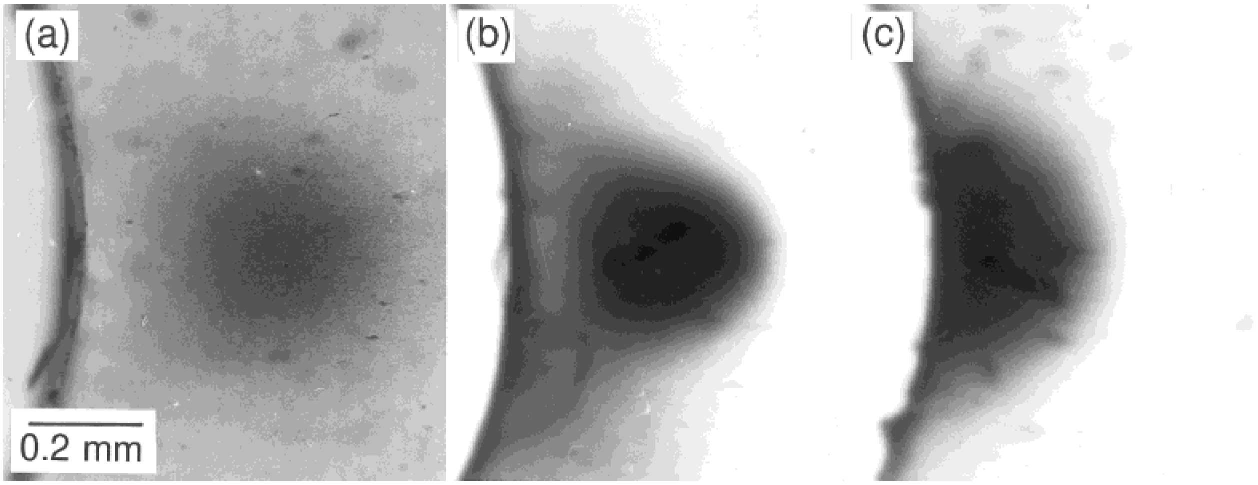

Figure 13 Optical micrographs of the damage zone taken during loading for PVC with 15 phr MBS deformed to about 80% of the yield stress at (a) 40°C, (b) 0°C, and (c) −40°C.

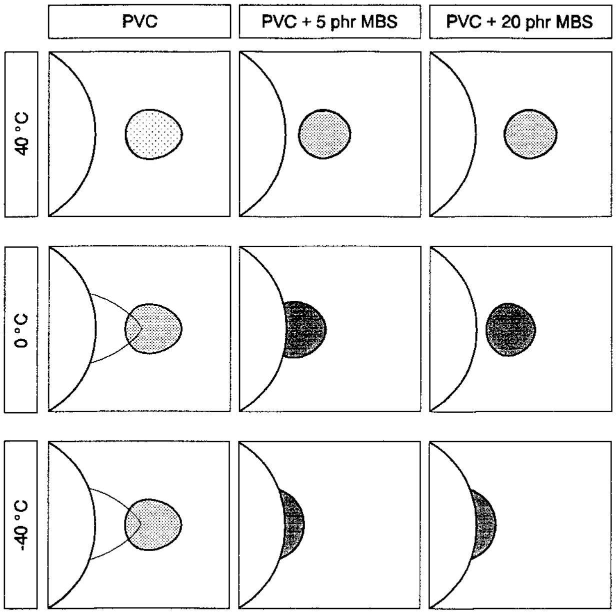

Figure 14 Schematic showing the effects of temperature and composition on the damage zone in PVC and PVC/MBS blends.

surface forming a crescent-shaped zone similar to that observed at room temperature in blends of PVC with chlorinated polyethylene (CPE).[7]

The combined effects of composition and temperature on the shape of the SWZ and its position relative to the notch root are summarized schematically in Figure 14. As the temperature decreased, the circular SWZ gradually shifted closer to the notch root until it started at the notch root without being preceded by a plastic zone. This indicated that with decreasing temperature, the cavitation condition approached the shear yielding condition until at some transition temperature cavitation occurred at the notch root before shear yielding. This transition temperature was about 0°C with 5 phr MBS. At this temperature, blends with higher rubber content still exhibited a small plastic zone since increasing the rubber content had the effect of shifting the SWZ away from the notch root. However, at −40°C, all the blends exhibited a crescent-shaped SWZ at the notch root similar to that described by Tse et al.

Damage Zone in PVC/CPE Blends Above Room Temperature

The damage zone ensuing at a semicircular notch in blends of PVC with a wide range of chlorinated polyethylenes (CPE) was studied was Tse et al.[7] At the same rubber loadings, the tensile stress-strain behavior of PVC/MBS blends was very similar to that of the PVC/CPE blends. However, failure at a semicircular notch in the PVC/CPE blends occurred by a crescent-shaped zone in the temperature range −40°C to room temperature. In contrast, a crescent-shaped zone in PVC/MBS blends was only encountered below −20°C. Thus, localized yielding was sensitive to rubber type considered. Based on the observations of a transition in the PVC/MBS blends, the range for studying the temperature dependence of the deformation mechanisms in PVC/CPE blends was extended to include the temperatures above ambient, to explore a potential change in the sequence of deformation modes.

The results obtained from the new experiments with the 10 phr CPE blends (experimental resin No. 5896[7]) are illustrated in Figure 15 with micrographs from specimens deformed to 75–80% of the yield stress. At 35°C, core yielding distinctly

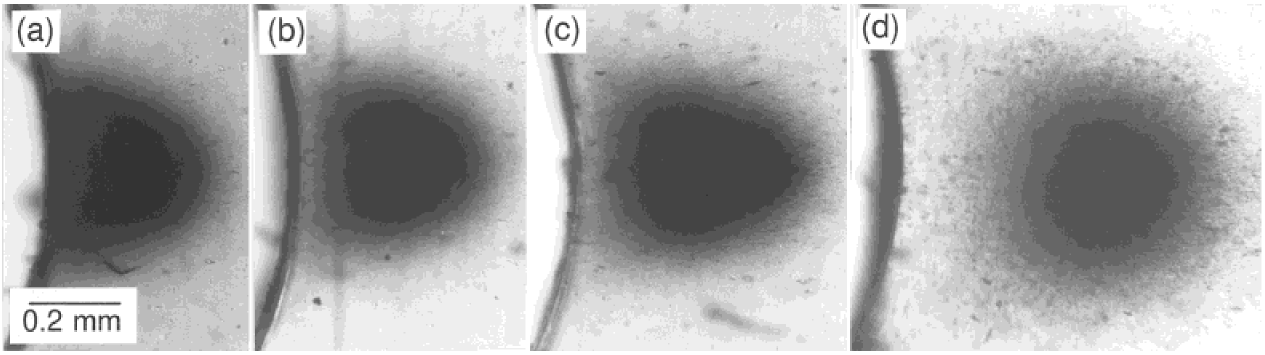

Figure 15 Optical micrographs of the damage zone for unloaded specimens of PVC with 10 phr CPE (5896) deformed to about 80% of the yield stress at: (a) 21°C, (b) 30°C, (c) 35°C, and (d) 45°C.

preceded the formation of a stress-whitened damage zone, and the distance of the initiation site from the notch root was 0.06 mm. The initiation site shifted outward to 0.22 mm when the temperature was further increased to 45°C. At 30°C, the zone exhibited a transitional behavior where stress whitening nucleated at the notch root but did not have the characteristic crescent shape.

Thus, neither the appearance of core yielding prior stress whitening nor the transition to a crescent-shaped zone is specific to PVC/MBS blends. Both PVC blends exhibit the same phenomena with a different transition temperature, which is approximately 30°C for CPE blends, and −20°C for MBS blends at 10 phr rubber loading. The ramifications of the different behavior for both blends will be discussed in the following paper.

CONCLUSIONS

The irreversible deformation modes in PVC and PVC/MBS blends were studied at a semicircular notch as a function of rubber content in the temperature range between −40 and 40°C. Observations can be summarized as follows.

1. In the macroscale, PVC invariably exhibited a constant plastic zone size at the notch root independent of temperature, prior to the onset of diffuse stress whitening at the tip of the plastic zone. In the blends, the plastic zone size preceding the onset of stress whitening was dependent on temperature and rubber content. Higher rubber content and temperature shifted the stress-whitened zone outward from the notch root, increasing the plastic zone size. Below 0°C, stress whitening initiated directly at the notch root and had a crescent shape similar to PVC/CPE blends.
2. In the microscale, AFM revealed voiding in PVC. In the blends, stress whitening was more intense and was caused by the cavitation of rubber particles, as shown by TEM. Based on these observations, it was suggested that cavitation in the blends was controlled by the material properties of the rubber as opposed to PVC, where it was a property of the polymer matrix.
3. In experiments with previously studied PVC/CPE blends above the ambient temperature, the crescent-shaped stress-whitened zone was shown to gradually shift outward from the notch root with increasing temperature. Thus, a temperature dependent stress-whitened zone is characteristic of both MBS and CPE blends. However, the transition from a crescent-shaped zone to one where shear yielding at the notch root precedes stress whitening is at a considerably higher temperature in PVC/CPE blends than in PVC/MBS blends.

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