Damage Zone in PVC and PVC/MBS Blends. II. Analysis of the Stress-Whitened Zone

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: Damage zone development in a triaxial stress state in poly(vinyl chloride) (PVC) and blends of PVC with methyl methacrylate–butadiene–styrene (MBS) core-shell rubber was analyzed as a function of temperature. The sequence of failure events at the notch root, core yielding and stress whitening, was shown to depend on the competition between the shear yield stress and the cavitation stress. The onset of cavitation was described by a critical mean stress and a critical volume strain. At low temperatures, a crescent-shaped stress-whitened zone formed at the notch root, and the critical mean stress was obtained by an elastic analysis. At temperatures in the ambient range and higher, shear yielding preceded cavitation at the notch root, and the critical mean stress was obtained by a plastic analysis. The transition from cavitation to shear yielding at the notch root coincided with a transition in the temperature dependence of the critical mean stress. Above the transition, the critical mean stress was much less sensitive to temperature than below the transition. Although this transition temperature was higher by about 30°C in blends of PVC with 10 phr CPE (chlorinated polyethylene) rubber, the temperature dependence of the critical mean stress in both blends was similar. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 715–723, 1997

Key words: poly(vinyl chloride); MBS; cavitation; critical mean stress; critical volume strain

INTRODUCTION

A comprehensive description of damage zone development ahead of a semicircular notch in poly(vinyl chloride) (PVC) and its transparent blends with methacrylate–butadiene–styrene (MBS) core/shell rubber was given in the previous article on this subject.[1] Two mechanisms of failure, shear yielding and stress whitening, were observed at the notch. Stress whitening in the blends was caused by rubber cavitation; while in unmodified PVC, it was attributed to the growth of preexisting microvoids. The onset of whitening, as well as the sequence of failure events at the notch, was found to depend on the rubber content in the blend and on temperature. At low temperatures, stress whitening was initiated at the notch root, and a crescent-shaped damage zone was observed. At temperatures in the ambient range and higher, shear yielding occurred first, and stress whitening was initiated at some distance away from the notch root at the tip of the yielded zone.

Previously, a critical mean stress criterion was used to describe the onset of cavitation in the triaxial stress state ahead of the semicircular notch.[2–5] Blends of PVC with chlorinated polyethylene (CPE) rubber[2] exhibited a crescent-shaped damage zone, with contours corresponding to those of the elastic mean stress distribution around the notch. Hence, the critical mean stress

Correspondence to: A. Hiltner.

was obtained by an elastic analysis. While the critical mean stress decreased as the amount of CPE in the blend was increased, the critical volume strain, calculated from the bulk modulus, was independent of composition and was thought to be the controlling parameter for stress-whitening. The same approach was also applied to describe the initiation and growth of internal multiple notch crazes in styrene-acrylonitrile (SAN).[3]

In several other polymeric systems, such as PVC,[4] and rubber modified polycarbonate,[5] stress whitening did not initiate at the notch but formed at a distance away from the notch root at the tip of a shear yielding zone emanating from the notch. The same sequence of events was also observed for a broad range of polymers prior to the onset of an internal craze in thick specimens.[6–8] Because shear yielding preceded cavitation, the critical mean stress was obtained by a plastic analysis that gives the triaxial stress intensification at the tip of the shear yielding zone.

This article focuses on the analysis of the macroscopic damage zones observed in PVC and PVC/MBS blends as a function of temperature. First, a competition between shear yielding and cavitation was invoked to explain the sequence of failure events at the notch root. The onset of cavitation was characterized by the critical mean stress criterion, which was obtained either by an elastic or plastic analysis, depending on the sequence of failure events at the notch. The critical volume strain was also calculated for each case. Finally, results obtained with PVC/MBS blends were compared with those for PVC/CPE blends at 10 phr rubber loading.

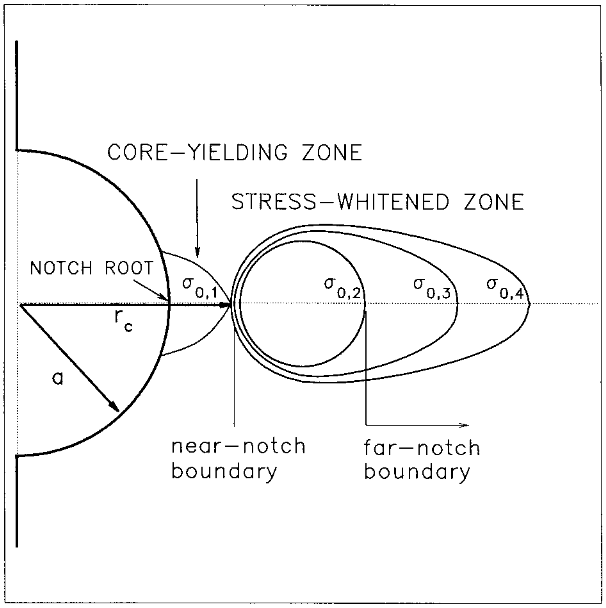

Figure 1 Schematic of damage evolution ahead of the semicircular notch for PVC and PVC/MBS blends in the ambient temperature range.

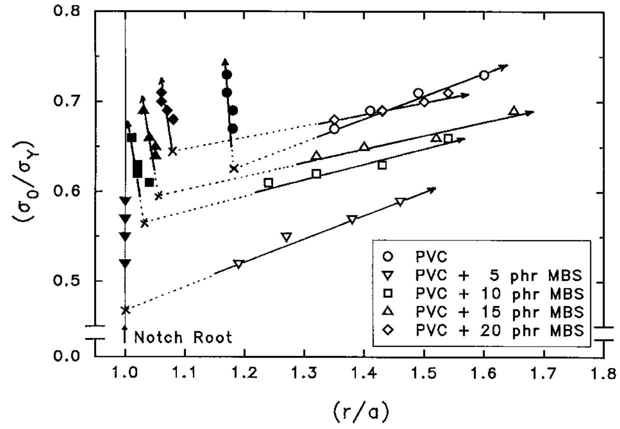

Figure 2 Growth of the stress-whitened zone in PVC and the blends as a function of stress at 0°C. The y-axis is the remote stress (σ_0) normalized with tensile yield stress (σ_Y); the x-axis is the distance from notch origin (r) normalized with the notch radius (a).

RESULTS AND DISCUSSION

Initiation and Growth of the Damage Zone

The prefracture damage evolution in PVC and PVC/MBS blends ahead of a semicircular notch was described in the preceding paper.[1] The typical sequence of failure events is schematically illustrated in Figure 1. In the ambient temperature range, shear yielding at the notch root was observed at remote stress $\sigma_{0,1}$. The yielded region, designated as the core-yielding zone,[9] contained sliplines in PVC. Even though sliplines were not discernible in the blends, core yielding was inferred based on the birefringent zone that was observed in the same region after the specimens were unloaded. With increasing remote stress $\sigma_{0,2}$, a stress-whitened zone (SWZ) appeared at the tip of the core yielding zone, at a distance r_c from the notch origin. The contours in Figure 1 represent the projection of the boundary of the SWZ onto the center plane through the thickness. With further increase in stress, $\sigma_{0,3}$ and $\sigma_{0,4}$, the SWZ grew in size outward from the notch.

The growth pattern of the zones in PVC and

Table I Initiation Location of the SWZ Measured from the Notch Origin (r_c) Normalized with the Notch Radius (a = 1 mm)

Temperature (°C)	PVC	5 phr MBS	10 phr MBS	15 phr MBS	20 phr MBS
40	1.20	1.12	1.18	1.22	1.24
21	1.17	1.06	1.09	1.15	1.18
0	1.18	1.00	1.04	1.06	1.07
−20	1.21	1.00	1.00	1.00	1.00
−40	1.20	1.00	1.00	1.00	1.00

the blends are compared in Figure 2 with data from micrographs taken during deformation at 0°C. Filled and open symbols indicate the positions of the near- and far-notch boundary of the SWZ as a function of stress, and both axes are normalized to present data in dimensionless form. For each material, the position of the near-notch boundary did not change significantly as the stress increased. In contrast, the far-notch boundary of the SWZ grew linearly outward from the notch with increasing remote stress. The slope of the line describing the position of the far-notch boundary decreased with increasing rubber content in the blend. Hence, with increased rubber loading, smaller stress increments were required to expand the SWZ. In the microscale, this indicates an increased tendency towards the previously described cooperative cavitation mechanism[1,10] with increasing amount of rubber.

The amount of rubber in the blend, as well as temperature, had a pronounced effect on the stress level required for whitening and on the position of the SWZ with respect to the notch root. For specimens deformed at 0°C, the SWZ was furthest from the notch root in PVC and closest to the notch in the 5 phr MBS blend, as seen in Figure 2. The SWZ moved away from the notch root with increasing MBS content. Because the initiation of stress whitening could not be determined accurately by direct observation, the remote stress at initiation and the initiation location were obtained by extrapolation and are indicated by crosses in Figure 2. The distance of the extrapolated initiation location on the x-axis from the notch origin, r_c, normalized with the notch radius, a (1 mm), is shown in Table I for PVC and the blends at five temperatures between −40 and 40°C. The condition $(r_c/a) = 1$ means that stress whitening initiated directly at the notch root and that no core yielding was observed. When core yielding was absent, the SWZ had a crescent shape at the notch, rather than the shape depicted in Figure 1.[1]

Relationship Between Stress Whitening and Shear Yielding

The remote stress at the initiation of stress whitening obtained by extrapolation ($\sigma_{0,c}$) is compared with the stress at shear yielding (k_0) in Figure 3. The shear yield stress is calculated from the yield stress in uniaxial tension (Fig. 4 in Bensason et al.[1]) and is shown by dashed lines. The remote stress at the onset of whitening, simply denoted as cavitation stress, is shown by solid lines. Because $\sigma_{0,c}$ was insensitive to the rubber content in the blend, all data for blends were presented by a single solid line. The cavitation stress of the blends was clearly less than that of PVC, an effect attributed to the presence of rubber in the blends. In PVC, the cavitation stress was always higher than the shear yield stress; while in the blends, $\sigma_{0,c}$ and k_0 were comparable. At low temperatures,

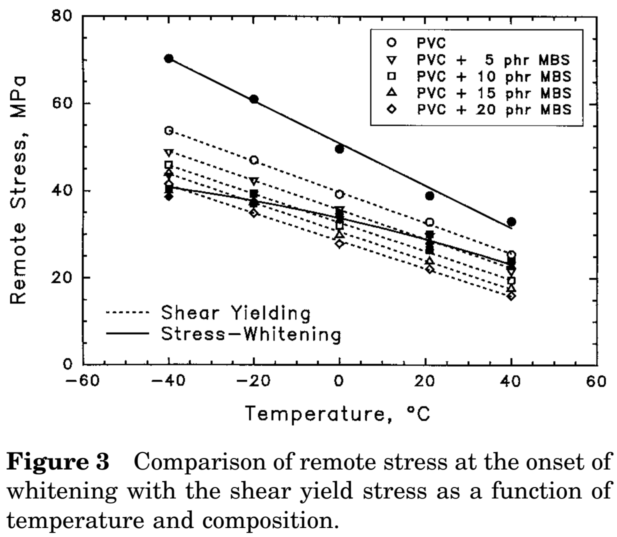

Figure 3 Comparison of remote stress at the onset of whitening with the shear yield stress as a function of temperature and composition.

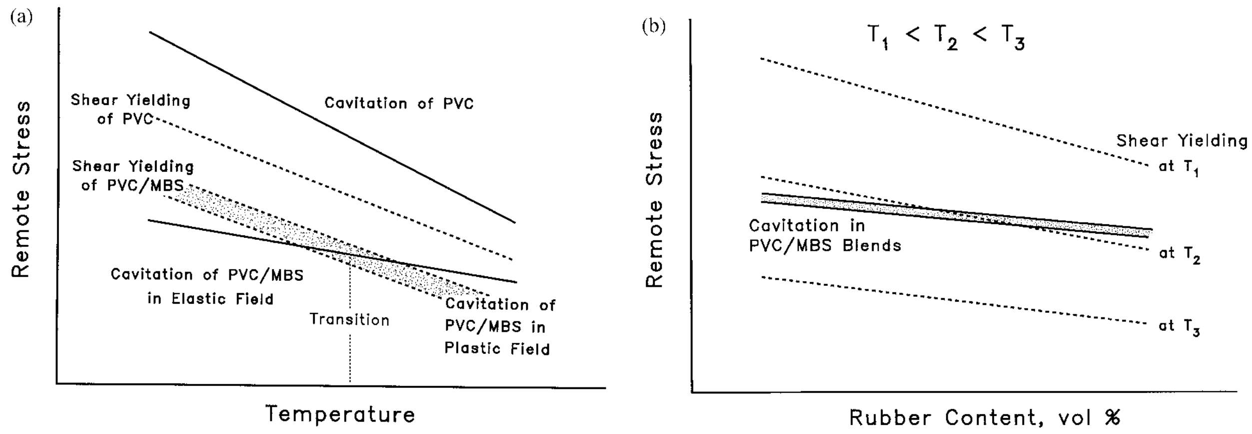

Figure 4 Schematic representation of the competition between the cavitation stress and the shear yield stress as a function of (a) temperature and (b) rubber content.

$\sigma_{0,c}$ was lower than k_0, and cavitation occurred in an elastic field. In contrast, blends that were deformed at higher temperatures exhibited cavitation only after shear yielding, as in PVC.

In extension to Figure 3, the effect of temperature and rubber content on the competition between shear yielding and cavitation is schematically illustrated in Figure 4(a,b). In PVC, the cavitation stress is higher than the shear yield stress at each temperature [Fig. 4(a)]. This is in agreement with the sequence of failure events in PVC, in which the SWZ was always observed to initiate away from the notch root, as seen in Table I. In contrast with PVC, the temperature dependence of the cavitation stress and the shear yield stress, the latter shown as a band in Figure 4(a), are different in the blends. The cavitation stress is less sensitive to temperature, and a cross over is observed. At higher temperatures, shear yielding precedes cavitation and a core yielding zone forms first at the notch root; at lower temperatures, cavitation occurs first at the notch root. When the cavitation band intersects the shear yield line, the conditions for cavitation and shear yielding are achieved simultaneously. The sensitivity of the initiation location of SWZ to temperature shown in Table I is in good agreement with the proposed scheme.

An alternative representation that emphasizes the effect of MBS content is shown in Figure 4(b). At the highest temperature, T_3, the shear yielding condition is reached before the cavitation condition in all the blends; while at the lowest temperature, T_1, cavitation precedes shear yielding. At the intermediate temperature, T_2, the cavitation band crosses the shear yielding line. Blends with higher MBS content yield first at this temperature, while blends with lower MBS content cavitate first.

Analysis of Stress Whitening

The onset of cavitation in a triaxial stress field can be characterized by a critical mean stress condition.[2–5] The method to evaluate the stress distribution around the notch is dictated by the sequence of yielding modes at the notch root, which is dependent on the amount of rubber in the blend, as well as the temperature. If shear yielding precedes stress whitening [Figure 5(a)], a plastic analysis is used to calculate the critical mean stress at the onset of cavitation. In contrast, when cavitation occurs first at the notch root, as in Figure 5(b), an elastic stress field is assumed.

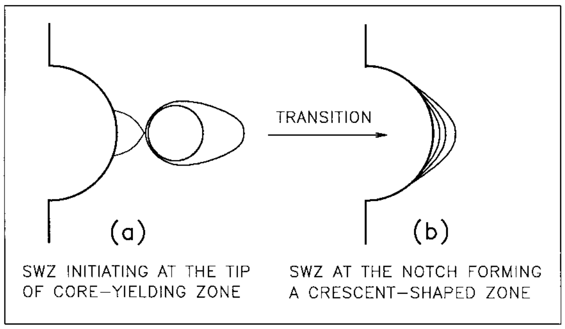

Figure 5 Schematic of stress-whitening zone when (a) shear yielding precedes cavitation at the notch root and (b) cavitation occurs first at the notch root.

Critical Mean Stress by Elastic Analysis

Depending on the rubber content in the blend, at temperatures lower than 0 to −20°C, stress whitening initiated at the notch root. Hence, elastic stress intensification at the notch root was high enough to cause cavitation before shear yielding. At low enough temperatures, the shape and growth pattern of the ensuing zones resembled the crescent-shaped damage zone, previously observed by Tse et al. in PVC/CPE blends[2] and in poly(4-methylpentene-1)[11] in the ambient and subambient temperature range. The same type of contours were also reported by Shin et al.[3] in SAN, where the damage occurred in the form of internal multiple notch crazes.

Previously, the initiation and growth of the crescent-shaped SWZ was described by an elastic critical mean stress condition, based on the excellent correspondence between the calculated elastic iso-mean stress contours and the observed contours of the crescent-shaped zone. Maunsell's exact solution for a semicircular notch in a semi-infinite plate under uniform tension[12] was used to calculate the two-dimensional stress distribution. For the plane strain condition, the third principal stress in the thickness direction σ_3 was calculated from the relationship $\sigma_3 = v(\sigma_1 + \sigma_2)$, using a Poisson's ratio of $v = 0.38$ for PVC.[2] The resultant mean stress distribution around the semicircular notch is shown in Figure 6.

To examine the applicability of the elastic critical mean stress criterion, mean stress values were calculated at 10 to 15 positions on the boundary of the SWZ from micrographs taken during the loading experiments. For PVC with 5 phr MBS deformed at −20°C, the elastic mean stress σ_m is plotted in Figure 7(a) as a function of position on the damage zone contour for several remote stress levels. Theta is the polar angle measured with the origin at the center of the semicircular notch. As seen in Figure 7(a), the mean stress along the zone contour varied only by a small amount as a function of position. Furthermore, the mean stress did not vary with increasing levels of remote stress. Hence, the elastic σ_m satisfactorily described the critical condition for stress whitening for PVC with 5 phr MBS and had an average value of 49 MPa at −20°C.

The critical mean stress criterion was considered valid only if readings of the mean stress along the damage zone contour had a deviation less than ±5% from the mean, within the first 5 MPa increment following initiation. The latter criterion was set to avoid large zones, where stress redistribution at the elastic-plastic boundary is expected. Blends of PVC with 5 and 10 phr MBS satisfied both criteria and gave good fits at −20°C and below, whereas blends with 15 and 20 phr MBS were amenable to a good fit only at −40°C. The resultant values of elastic critical mean stress are shown in Table II.

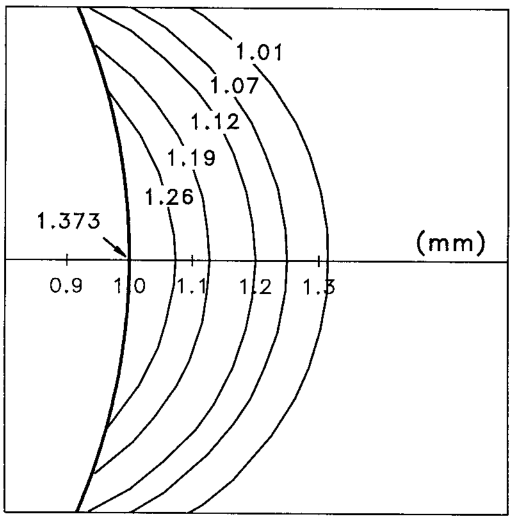

Figure 6 Elastic (iso)mean stress contours around the notch, normalized with the remote stress (from Shin et al.).[3]

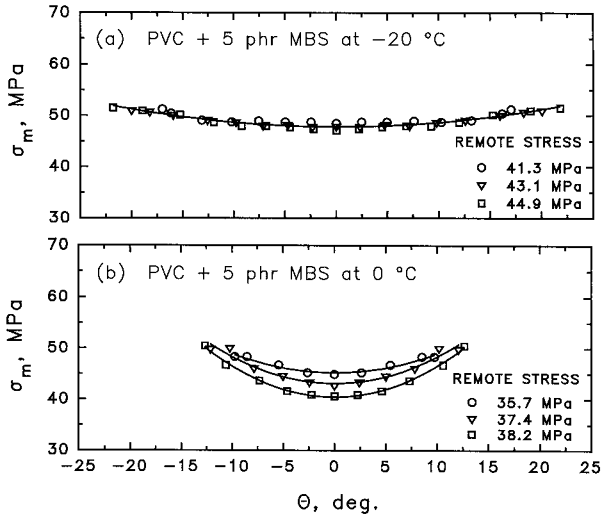

Figure 7 Elastic mean stress at the boundary of the stress-whitening zone measured as a function of polar angle Θ at several remote stresses: (a) 5 phr MBS blend deformed at −20°C and (b) 5 phr MBS blend deformed at 0°C.

Table II Critical Mean Stress Values (MPa) Obtained by Elastic Analysis

Temperature (°C)	5 phr MBS	10 phr MBS	15 phr MBS	20 phr MBS
−20	49.0	47.9	n/a	n/a
−40	60.4	52.9	52.5	50.9

At higher temperatures, the crescent-shaped zones became more elongated in the growth direction, and the elastic mean stress at the boundary of SWZ as a function of both position and remote stress was no longer a constant. An example of such a case is shown in Figure 7(b) for PVC with 5 phr MBS at 0°C. The variation in mean stress was attributed to the fact that in transitional cases, shear yielding and cavitation conditions were virtually identical at the notch root. Subsequently, in these cases, a plastic analysis was used to evaluate the critical mean stress.

Critical Mean Stress by Plastic Analysis

With increasing temperature, the zones gradually lost their characteristic crescent shape amenable to elastic analysis, as shown in Figure 7(b). At higher temperatures, about 0°C, a core yielding zone became apparent in all blends except for PVC with 5 phr MBS, and the zones shifted away from the notch. In such cases, the cavitation condition was attained by the triaxial stress intensification at the tip of the core yielding zone advancing into the elastic material. The stresses at the elastic-plastic boundary of the core-yielding zone are calculable by Hill's slip line field analysis, which gives the plastic principle stresses at a deep semicircular notch for a nonwork hardening, perfectly plastic material in plane strain.[13] Modified by Narisawa et al.[6] to accommodate a pressure-dependent yield criterion, the plain strain mean stress along the x-axis is given as follows:

$$\sigma_m = \frac{(\sigma_{rr} + \sigma_{\theta\theta} + \sigma_{r\theta})}{3} = \frac{k_0}{\mu}\left[1 - \left(\frac{1}{1+\mu}\right)\left(\frac{r}{a}\right)^{-2\mu/1+\mu}\right] \quad (1)$$

where k_0 is the shear yield stress, which was obtained from the uniaxial tensile yield stress using the von Mises yield criterion; μ is the pressure dependence parameter in the modified von Mises equation, which was taken as 0.11 for PVC,[4] r is the distance along the x-axis from the notch origin; and a is the notch radius. The critical mean stress for cavitation $\sigma_{m,c}$ is obtained by inserting (r_c/a) ratio into eq. (1), together with k_0 values for each material at each temperature.

In PVC, the (r_c/a) ratio was a constant independent of temperature, and the critical mean stress obtained by eq. (1) was proportional to the shear yield stress. In contrast, the (r_c/a) ratio in the blends was dependent both on rubber content and temperature. With decreasing shear yield stress, due to either increasing rubber content or temperature, the SWZ initiated further away from the notch root. Therefore, $\sigma_{m,c}$ decreased less with increasing temperature, in comparison to the shear yield stress. All values obtained by plastic analysis are shown in Table III. The addition of 5 phr MBS rubber to PVC reduced the critical mean stress by about 25% at each temperature. Yet further addition of rubber into the blend reduced the critical mean stress only by a modest amount, typically by 5% per each additional 5 phr increment. Also included in Table III, shown in parentheses, are the critical mean stress values for transitional cases, which exhibited no core yielding but considerable variation in elastic mean stress (5 phr MBS blend at 0°C, 15, and 20 phr MBS blend at −20°C). Because the ratio (r_c/a) ratio had a value of 1 for transitional cases, the plastic critical mean stress obtained by eq. (1) was equivalent to 0.9 k_0.

Temperature Dependence of the Critical Mean Stress

The critical mean stress values obtained by elastic and plastic analyses are plotted as a function of temperature in Figure 8. PVC exhibited a linear relationship over the entire temperature range, and the critical mean stress was proportional to the shear yield stress. The critical mean stress values for the blends were lower than PVC and exhibited two regimes, with a transition at about

Table III Critical Mean Stress Values (MPa) Obtained by Plastic Analysis

Temperature (°C)	PVC	5 phr MBS	10 phr MBS	15 phr MBS	20 phr MBS
40	33.6	26.0	25.2	23.9	22.1
21	42.0	32.7	30.5	29.8	28.5
0	50.8	(35.7)	34.2	33.0	31.3
−20	62.9	n/a	n/a	(37.4)	(34.9)

Values in parentheses indicate the cases in which stress whitening initiated at the notch root with $(r_c/a) = 1$.

−20°C. In the plastic regime between 40°C and the transition, the critical mean stress was not affected significantly by temperature and appears to reflect the cavitation resistance of the specific rubber in the blend. In contrast, the critical mean stress values obtained by elastic analysis at lower temperatures were higher and did not follow the trend set by the plastic regime. With decreasing temperature, the critical mean stress for the blends approached that of PVC, the latter a property of the matrix rather than the rubber. Even though the trend at lower temperatures reflects an increased resistance to cavitation, the temperature range of the transition is still considerably above the glass transition temperature of the MBS rubber (−70°C). However, the temperature range of the transition seems to correspond to the minimum achievable ductile–brittle transition temperature in polycarbonate toughened with optimal amount of MBS rubber.[5]

The Critical Volume Strain

The onset of dilational yielding can also be characterized by the critical volume strain, defined as[2,14]

$$V_c = \frac{\sigma_{m,c}}{K} = \frac{3(1-2\nu)\sigma_{m,c}}{E} \quad (2)$$

where K is the bulk modulus, E is the tensile modulus, ν is the Poisson's ratio, and $\sigma_{m,c}$ is the critical mean stress. Previously, the critical volume strain V_c was found to be a temperature-independent material parameter with a value of 0.8% for PVC/CPE blends.[2] In comparison, blends of polycarbonate with MBS rubber V_c had a larger value (1.2%).[5]

The critical volume strain for PVC and PVC/MBS blends, obtained by assuming a temperature-independent Poisson's ratio, is shown in Figure 9. The values ranged from 1.2% at low temperatures to 0.8% at high temperatures. The temperature dependence of the critical volume strain was

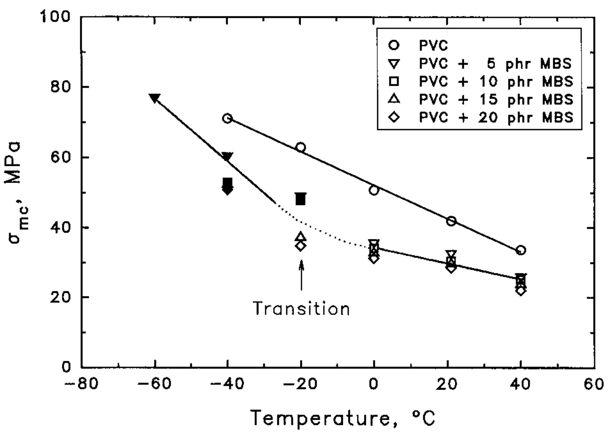

Figure 8 The critical mean stress as a function of temperature. Open symbols denote data obtained by plastic analysis; filled symbols denote data obtained by elastic analysis.

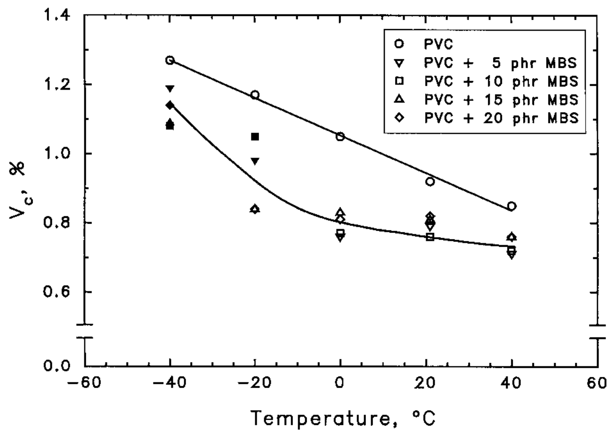

Figure 9 The critical volume strain as a function of temperature. Open symbols denote data obtained by plastic analysis; filled symbols denote data obtained by elastic analysis.

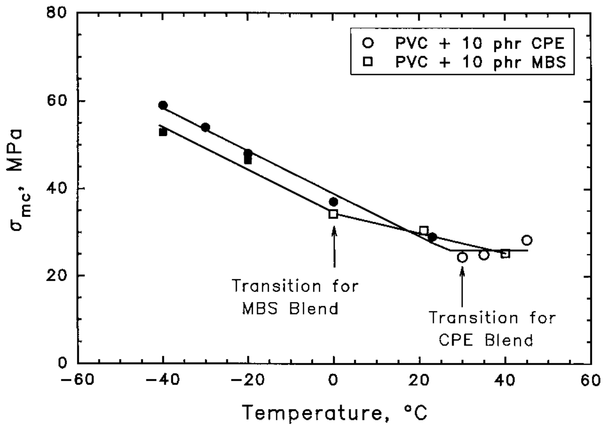

Figure 10 Comparison of the temperature dependence of critical mean stress for PVC modified with 10 phr CPE and 10 phr MBS. Open symbols denote data obtained by plastic analysis; filled symbols denote data obtained by elastic analysis.

less than that of the critical mean stress. However, a constant value of 0.8% as in the case of PVC/CPE blends was not observed. Hence, the critical volume strain may be as relevant as the critical mean stress for characterizing the onset of stress whitening in PVC and PVC/MBS blends.

Comparison of PVC/MBS with PVC/CPE Blends

The critical mean stress values obtained for PVC/CPE blends were compared with those of PVC/MBS blends to examine the effect of rubber type on stress whitening. The $\sigma_{m,c}$ values obtained from new data for PVC with 10 phr CPE above room temperature,[1] together with those reported by Tse et al. between −40°C and room temperature,[2] are shown in Figure 10. Also included in Figure 10 are results for PVC with 10 phr MBS for comparison. For CPE blends, the transition in the initial mode of failure at the notch root was observed at 30°C. The transition temperature was considerably closer to the glass transition temperature of this CPE resin, which was reported as 17°C at 1 Hz.[2] As in the case of MBS blends, the transition in the failure modes in CPE blends also coincided with a transition in the temperature dependence of the critical mean stress. The linearly decreasing trend in $\sigma_{m,c}$ with temperature leveled off abruptly at 30°C, and the critical mean stress was not affected by temperature above 30°C. The plastic critical mean stress in both blends was quite similar, about 27 ± 2 MPa. Although the transition temperature was about 30°C higher in PVC/CPE blends, the critical mean stress for cavitation was very similar in both blends over the whole temperature range, regardless of whether the mean stress was obtained by the elastic or plastic analysis.

CONCLUSIONS

Analysis of the damage zone development in PVC and PVC/MBS blends ahead of a semicircular notch led to the following conclusions:

1. The sequence of failure events at the notch root, core yielding and stress whitening, depended on the competition between shear yield stress and cavitation stress at the notch root. At higher temperatures, shear yielding preceded cavitation, and a core yielding zone formed at the notch root, followed by stress whitening some distance away from the notch; at lower temperatures, cavitation occurred first at the notch and formed a crescent-shaped zone.
2. The onset of stress whitening was characterized by a critical mean stress. Depending on the sequence of failure events at the notch, either an elastic or a plastic analysis was used. The critical mean stress for blends decreased slightly with rubber content and was significantly lower in the blends in comparison to PVC. Two regimes of temperature dependence were observed. At temperatures above −20°C, when core yielding preceded cavitation, the critical mean stress exhibited little sensitivity to temperature. At lower temperatures, where a crescent-shaped zone was observed, the temperature dependence was stronger.
3. The critical volume strain for PVC was larger than in blends. The values ranged between 0.8% at high temperatures and 1.3% at low temperatures.
4. The transition from a crescent-shaped zone to a core-yielding zone at the notch root was about 30°C higher in blends of PVC with 10 phr CPE than in MBS blends of the same rubber content. However, the critical mean stress values for both blends were similar over the temperature range studied.

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