

Irreversible Deformation of Plasticized and Impact-Modified Poly(vinyl Chloride)

A. SIEGMANN and A. HADAS, *Department of Materials Engineering, Technion, Israel Institute of Technology, Haifa 32000, Israel*

Synopsis

Tensile mechanical properties of DOP-plasticized poly(vinyl chloride) (PVC) and methyl methacrylate-butyl acrylate copolymer (MMA-BA) or ethylene vinyl acetate-vinyl chloride copolymer (EVA-VC) modified PVC have been studied. The irreversible deformation processes have been investigated using optical microscopy. Thermal analysis and x-ray diffraction were used to investigate the structure of the PVC blends. The differences in behavior observed for the modified and plasticized PVC are discussed on the basis of their morphology.

INTRODUCTION

Poly(vinyl chloride) (PVC) is probably the most frequently modified polymer on both the laboratory and commercial scale. A very wide range of properties can thus be attained depending on the type and amount of modifiers (such as plasticizers and rubbery modifiers). The mechanical behavior of the large family of PVC depends, among other things, on the system morphology. In this respect, plasticized and elastomer-modified PVC are very different. The plasticized polymer is considered a homogeneous one-phase system that contains aggregates on several size scales.^{1,2} In this structural hierarchy, the smallest structural units (approximately 100 Å) were found to be affected by plasticization; plasticizer diffuses into these units and causes their size increase. On the other hand, all rubber-modified PVC systems consist of two-phase structures, the morphology of which depends on the type and content of the modifier as well as the processing conditions.³⁻⁵ These systems contain the primary 1- μm PVC flow units, and the modifier is either discretely dispersed (mainly at low content) or forms a network structure enveloping the primary particles. Under the influence of external stresses, in the plasticized polymer the PVC morphological units are deformed whereas in the modified PVC most of the deformation takes place in the rubber phase.^{3,6,7} It is therefore the purpose of the present work to compare the tensile behavior and the irreversible microdeformation mechanisms and their relationship in plasticized and impact-modified rigid PVC.

EXPERIMENTAL

The materials used in this study include PVC (K value of 70) supplied by Israel Electrochemical Industries (suspension polymerized grade 37I), methyl methacrylate-butyl acrylate copolymer (MMA-BA, Acrylaid K323) supplied by Rohm and Haas, ethylene vinyl acetate-vinyl chloride copolymer (EVA-VC

containing 50% VC, EVA contains 45% VA, Vestolet HIS 7587) supplied by Huls, dioctyl phthalate (Fluka AG), and Igrastab 17M stabilizer (Ciba Geigy). The blends were prepared by first dry mixing the components and then roll milling at 175°C for 7 min. Sheets were compression molded in a preheated press at 190°C and 3500 psi for 5 min and then cooled in the mold under pressure. All blends contained 1 phr stabilizer and up to 20 phr either plasticizer (DOP) or impact-modifying elastomer (either MMA-BA or EVA-VC). No other additives commonly used in practical applications were included.

Tensile specimens were cut from about 0.5 mm thick molded sheets in accordance with ASTM D638 and tested using an Instron machine at a strain rate of 0.5 and 1.3 min^{-1} . The average results of at least five specimens are reported for each composition.

Irreversible deformation was followed by observation of deforming rectangular specimens, 5 × 0.5 cm, using a stretching jig under an Olympus optical microscope.

The glass transition temperature of all blends was determined using a Mettler TA 3000 DSC at a heating rate of 20°C/min. The wide-angle x-ray diffraction patterns of DOP-containing blends were obtained using a Phillips diffractometer (CuK_α radiation).

RESULTS

Stress-strain curves of PVC and its blends with DOP, EVA-VC, and MMA-BA are shown in Figures 1 through 3. The additives have a pronounced effect, mainly on the tensile behavior in the yield region and on the ultimate elongation. In the plasticized PVC, the addition of DOP first results in a

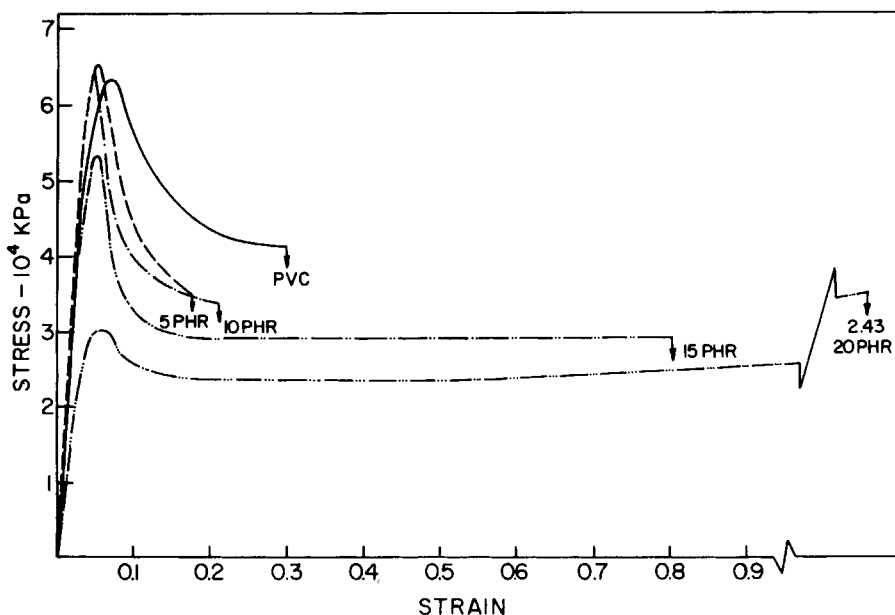


Fig. 1. Stress-strain curves of DOP-plasticized PVC ($\dot{\epsilon} = 1.3 \text{ min}^{-1}$).

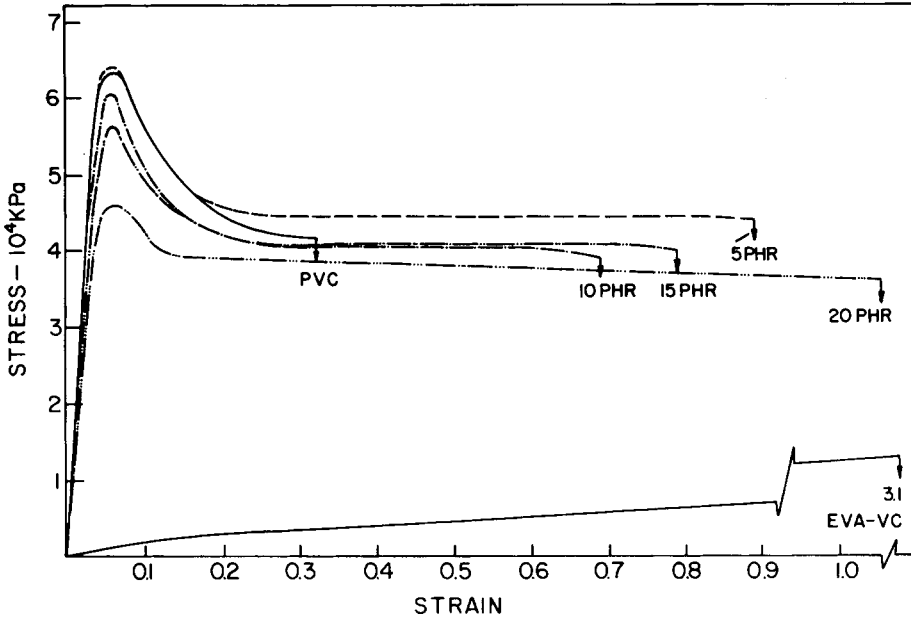


Fig. 2. Stress-strain curves of PVC/EVA-VC blends ($\dot{\epsilon} = 1.3 \text{ min}^{-1}$).

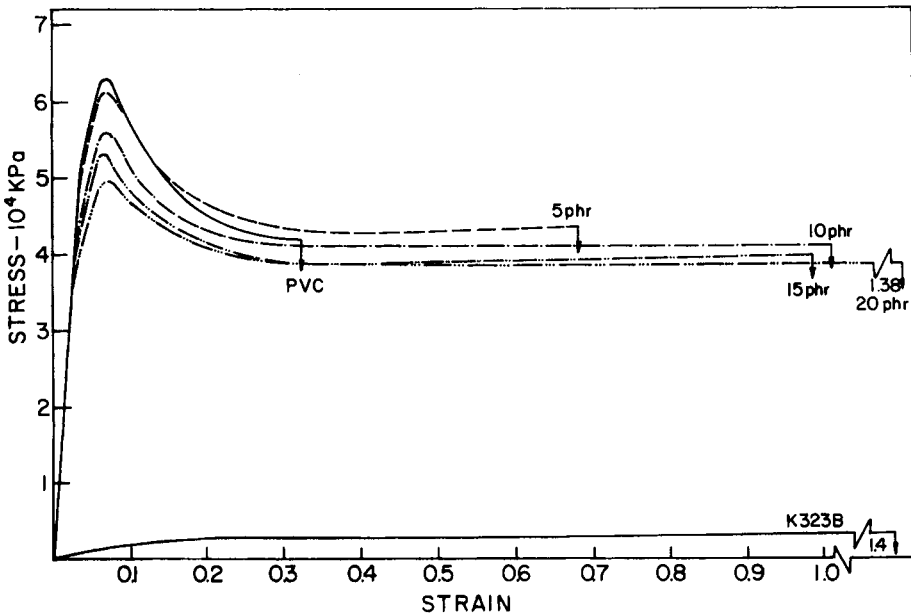


Fig. 3. Stress-strain curves of PVC/MMA-BA blends ($\dot{\epsilon} = 1.3 \text{ min}^{-1}$).

narrower yield zone than observed for PVC, as well as a slight increase in the yield stress and a decrease in the yield strain. Only upon the addition of 20 phr DOP does the yield zone broaden and the yield stress markedly decline. Simultaneously, appreciable deformation relative to that of PVC is only obtained in blends containing more than 15 phr DOP; at lower DOP contents the ultimate elongation is even lower than that of PVC. The lower DOP concentration blends exhibit a more pronounced yield instability than that of PVC. However, at higher DOP content the yield stress is reduced and the yield instability then becomes less pronounced. Stress-strain curves obtained at the lower strain rate (not shown) exhibit gradually decreasing yield stresses with increasing DOP content. However, the changes in the yield zone shape are similar to those observed at the higher strain rate. Moreover, much higher ultimate strains are attained at the lower strain rate. It is interesting to note that the rate sensitivity of the elongation at break decreases markedly with increasing DOP content. In PVC-EVA-VC blends, more gradual changes with composition are observed in the yield region of the stress-strain curves. However, the addition of only 5 phr EVA-VC results in a much higher ultimate strain compared with that of PVC (90 and 30%, respectively). Further increasing the EVA-VC content does not significantly affect blend deformability. The broadening of the yield zone with increasing modifier content is more pronounced when tested at the lower than at the higher strain rate. Interestingly, the ultimate strains of the blends attained at the lower strain rate are not much higher than for PVC; they are not as rate sensitive as PVC. This indicates the advantage of EVA-VC modification mainly at high strain rates for which it is commercially designed. PVC-MMA-BA blends exhibit a very gradual acrylic content effect on the yield region of the stress-strain curves; the yield zone becomes increasingly broader although the yield stress does not significantly change. Such gradual change is also observed in the ultimate strain, which increases with MMA-BA content, attaining quite high values. It is also interesting to note that the flow stress and thus the stress at break of PVC is not significantly affected by the presence of the plasticizer and only slightly by the rubbery modifier. This suggests that the PVC particles actively participate in the deformation processes of both systems, which was not observed in previous microscopic studies of deformed modified PVC.⁷

Observation of the various specimens undergoing deformation in the Instron is quite informative. Yielding in PVC is associated with the formation of a single macroscopic shear band from which a sharp neck develops. The PVC neck stability strongly depends on the strain rate; at the higher rate it propagates only for a short distance before fracture occurs. In PVC-DOP blends several shear bands develop along specimens drawn even at the higher rate followed by the development of a single neck, the extent of which increases with DOP content. Only upon the addition of 20 phr is a so-called homogeneous deformation observed; there is no identifiable necking, but profuse shear banding is observed all over the drawn specimen (such homogeneous deformation was not observed in the other blends). At the lower strain rate the specimens behave visually in a very similar manner although the extent of neck propagation is much higher. All specimens but those containing 20 phr DOP stayed transparent throughout the deformation process. Blends

of PVC with either of the studied impact modifiers exhibit a different behavior during deformation. Yielding of these blends is accompanied by the formation of shear bands that increase in number with modifier content. The narrow yield zone, characteristic of PVC, becomes broad, and shear banding is not restricted to the neck zone but occurs all over the specimen. The neck propagates through the specimens of all modified PVC, which turn first translucent and then become opaque white (the PVC-acrylate blends are translucent to start with and become opaque upon deformation). With increasing modifier content the neck formation is more retarded: the specimens first seem to homogeneously deform, and only later, at increasing strains beyond the yield strain (as defined by the stress-strain curve), is the neck formed. It also seems that the PVC-acrylate blends are more densely shear banded than the PVC-EVA-VC blends of the same PVC content. In both blend systems of all compositions, the deformation processes advance through necking and even at the 20 phr modifier-containing blends no homogeneous deformation was observed. This behavior is different from the homogeneous deformation previously observed in PVC-CPE blends containing only 13% modifier.⁷

Prior to further discussions of the mechanical behavior, investigation of the effect of the various additives on the PVC glass transition temperature and crystallinity will be described. The single observed T_g in PVC-DOP blends was found, as expected,^{8,9} to linearly decrease with DOP content from a value of 75°C for PVC to 48°C for a blend containing 20 phr plasticizer. Moreover, the 10 and 15 phr DOP-containing blends exhibit a quite sharp excess enthalpy endotherm coupled with the glass transition; but the blend containing 20 phr DOP exhibits a rather shallow and broad endotherm. The experimentally determined T_g values are significantly lower than values calculated using the Fox equation.¹⁰ This may indicate that DOP does not form a simple miscible blend with PVC but instead forms a heterogeneous structure.⁹ The T_g of PVC was not affected by the incorporation of either modifiers in the whole range of compositions studied, indicating a complete phase separation. Some effect on the PVC T_g was anticipated, however, in blends with EVA-VC. Hardt¹¹ and Hammer,¹² for example, found that compatible blends can be obtained provided the EVA contains 60–75 wt% vinyl acetate. Marcincin et al.¹³ have found that even when the EVA contains only 45% vinyl acetate there is a shift of the PVC transition region (as measured by dynamic loss modulus), indicating a certain extent of molecular mixture. In our system (VA content of 45%), such a mixture is expected, at least because of the VC segments in the EVA-VC copolymer, which should not significantly affect the PVC glass transition, however. The wide-angle x-ray diffraction (WAXD) patterns for PVC and its blends with DOP are shown in Figure 4. All are characteristic of low-crystallinity polymers. With increasing DOP content the WAXD patterns become sharper and the relative intensity of the diffraction peaks, especially that at $2\theta = 17.5^\circ$, gradually increase, which is in good agreement with values reported in the literature.¹⁴ The relative intensity at $2\theta = 17.5^\circ$ levels off at a DOP content of 15 phr (not shown). It actually attains a maximum at that DOP level, which can be observed when a concentration correction is introduced. This increase in semicrystalline order can by itself explain the unique changes in the PVC mechanical behavior

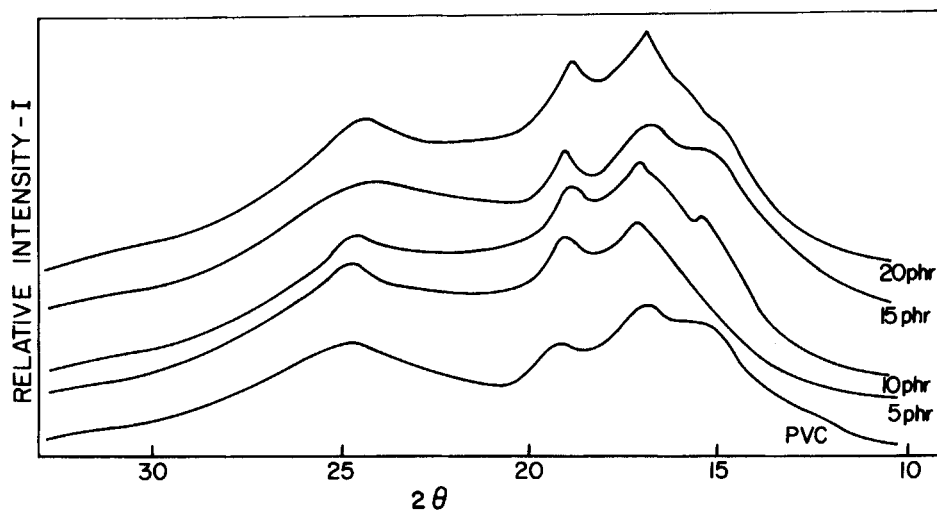


Fig. 4. Wide-angle x-ray diffraction patterns of PVC and DOP-plasticized PVC.

observed upon the incorporation of a relative low content of DOP (shown below).

The elastic modulus (the initial slope of the stress-strain curve) linearly decreases with increasing the content of either rubbery impact modifiers (Fig. 5). However, low DOP levels were found to impart PVC higher modulus values, which is in agreement with results reported in the literature.^{15,16} Further addition of DOP (> 10 phr) results in a sharp modulus decline to a value far below that of the PVC by itself. This modulus rise, accompanied by declining impact strength, has been called antiplasticization. Moreover, a minimum impact strength was recently obtained at a plasticizer level ($\sim 10\%$)

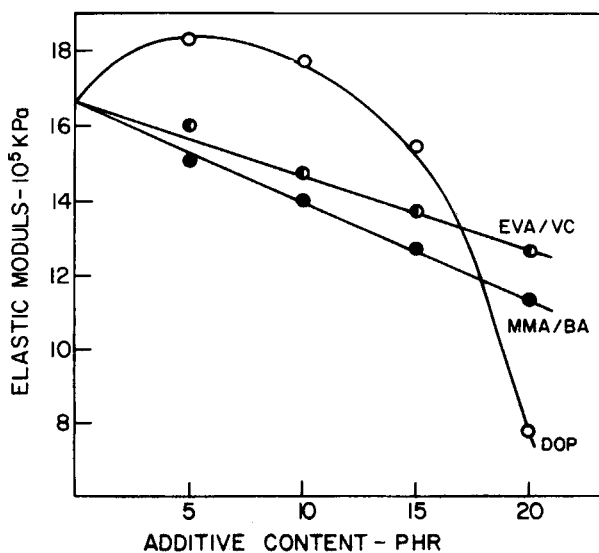


Fig. 5. Elastic modulus of PVC blends as a function of additive content ($\dot{\epsilon} = 1.3 \text{ min}^{-1}$).

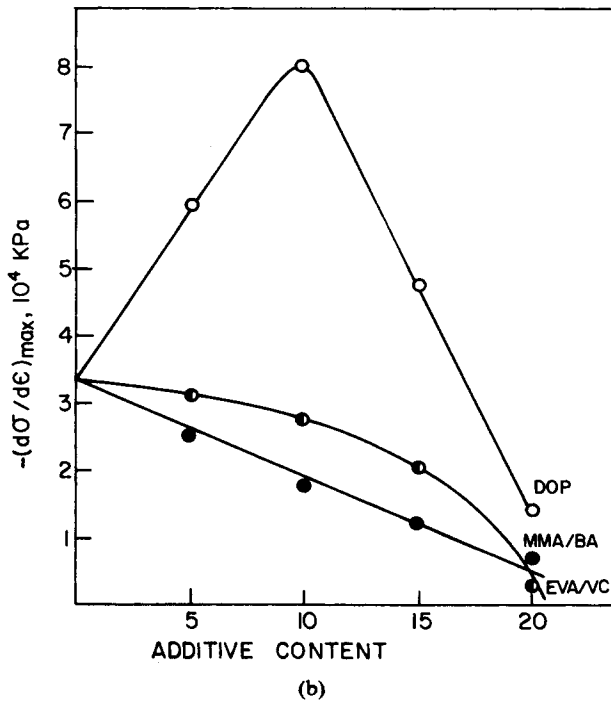
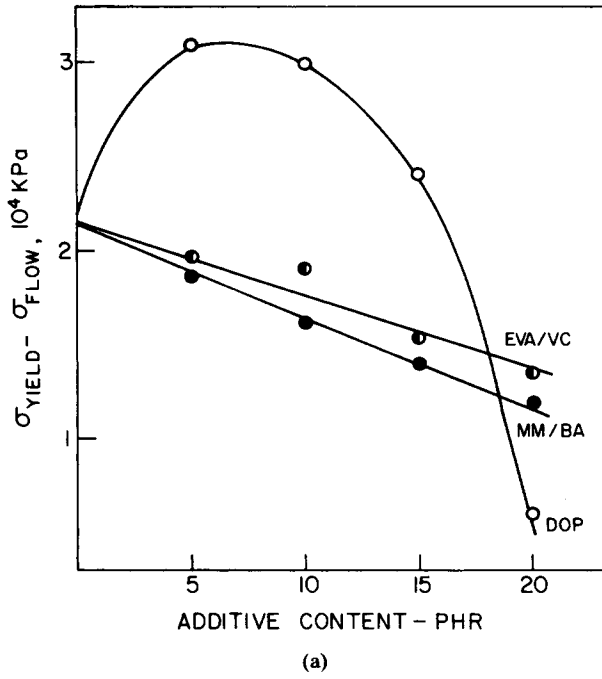


Fig. 6. (a) The stress drop $\Delta\sigma$, and (b) the maximum negative slope $-(d\sigma/d\epsilon)_{max}$ in the yield region of PVC blends.

at which the elastic modulus attains a maximum.¹⁷ Brown and Stevens¹⁷ attributed the minimum in impact strength to a combined effect of the stress necessary to initiate a craze at the crack tip and the maximum value the elastic modulus attains at that plasticizer level.

The yield behavior of the PVC blends is strongly affected by the type and level of additive. The yield strain for both polymer blends was not affected by the polymeric additive; however, that of DOP blends first decreases upon the incorporation of DOP, attaining a minimum value at about 10 phr DOP, and then gradually increases. Simultaneously, the yield stress linearly decreases with increasing the acrylic rubber content, although not as sharply as was reported for PVC-CPE blends.⁷ At the same time, the yield stress of PVC blends with EVA-VC or DOP is not significantly affected up to a level of about 10 phr additive (an important fact from an engineering point of view) but sharply declines at higher additive contents to values much lower than those obtained for the PVC-acrylic rubber blends. The most pronounced effect the additives have on the yielding of PVC is on the slope of the stress-strain curve in the yield region. This yield zone becomes broader with increasing additive content, indicating a more homogeneous, delocalized deformation process. The strain-softening process occurring during yielding can be characterized by its intensity—the difference between the upper and lower yield stresses $\Delta\sigma_y$, and by its rate—the maximum negative slope of the stress-strain curve $(d\sigma/d\epsilon)_{\max}$. As seen in Figure 6, both gradually decrease with increasing the content of either rubbery additive, as recently reported for PVC-CPE blends⁷ but not as sharply. It is rather interesting to observe the change in the two parameters describing the yield zone in PVC-DOP blends. The $\Delta\sigma_y$ first markedly increases upon the addition of DOP, attaining a maximum at a

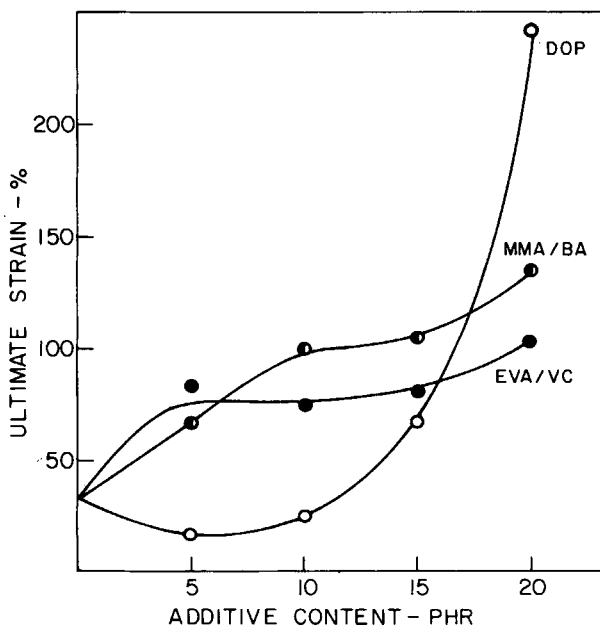


Fig. 7. Ultimate elongation of PVC blends as a function of additive content ($\dot{\epsilon} = 1.3 \text{ min}^{-1}$).

DOP content between 5 and 10 phr and then sharply decreases to a value lower than 1 kg/mm^2 . At the same time, the rate parameter $-(d\sigma/d\epsilon)_{\text{max}}$ sharply increases to a maximum value at 10 phr DOP, followed by a steep decline, attaining about the same value exhibited by the other blends, all containing 20 phr additives.

It is not worth paying too much attention to the blend's tensile strength since it is mainly determined by its deformability. In cases in which the material is deformed through a fully developed neck, the tensile strength is higher than the flow stress and in certain cases, even higher than the yield stress. In all cases in which the neck is only partially developed, the tensile strength is either equal to the flow stress or, if failure occurs just beyond yielding, the material fails at a stress level between the yield and flow stresses. Therefore, the more significant characteristic of failure is the ultimate strain, which is strongly affected by the various additives through their influence on the irreversible deformation mechanism. As can be seen in Figure 7, the elongation at break of PVC-DOP blends first decreases, attaining a minimum value at 5–10 phr DOP, and then sharply increases up to about 240% at 20 phr DOP. One should actually expect a gradual increasing ultimate strain as a result of the linearly decreasing blend T_g (mentioned above), which is the case for blends containing DOP at levels higher than 15 phr. However, at the lower plasticizer contents the dominating factor is instead the increasing crystallinity reported above (crystal morphology and DOP location also should be considered). As was shown in Figure 4, the crystallinity increases in blends containing up to 10 phr DOP. At higher DOP content the conventional plasticizer effect takes over, resulting in rising ultimate elongations. Thus, at low DOP contents the PVC undergoes a very nonuniform deformation, which is reflected by an intensely high-rate stress-softening process (see Fig. 6); only a few coarse shear bands are formed, no neck is developed, and an early failure occurs. On the other hand, at the higher DOP contents the PVC is deformed in a rather uniform manner so that failure is postponed to very high elongations. The two blend systems containing increasing amounts of rubbery modifiers exhibit gradually increasing elongations at break (see Fig. 7). Their efficiency in postponing failure is slightly different, and both are much less

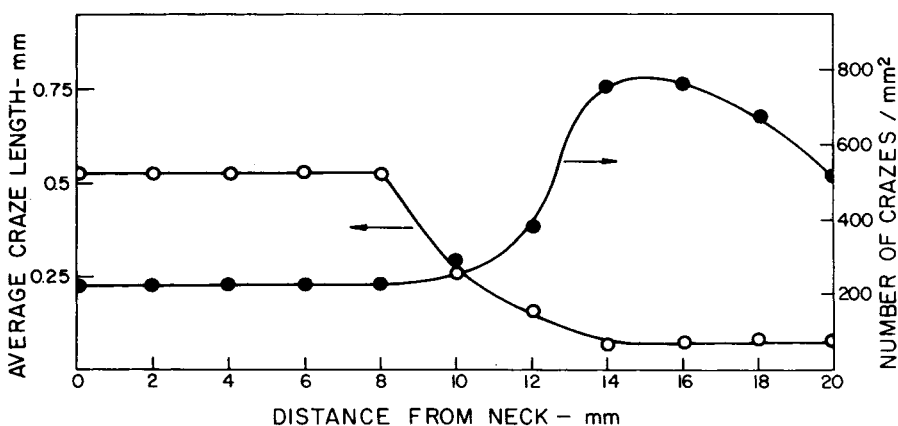


Fig. 8. The changes of length and density of crazes along a stretched rigid PVC specimen.

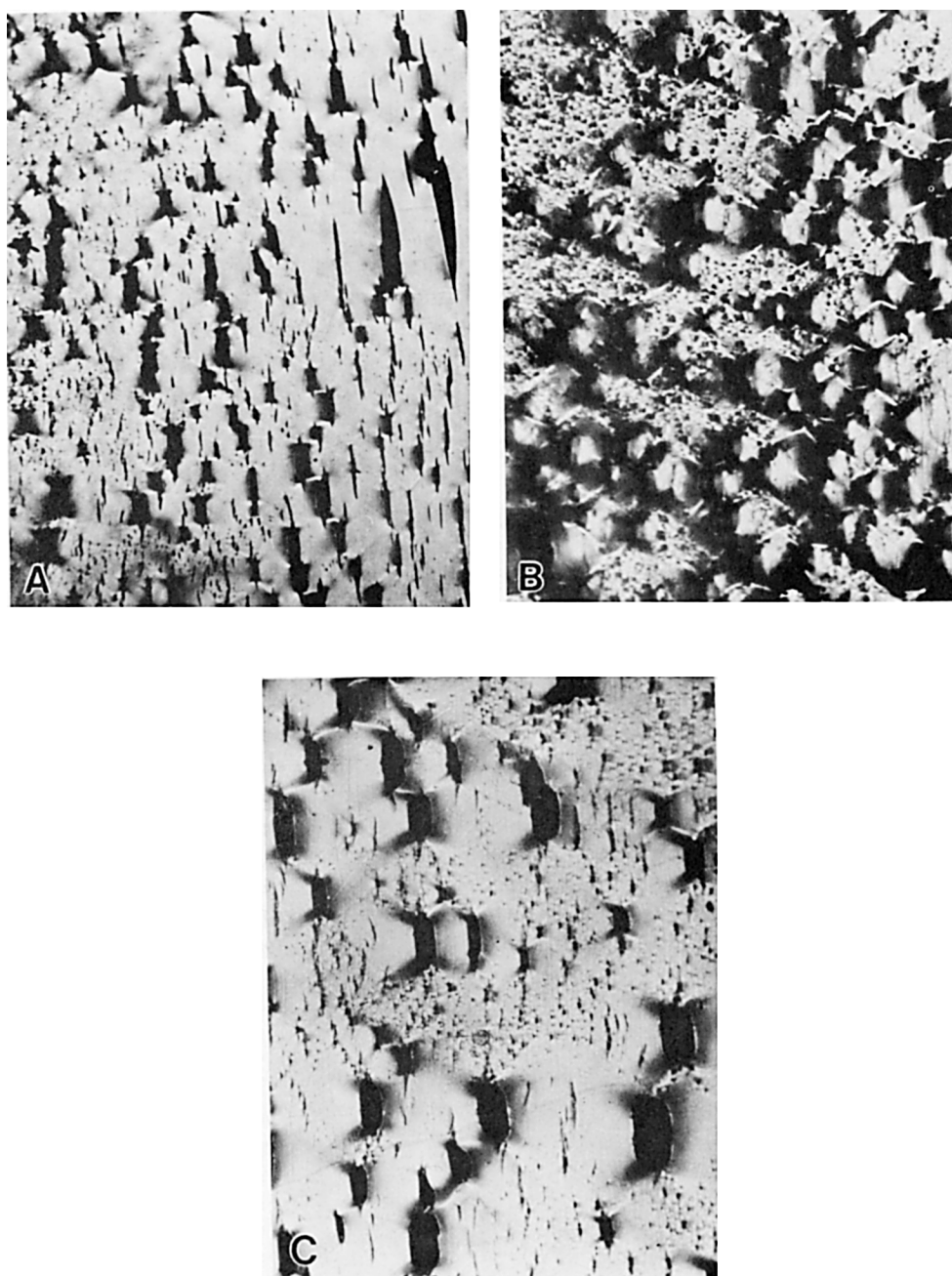


Fig. 9. Optical micrographs of the necked-unecked transition region in stretched rigid PVC: (a) crazes in the transition region; (b) crazes terminated by shear bands at their tips; (c) a higher magnification of the region shown in (b).

effective in this regard than CPE.⁷ The latter raises the PVC ultimate elongation to 150%, already at a 2% level, whereas the currently studied polymers require 20 phr in order to attain similar values. Nevertheless, increasing amounts of the modifiers result in a more homogeneous deformation, as has been shown in Figure 6. At this point it should be noted that in spite of the rather high ultimate elongations in some of the ductile materials, no high values of tensile strength were obtained, indicating that no significant PVC molecular orientation occurred. Thus, in the plasticized systems, high strains are achieved through molecular sliding, whereas in the modifier-containing blends the high elongations obtained may mainly result from their two-phase morphology.³⁻⁵ As can be seen in Figures 2 and 3, the stress-strain curves of the two rubbery modifiers exhibit very low stresses and very high ultimate elongations relative to those of PVC. This rubbery behavior is not fully reflected by the tensile behavior of the blends owing to their morphology.

The microdeformation mechanisms in PVC and its blends were studied by stretching the materials in the optical microscope. The observations made during the stretching of PVC were very similar to those recently reported⁷ for another PVC grade; however, additional important observations were made during the present work (for the convenience of the reader the complete picture will be described). When PVC is stretched a sharp neck is first formed. As recently shown,⁷ no further stretching is required because crazing, a time-dependent process, is initiated adjacent to the sharp neck edge. With

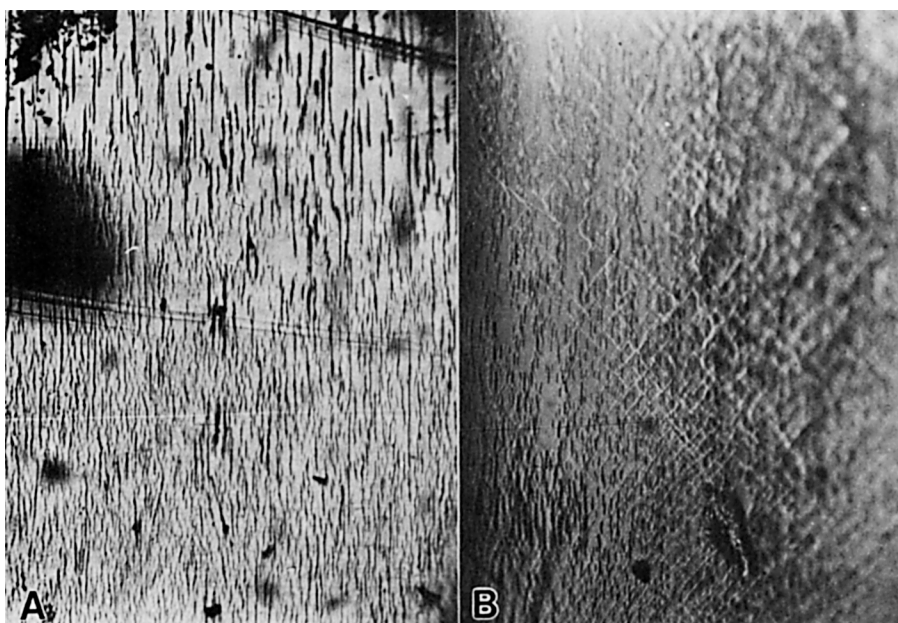


Fig. 10. Optical micrographs of the necked-unnecked transition region in stretched and plasticized (10 phr) PVC: (a) profused crazing in the unnecked zone; (b) interaction between pre-existing crazes and shear bands formed in the necked zone.

time and/or stress, the crazed region gradually extends farther into the unnecked region and the crazes grow in number as well as in size. Siegmann et al.⁷ have followed the time dependence of craze nucleation and growth at a constant distance of about 1 mm from the neck edge. They have observed that initially the number of crazes sharply increases with time and then levels off at about 500 crazes mm^{-2} . Simultaneously, the average craze length increases linearly with time (during an observation time of 22 min), with no tendency to level off. In the present study, the equilibrium distribution of craze density and length along the stretched specimens, rather than their time dependence at a certain location, were measured. Optical micrographs were taken every 2 mm along the longitudinal axis of the specimen. Since crazing is a time-dependent process, the first micrograph was taken an hour after stretching the specimen to an extent required for neck formation (assuming that by then the tensile stresses have relaxed to below the critical values for crazed initiation). Rather interesting profiles were obtained, as seen in Figure 8. At a distance up to 8 mm from the neck edge, both craze average length and density were found to be constant, ~ 0.5 mm and ~ 200 mm^{-2} , respectively. In this region the stresses were sufficiently high to form a craze network in which the density is relatively low and the average length is quite high, probably due to coalescence of crazes, at least as observed by optical microscopy. With greater distance from the neck edge, the craze density first increases, attains a maximum value of approximately 800 mm^{-2} , and then decreases until no crazes are further observed. Simultaneously, the average craze length gradually decreases. (At the far end of the specimen the measured values are not accurate because of the difficulties encountered in taking into account the



Fig. 11. Shear banding in homogeneously deformed plasticized (20 phr) PVC.

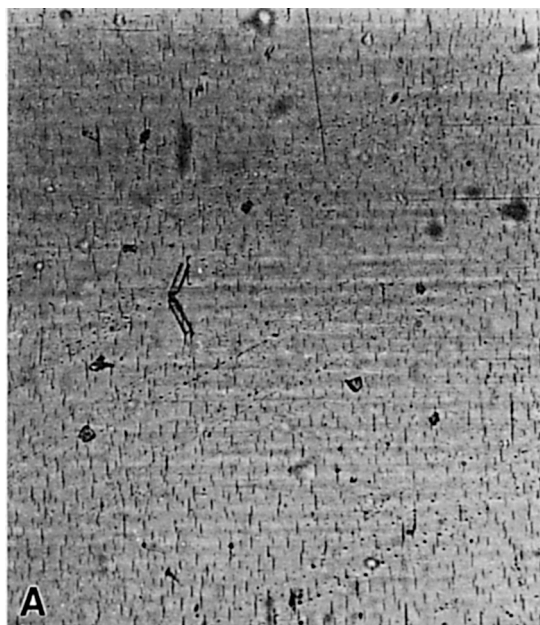


Fig. 12. Optical micrographs of stretched PVC/EVA-VC blends: (a) crazing in an unstretched region; (b) crazing and cavitation in the necked region.

very small crazes). The shape of the profiles at a distance from the neck edge (> 8 mm) stems from the actual decrease in craze number and length and therefore also from the decrease in craze coalescence. It is therefore only farther out that the real craze density and length are measured, with density declining with distance; length is constant. The decreasing average length, however, is due to the declining stress profile along the strained specimen.

Upon further stretching the already necked specimen, it was especially interesting to observe the transition region between the necked and unnecked regions. In this region two main phenomena were observed, namely, interaction between crazes and shear bands and a very pronounced craze widening (see Fig. 9). The craze-shear band interactions, which were also observed in PMMA and polycarbonate,¹⁸⁻²⁰ determine the shape of the crazes. The shear bands formed at the tip of existing crazes have a blunting effect,¹⁸ preventing further craze propagation. Hence, the formation of shear bands on both craze tips results in short and "fat" crazes (see Fig. 9c), whereas shear bands formed only at one tip result in asymmetric crazes (see Fig. 9a), which continue to propagate only at one end. It is interesting to note in Figures 9a and c that the craze tips are also seen beyond the shear bands; nevertheless, they seem to be arrested and thus not able to propagate further longitudinally. At this stage it also seems that the crazes have turned into cracks; no fibrillar structure could be observed.

In PVC-DOP blends the observed irreversible deformation process was found to be dependent on the DOP content. In blends containing up to 15 phr DOP, crazes were observed in stretched strips even prior to necking. They seem to grow faster and denser with increasing DOP content (see Fig. 10a). This profuse crazing is accompanied by delayed neck formation, which is more pronounced with increasing DOP content. The plasticizer seems mainly to enhance craze nucleation by reducing the critical stress required for crazing. Upon further stretching, which is accompanied by necking, the interaction between the already existing crazes and the newly formed shear bands is very pronounced (see Fig. 10b). Since crazing is a time-dependent process, crazes of different lengths were formed that were fixed by the necking process due to the blunting effect of the shear bands. Blends containing a higher DOP content (20 phr) are quite different, undergoing homogeneous deformation and no necking, which is accompanied by profuse shear banding (no crazing), as seen in Figure 11.

In the polymer-modified PVC the observed microdeformation process is very similar to that observed in PVC-CPE.⁷ The craze density is higher than in the unmodified PVC, and the crazes are much shorter (see Fig. 12a). With increasing modifier content more shear bands are also observed in the unnecked region, and the density of the shorter crazes appears to decrease while profuse cavitation, which accompanies the deformation, is taking over (see Fig. 12b). At high modifier content the voiding density is very high, making optical microscopic examination impossible.

DISCUSSION

The tensile mechanical properties of the PVC studied here and its blends are very sensitive to deformation rate. Changing the latter from 0.51 to only 1.3 mm^{-1} reduces, for example, the ultimate elongation of the PVC from 160

to 39%. This large rate effect may be due to the specific choice of deformation rates, which are for the currently studied PVC on two opposite sides of the ductile to brittle transition. Uitenham and Geil²¹ have reported such a transition at a rate of about 0.3 min^{-1} for an extruded rigid PVC. However, plasticization was found to lower this rate sensitivity. The tensile behavior of the plasticized PVC was found to be determined by two competing effects, namely, crystallinity and plasticization. At low DOP contents the predominating effects of crystallinity and profuse crazing result in an inhomogeneous deformation and a rather brittle fracture, even more brittle than that of rigid PVC. At high plasticizer content, plasticization and profuse shear banding result in a homogeneous and ductile deformation. Both elastomeric modifiers result in increasing ductility, even at a content as low as 5 phr. Their incorporation in increasing amounts probably reduces the stress required for shear banding initiation, resulting in fine shear band formation throughout the sample and a more homogeneous deformation and thus enabling the material to attain a higher ultimate elongation. In the lower deformation rate experiments (not shown), the plasticized blends exhibit a gradually increasing elongation with DOP content instead of the first decreasing elongation obtained at the higher strain rate. This different behavior may stem from the energy-absorbing profuse crazing described above, which at lower deformation rates has sufficient time to develop (crazing is a time-dependent phenomenon²²). Moreover, these crazes are arrested by shear bands, as shown above, and so are prevented from developing into cracks. On the other hand, the addition of the rubbery modifiers up to a content of 10 phr also results in increasing elongation, similar to that of the PVC-DOP blends of the same additive content. However, at higher modifier content the ultimate elongation gradually decreases in spite of the deformation mechanism, which should have led to a more homogeneous deformation. The difference in behavior between plasticized and modified PVC is probably mainly due to the difference in their morphology, namely, a one- or two-phase structure. In plasticized PVC, the homogeneous single-phase PVC-DOP blend particles are the morphological units, which all undergo similar deformation, whereas in the modified two-phase system the rubbery phase undergoes a much higher deformation than the primary PVC particles.⁷ The difference between the two is more pronounced in the low-rate experiments in which the ultimate elongations are much higher than in the high-rate tensile tests.

The stress at fracture in plasticized PVC decreases with DOP content as a result of the decreasing flow stresses (lower T_g). However, in the two-phase modified PVC (constant T_g), the flow stresses are only slightly affected by the modifier content. Since no significant strain-hardening effects were observed, the ultimate stress is quite similar to the flow stress and therefore is also only slightly affected by the modifier content.

The elastic modulus of modified PVC linearly decreases with increasing content of either rubbery additives, obeying a linear mixing rule. In the plasticized system, on the other hand, the modulus is predominantly affected by the increasing crystallinity at low DOP content and by the plasticization at high DOP content.^{14,16} Similar general behavior is exhibited by the yield stress, which is also a structure-sensitive mechanical property. Our modifiers are not as effective in reducing the yield stress as CPE.⁷ The latter is similar in this respect to the plasticizer. The yield zone in the stress-strain curves is

very sensitive to the PVC blend composition. The two parameters describing the yield zone, $\Delta\sigma_y$ and $(d\sigma/d\epsilon)_{\max}$, change differently for the modified and plasticized PVC. Both gradually decrease with increasing rubbery modifier content, reflecting the increasing strain delocalization and thus increasing strain homogeneity, which stem from the increasing shear band density.^{23,24} On the other hand, when increasing amounts of plasticizer are added to the rigid PVC, the yielding zone parameters first sharply increase, attaining their maximum values at about 10 phr DOP, and then rapidly fall to values below those obtained for the modified material. This behavior is also a result of the competition between the plasticization and crystallization effects. These changes in the yield zone of the stress-strain curves are different from those obtained for PVC-CPE blends.⁷ In the latter, the addition of just 2 wt% CPE caused a large change in the maximum negative slope; further addition of CPE results in gradually decreasing values of the parameters chosen to describe the yield zone. These differences probably stem from the different morphology of the various two-phase modified PVC.

The microdeformation observed in PVC sheets was found generally to be in agreement with recently published observations.¹⁷ PVC reacts to external stresses by the formation of both crazes and shear bands. Since crazing is a time-dependent process, shear banding is the predominant mechanism, despite the higher critical stresses required for shear banding than for crazing. The interaction between the two mechanisms of irreversible deformation is rather intriguing and was found to be pronounced in the necked-unnecked transition zone. The important role played by the shear bands in arresting the crazes was very clearly demonstrated. The addition of increasing amounts of plasticizer to the rigid PVC causes lowering of the critical stress for crazing, resulting in faster and denser craze growth as well as delayed necking. The craze-shear band interaction in plasticized PVC is even more pronounced than in the plain polymer. At high plasticizer content (> 20 phr), the critical stress for shear band initiation becomes lower than that for crazing so that profuse shear banding and no crazing is observed, resulting in a homogeneous deformation and thus high ultimate elongation. In the rubber-modified PVC, increasing amounts of modifier reduce the shear band initiation stress, resulting in the formation of more shear bands and fewer crazes. In blends containing a high modifier concentration, deformation is accompanied by dense cavitation, which is not observed in the plasticized PVC. The absence of cavitation in the latter may be one of the major reasons for the much higher ultimate elongations observed in plasticized PVC compared with rubber-modified polymer.

The comparison made here between the effect of a plasticizer and a rubbery modifier on the mechanical behavior of rigid PVC sheds more light on the deformation mechanism of polymers in general and of PVC and its blends in particular.

References

1. D. M. Gezovich and P. H. Geil, *Int. J. Polym. Mater.*, **1**, 3 (1971).
2. C. Singleton, J. Isner, D. M. Gesovich, P. K. C. Tsou, and P. H. Geil, *Polym. Eng. Sci.*, **14**, 371 (1974).
3. F. Haaf, H. Brewer, and J. Stabenow, *Angew. Makromol. Chem.*, **58/59**, 95 (1977).

4. D. Flischner, E. Fischer, and J. Brandrup, *J. Macromol. Sci. Phys.*, **B14**, 17 (1977).
5. A. Siegmann and A. Hiltner, *Polym. Eng. Sci.*, **24**, 869 (1984).
6. H. Brener, F. Haaf, and J. Stabenow, *J. Macromol. Sci. Phys.*, **B14**, 387 (1977).
7. A. Siegmann, L. K. English, E. Baer, and A. Hiltner, *Polym. Eng. Sci.*, **24**, 877 (1984).
8. W. P. Brennan, Perkin Elmer Therm. Anal. Study No. 22, 5 (1977).
9. H. E. Bair, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981 p. 878.
10. T. G. Fox, *Bull. Amer. Phys. Soc.*, **1**, 123 (1956).
11. D. Hardt, *Brit. Polym. J.*, **1**, 225 (1969).
12. C. F. Hammer, *Macromolecules*, **4**, 69 (1971).
13. K. Marcincin, A. Romanov, and V. Pallak, *J. Appl. Polym. Sci.*, **16**, 2239 (1972).
14. J. V. Koleske and L. H. Wartman, *Poly(Vinyl Chloride)*, Gordon and Breach, New York, 1969.
15. N. Kinjo and T. Nakayawa, *Polym. J.*, **4**, 143 (1973).
16. K. A. Burghansen and K. P. Paul, *Kunstst.*, **70**, 7 (1980).
17. H. R. Brown and G. Stevens, *J. Mater. Sci.*, **13**, 2373 (1978).
18. R. P. Kambour, *J. Polym. Sci., Macromol. Rev.*, **7**, 1 (1973).
19. S. B. Newman and I. Wolock, *J. Res. Nat. Bur. Stand.*, **58**(6), 339 (1957).
20. G. Jacoby and E. Cramer, *Rheol. Acta.*, **7**, 23 (1968).
21. L. C. Uitenham and P. H. Geil, *J. Macromol. Sci.-Phys.*, **B20**, 593 (1981).
22. A. S. Argon, R. E. Cohen, O. S. Gebizlioglu, and C. E. Schwier, *Advan. Polym. Sci.*, **52 / 53**, 275 (1983).
23. P. B. Bowden, *Phil. Mag.*, **32**, 455 (1970).
24. P. B. Bowden and S. Raha, *Phil. Mag.*, **32**, 463 (1970).

Received March 10, 1986

Accepted August 12, 1986