

The deformation behaviour of thin films of poly(styrene–acrylonitrile)/poly(styrene–maleic anhydride) blends

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The deformation behaviour of thin films of poly(styrene–acrylonitrile) (SAN) and poly(styrene–acrylonitrile)/poly(styrene–maleic anhydride) (SAN/SMA) blends was investigated at a range of different temperatures and strain rates. It is found that SAN shows a transition from shear yielding to disentanglement-induced crazing with rising temperature or decreasing strain rate. Addition of SMA leads, in the regime where SAN shows shear yielding, to more crazing and thus a more brittle behaviour. In the regime where SAN shows disentanglement crazing, addition of up to 50 wt% of SMA apparently leads to a rise in the monomeric friction coefficient in the blend, and therefore to a suppression of the disentanglement crazing mechanism. Still higher levels of SMA addition lead to pure crazing.

(Keywords: crazing; disentanglement; entanglements; miscible blend; styrene–acrylonitrile; styrene–maleic anhydride; monomeric friction coefficient)

INTRODUCTION

The deformation mechanism in thin films of amorphous polymers has been studied rather extensively over the past years¹. Most of these studies have focused on films of a single homo- or copolymer. Less is known, however, about the way in which two mutually miscible polymers influence each other's molecular deformation mechanisms. In this study the deformation behaviour of a blend of a low-entanglement-density polymer, poly(styrene–maleic anhydride) (SMA), and a higher-entanglement-density polymer, poly(styrene–acrylonitrile) (SAN), is investigated.

When thin films of amorphous polymers like SAN and polycarbonate (PC) are strained in tension, two modes of deformation may be observed, shear deformation and crazing¹. Shear deformation zones (DZs) are localized shear-necked zones; crazes are fibrillated structures that are still load-bearing. The formation of crazes is accompanied by the loss of entanglement. This loss can be brought about by either chain scission or chain disentanglement.

In the case of craze formation via chain scission, the energy to create new void surface area is not just the van der Waals surface energy of intermolecular separation, γ , but will also include the energy needed to break the primary covalent bonds of the chains that must undergo scission. The resulting surface energy Γ is given by Kramer¹ as:

$$\Gamma = \gamma + d\nu_e U/4 \quad (1)$$

with d the root-mean-square end-to-end distance of a chain of molecular weight M_e (the entanglement molecular weight), ν_e the density of chains between entanglement junction points and U the energy needed to break a single primary polymer chain bond. Since ν_e depends on the entanglement molecular weight M_e as:

$$\nu_e = \rho N_A / M_e \quad (2)$$

with ρ the density and N_A Avogadro's number, and d depends on M_e as:

$$d \propto (M_e)^{1/2} \quad (3)$$

it is clear that the energy needed for the formation of new surface during the growth of a craze rises with increasing entanglement density (or decreasing M_e). Berger and Kramer² relate Γ to the critical stress for craze propagation, S_c , at a given strain rate $\dot{\epsilon}$ as:

$$S_c \propto [\Gamma \sigma_y(T)]^{1/2} (\dot{\epsilon})^{1/(2n)} \quad (4)$$

where n is an empirical constant (typically between 10 and 20) and $\sigma_y(T)$ the yield stress. The equivalent expression for localized shear deformation is given by Berger and Kramer² as:

$$S_{DZ} \propto \sigma_y(T) (\dot{\epsilon})^{1/n} \quad (5)$$

When the entanglement density increases, Γ will rise and so will the critical crazing stress S_c . The value of S_{DZ} is independent of Γ and therefore, going from low- to higher-entanglement-density polymers, one finds a transition from crazing to shear yielding when deformation is performed at moderate conditions.

When two miscible polymers are mixed, the entanglement density ν_e of the resulting blend lies in between the ν_e

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values of the original materials. Wu³ has studied the entanglement density in miscible polymer blends. He shows that in Θ blends, where the Flory–Huggins interaction parameter $\chi=0$, the entanglement density is linearly additive with respect to the volume fraction of blend composition. However, in blends with $\chi<0$, the entanglement density was found to be smaller than linear additivity. The deviation increases with increasing strength of interchain interaction (i.e. decreasing χ). Thus, one expects the deformation behaviour of a high-entanglement-density polymer to change, at moderate conditions, from shear-dominated towards crazing-dominated when a low-entanglement-density polymer is added (whether χ be zero or smaller than zero). This is because the entanglement density of the resulting blend will be lower than that of the pure high-entanglement-density polymer.

As pointed out above, low-entanglement-density polymers like polystyrene and SMA deform at room temperature by the formation of crazes. There is indeed substantial evidence^{4,5} that this crazing is preceded by breaking of part of the polymer chains in order to create the fibrillar structure. Closer to T_g , however, the mechanism can change and the films can form deformation zones upon straining. At these higher temperatures the polymer chains are more free to move and redistribute the applied strains without the necessity of breaking chains. In other words, S_{DZ} drops faster than the crazing stress with rising temperature.

High-entanglement-density polymers, such as, for instance, polycarbonate (PC), poly(ether sulfone) (PES) and — to a lesser extent — SAN, form DZs upon straining at room temperature. However, at temperatures closer to T_g , these polymers can form crazes and are known to show brittle failure under certain circumstances⁶. Plummer and Donald^{5,7} have shown that during the formation of these crazes in PC and PES the chains disentangle rather than break. McLeish *et al.*⁸ have modelled this as a forced reptation mechanism. At these higher temperatures chain movements are relatively easy. Under the applied load the chains are forced to move in a certain direction and the chain ends are able to disentangle.

As can be expected, the appearance of this kind of crazing is dependent on the molecular weight M_w , monomer molecular weight M_0 , strain rate, temperature and the friction between the polymer chains. The frictional force, f_d , acting along the polymer chain, is then given by⁹:

$$f_d \propto v \zeta_0 M_w / M_0 \quad (6)$$

where v is assumed to be proportional to the applied deformation rate $\dot{\epsilon}$. ζ_0 is the monomeric friction coefficient, which is dependent on temperature through an Arrhenius factor $\zeta_0 = A \exp(E/RT)$. The monomeric friction coefficient is the inverse of the monomeric mobility μ_0 , and therefore will change when the environment of the polymer chain under consideration changes.

Now consider a chain in a polymer that shows disentanglement crazing above a certain temperature. Addition of a small amount of a second polymer changes not only the M_e , but also the environment of the chain and therefore the monomeric friction coefficient. The frictional force working on the chain when the material is stressed will change with ζ_0 . It might therefore be

possible to slow down or accelerate the disentanglement process that leads to crazing by addition of a small amount of a different component.

Thus, a rise in the frictional force due to changing blend composition may make chain disentanglement less likely to occur and change the deformation behaviour to either crazing via chain scission or shear deformation. This effect will probably be most significant in the regime where disentanglement crazing of the first polymer just becomes a viable mechanism.

So, a change in composition of a miscible blend leads to a different M_e as well as ζ_0 . Apart from the dominant effect that the altered M_e will have on the deformation behaviour of the blend, a change in ζ_0 can, in certain regimes, also have an influence.

The third parameter that can change when blend composition is altered is the T_g . The relative distance from T_g is important for the way in which a polymer system will deform under applied stress. Low-entanglement-density polymers will show an increased tendency to shear when deformed closer to T_g , whereas high-entanglement-density polymers will show an increased tendency towards disentanglement crazing.

SAN and SMA are miscible over a certain range of copolymer composition. Addition of SMA to the SAN will probably result in a lowering of the entanglement density and an embrittlement of the system.

Also, Kim *et al.*¹⁰ report a weak exothermic interaction between monomeric maleic anhydride and acrylonitrile. Thus, there might be an enhanced interaction in SAN/SMA blends, which could lead to a higher friction coefficient. Therefore, in spite of the fact that SMA is a lower-entanglement-density polymer and therefore intrinsically more brittle than SAN, SMA might, when added in small amounts, suppress the disentanglement crazing that SAN is expected to show at higher temperatures or lower strain rates.

Addition of SMA to SAN will result in an increase in T_g of the system. What influence this will have on the resulting deformation behaviour is not obvious *a priori*.

EXPERIMENTAL

Two different molecular weights of either SAN and SMA are used. All four polymers had approximately the same copolymer content. The materials used can be found in Table 1. The solvent used for processing the films is methyl ethyl ketone (MEK). Films are made using a method based on that developed by Lauterwasser and Kramer¹¹. The different polymers and blend compositions are dissolved in MEK. A slide is dipped in the solution and drawn out at a constant rate.

Table 1 Materials

Type	Copolymer content (% AN)	M_w (kg mol ⁻¹)	M_e^a (kg mol ⁻¹)
SAN1	25.8	200	9.5
SAN2	27.3	125	
Type	Copolymer content (% MA)	M_w (kg mol ⁻¹)	M_e^a (kg mol ⁻¹)
SMA1	29	210	21
SMA2	29	66	

^a Determined from the plateau modulus in the rubbery regime

Appropriate-sized pieces of film are cut out with a scalpel and floated off on a water bath. The films are then picked up on copper grids, which have been coated previously with the same polymer. In order to bond the films to the grids they are exposed to solvent vapour for a few seconds. The films are then dried at room temperature under vacuum for at least one night.

Films are tested by straining the grids in a mini tensile testing machine, the Minimat from Polymer Laboratories. The strain rate can be varied between $\dot{\epsilon} = 10^{-2}$ and 10^{-6} s^{-1} . Testing temperature can be varied from room temperature up to 200°C . An optical microscope with a magnification of $100\times$ is fitted on the Minimat in order to follow the deformation process. After deforming the samples, they are investigated under an optical microscope (Carl Zeiss Jenapol) at a magnification of $320\times$ in reflected light.

Individual grid squares may be cut out for investigation in a transmission electron microscope. The TEM used is a JEOL JEM 2000 operated at 200 kV.

Films were strained at different strain rates and different temperatures. The strain at which the first visible deformation occurred was monitored and the nature of the deformation, i.e. crazing, localized shear yielding (DZs) or mixed mode, was investigated under the optical microscope and in the TEM.

RESULTS

Poly(styrene-acrylonitrile)

The critical strain at which visible deformation occurs (strain for deformation onset, *SDO*) as a function of temperature for pure SAN1 films at a strain rate of 10^{-3} s^{-1} is shown in *Figure 1*. Investigation of different films with TEM reveals that the deformation mechanism of the films changes with changing temperature. At room temperature the main mechanism is the formation of DZs; very little fibrillation is found in the deformed regions. The *SDO* for DZs is relatively high. On raising the

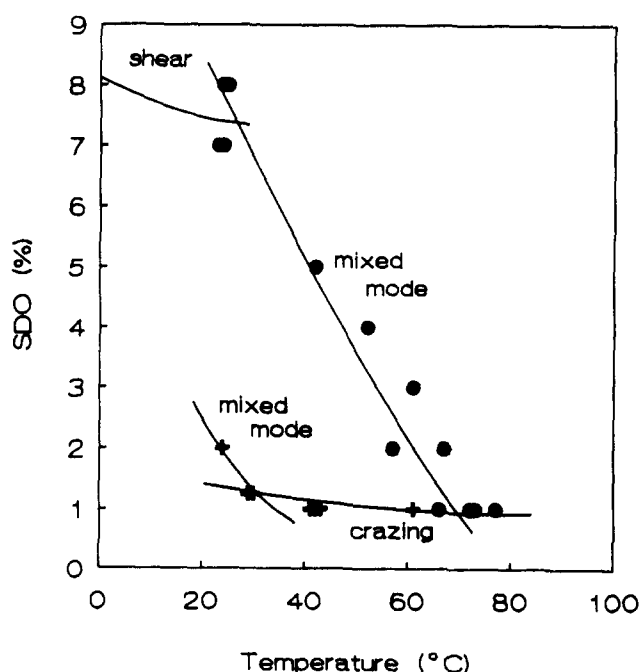


Figure 1 Percentage strain for deformation onset for SAN1 as a function of straining temperature: (●) $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$; (+) $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

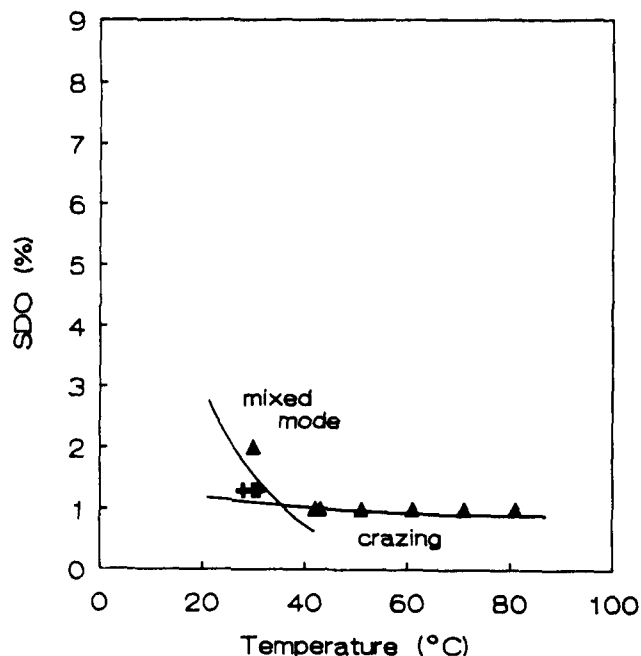


Figure 2 Percentage strain for deformation onset for SAN2 as a function of straining temperature: (▲) $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$; (+) $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

temperature crazing becomes more and more important, but shear deformation still exists, mainly at the craze tips. This is clearly a mixed-mode mechanism. At an even higher temperature, a rather pronounced transition to a pure crazing mechanism occurs. Pure crazing occurs at a very low *SDO*. As can be seen in *Figure 1*, the *SDO* drops from about 8% for the shear-dominated mechanism to 1% for the pure crazing mechanism.

When the strain rate is lowered to 10^{-5} s^{-1} a profound change occurs in the deformation mechanisms as a function of temperature (*Figure 1*). Crazing is the principal deformation mechanism over almost the whole temperature range and only below 40°C does some shear deformation occur near the craze tips. The *SDO* is correspondingly lowered compared with that in the $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$ case. The pure shear regime is not found in this case.

SAN2, which has a lower molecular weight than SAN1, behaves in a more brittle fashion. At a strain rate of 10^{-3} s^{-1} the films tear at a strain of 3% or less. It is not clear whether there has been any crazing preceding film breakage.

The results for the strain rates 10^{-4} and 10^{-5} s^{-1} are given in *Figure 2*. From TEM it is seen that at 30°C there is a strongly crazing-dominated mixed-mode mechanism. At higher temperatures there is only crazing.

Poly(styrene-acrylonitrile)/poly(styrene-maleic anhydride) blends

As is shown for the pure SAN case, a high strain rate leads to a high *SDO* and shear-like behaviour, whereas lowering of the strain rate leads to lower *SDO* and a more brittle behaviour. The general trends are that addition of SMA leads to embrittlement of the blend and lowering of the *SDO* in the case of the high strain rate and shear-like behaviour. At lower strain rates and low *SDOs*, however, addition of a little SMA slightly raises *SDO* and the proportion of shear in the deformation. Addition of more SMA then leads to lowering of the *SDO* and a pure crazing behaviour (see *Figure 3*).

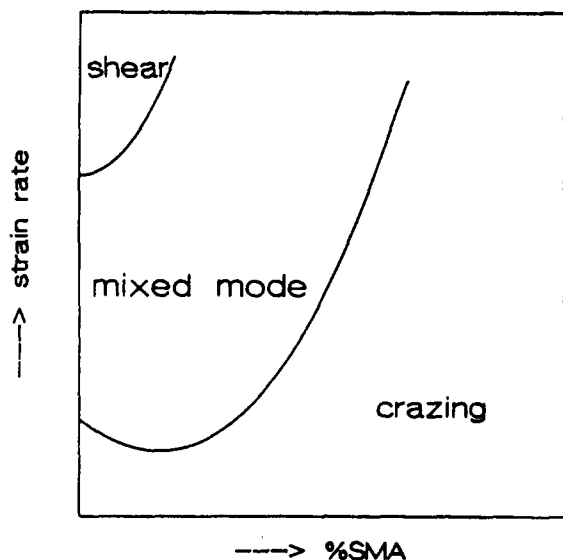


Figure 3 Qualitative representation of the influence of blend composition and strain rate on the mechanical behaviour of the films

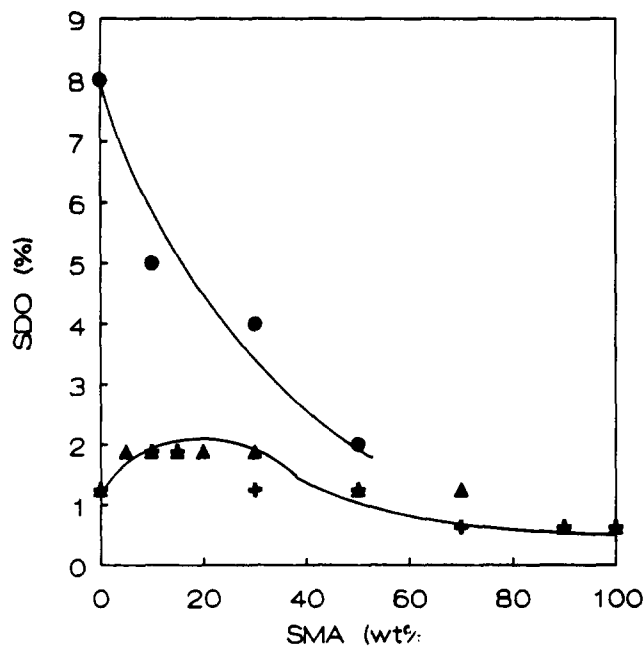


Figure 4 Percentage strain for deformation onset at 28°C for SAN1/SMA1 blends as a function of SMA content: (●) $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$; (▲) $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$; (+) $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

At a strain rate of 10^{-3} s^{-1} the *SDO* at room temperature decreases upon adding SMA1 to SAN1 (see Figure 4). The deformation mechanism changes from shear-dominated for 0 wt% SMA1 to mixed-mode up to 30 wt% SMA1. Above 50 wt% SMA1, the films break in a brittle way. The temperature (T_i) at which the transition from mixed mode to pure crazing takes place is given in Figure 5. This temperature is not affected by the percentage of SMA1 added. The blend with 90 wt% SMA1 and the pure SMA1 are also brittle at higher temperatures.

At a strain rate of 10^{-4} s^{-1} at room temperature, pure SAN1 deforms via a mixed-mode mechanism in which crazing dominates. Upon adding a small amount of SMA1 the deformation becomes more dominated by shear, although it is still mixed-mode. The *SDO* rises from 1.3% for pure SAN1 to 1.9% for a blend with an amount

of SMA1 up to 30 wt% (see Figure 4). Also these blends show visually an increased tendency to shear. For higher amounts of SMA1 the *SDO* falls again to 1.3% and eventually to 0.6%. (These differences may seem small, but they are certainly significant. For instance, at a strain rate of 10^{-5} s^{-1} an *SDO* of 0.6% means that deformation starts after straining for 10 min, while an *SDO* of 1.9% only gives visible deformation after more than 30 min of straining.) Films with 90 wt% SMA1 or more break in a brittle way upon straining. The temperature at which the transition from mixed mode to crazing takes place is given in Figure 5 as a function of the blend composition. The transition temperature rises with the amount of SMA1 added from 43°C for a pure SAN1 film to 61°C for a 50/50 wt% blend. Compositions with more than 50 wt% SMA1 show pure crazing over the whole temperature regime, or are brittle (90 and 100 wt% SMA1).

For $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ the *SDO* at 28°C for different blend compositions is given in Figure 4. It can be seen that there is a maximum in *SDO* of 1.9% for blend compositions with 10 and 15 wt% SMA1. TEM investigation of these blends reveals an increased tendency to shear. The films show mixed-mode behaviour up to a composition of 50 wt% of SMA1. The 70 and 90 wt% SMA1 compositions show crazing and even the pure SMA1 films sometimes visibly craze before they tear. The transition temperature from mixed-mode to pure crazing behaviour is given in Figure 5; this temperature seems to be essentially independent of blend composition. Films with an SMA1 content of 50 wt% or more show pure crazing over the whole temperature regime.

Upon adding low-molecular-weight SMA2 ($M_w = 66\,000$, approximately three times the SMA entanglement molecular weight, $M_{e,SMA} = 21 \text{ kg mol}^{-1}$) the *SDO* at room temperature and $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$ falls quite rapidly from 8% for pure SAN to 3% for 90 and 70 wt% SAN1

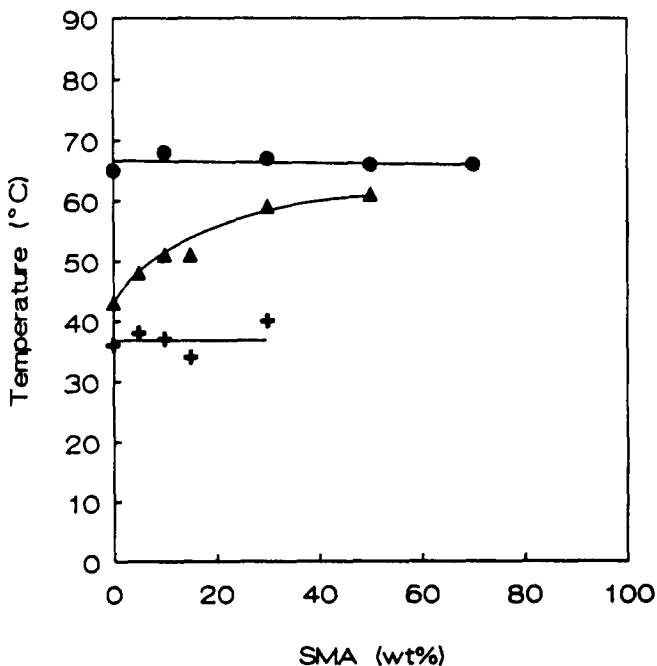


Figure 5 The transition temperature from mixed mode to crazing for SAN1/SMA1 blends as a function of SMA content: (●) $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$; (▲) $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$; (+) $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

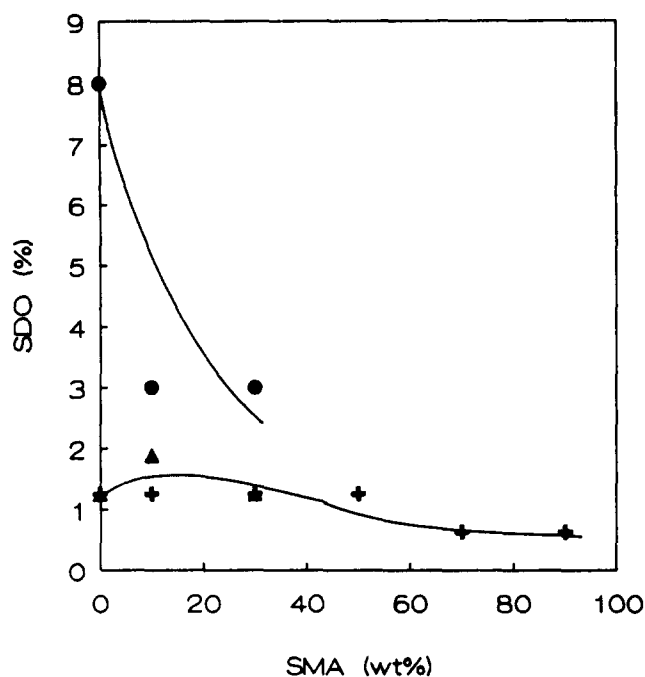


Figure 6 Percentage strain for deformation onset at 28°C for SAN1/SMA2 blends as a function of SMA content: (●) $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$; (▲) $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$; (+) $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

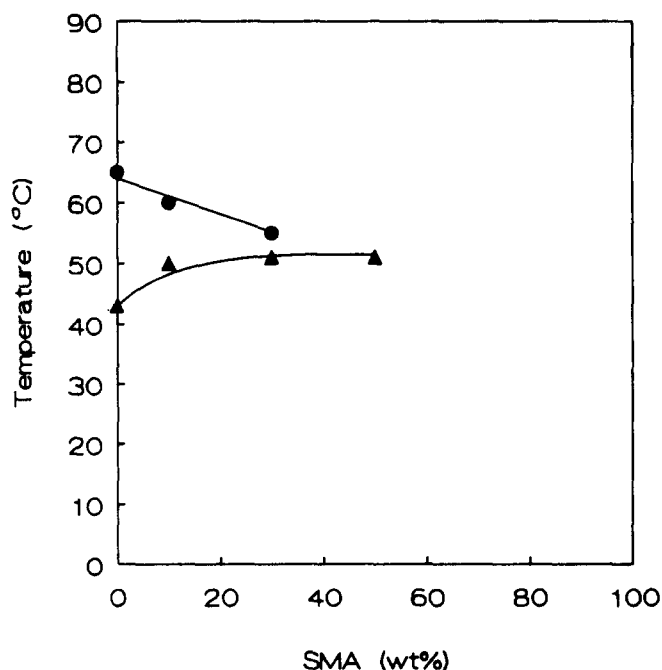


Figure 7 The transition temperature from mixed mode to crazing for SAN1/SMA2 blends as a function of SMA content: (●) $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$; (▲) $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$

blends, and the deformation becomes mixed-mode (Figure 6). The temperature at which the transition from mixed mode to crazing takes place drops as a function of composition (Figure 7). Blends with an SMA2 content of 50 wt% or more could not be measured because they were so brittle that they tore upon straining.

At 10^{-4} s^{-1} the low-molecular-weight SMA2 acts like the high-molecular-weight SMA1 in raising the strain for deformation onset (see Figure 6). Only the blends with

10 and 30 wt% SMA2 could be measured at room temperature, the other blends being too brittle. The transition temperature from mixed mode to crazing rises from 43°C for pure SAN1 to $\approx 50^\circ\text{C}$ for the 10, 30 and 50 wt% SMA blends, as can be seen in Figure 7. The other blends were too brittle at these temperatures.

The SDO at $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ only rises slightly at this strain rate with increasing SMA2 content, but this is hardly significant (Figure 6). The transition temperature from mixed mode to crazing was not measured exactly, but lies between 31 and 41°C.

DISCUSSION

Pure SAN1 films show shear-dominated deformation behaviour at room temperature and high strain rates. The fact that upon raising the temperature or lowering the strain rate the deformation becomes more and more craze-dominated indicates that this crazing is predominantly caused by disentanglement of the polymer chains, although there may of course also be some chain scission present. The entanglement molecular weight of SAN is approximately 9.5 kg mol^{-1} . For PS the M_e is ca. 19 kg mol^{-1} and for PC ca. 2 kg mol^{-1} . One would therefore expect the behaviour of SAN to lie in between the behaviour of these two. SAN shows disentanglement crazing like PC, but it shears less readily than PC.

As expected, the lower-molecular-weight SAN ($M_w = 125 \text{ kg mol}^{-1}$) behaves in a more brittle way than the high-molecular-weight samples ($M_w = 200 \text{ kg mol}^{-1}$). The shorter chains are easier to disentangle; consequently shear deformation is suppressed and the films show a lower SDO. Apparently at this lower molecular weight the crazes are less stable, and at the highest strain rate the films tear without clear crazing preceding the fracture.

Deformation in SMA, as in PS, is scission-craze-dominated ($M_{e,SMA} = 21 \text{ kg mol}^{-1}$). Therefore, one would expect that the addition of SMA1 to SAN1 would result in an increased tendency of the blend to craze and a subsequent lowering of the SDO. At the highest strain rate (10^{-3} s^{-1}) this is indeed the case. The blends show more and more crazing and less shear as the percentage of SMA1 is increased. Above 50 wt% of SMA1 no more crazing is observed and the films break in a brittle way at a strain of 1%. It is not clear whether in these cases crazes are formed at all, or if the films just break without any crazing.

More surprising is the fact that at strain rates of 10^{-4} and 10^{-5} s^{-1} the SDO rises slightly upon adding as little as 5 wt% of SMA1 to the SAN1. Also unexpected is that the transition temperature from mixed mode to crazing (T_c) as a function of SMA1 content of the blend (Figure 5) shows, for a strain rate of 10^{-4} s^{-1} , an increase with increasing SMA1 content. If one takes a temperature of, for instance, 55°C , a pure SAN1 film will craze at a strain rate of 10^{-4} s^{-1} ; adding SMA1 (ca. 25 wt%) then results in a transition from crazing to mixed-mode behaviour.

The T_g rises with increasing SMA content of the blend. A plot of the difference between the transition temperature and T_g as a function of SMA content is given in Figure 8. As can be seen, for the high strain rate, the difference between the transition temperature and T_g becomes larger when 30 wt% or more SMA1 is added (below this level there is little change). This means that the temperature regime where crazing takes place becomes broader, and

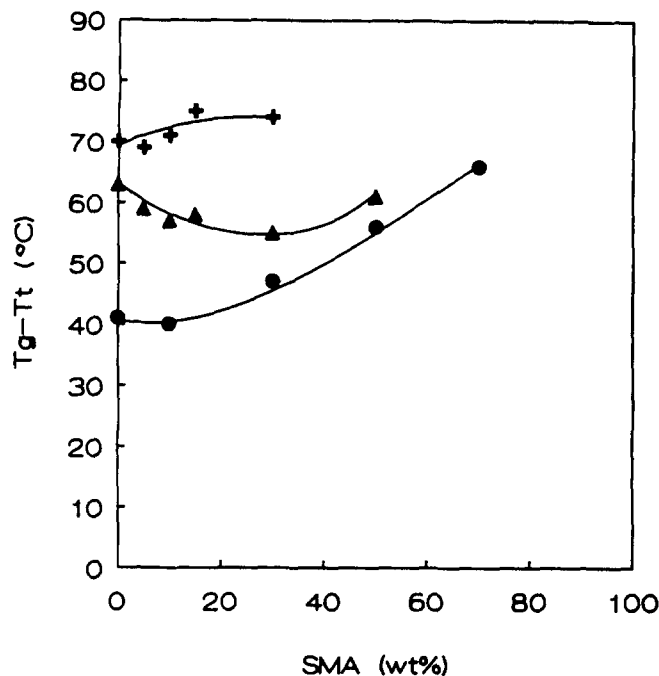


Figure 8 Plot of glass transition temperature minus the transition temperature from mixed mode to crazing (i.e. $T_g - T_t$) for SAN1/SMA1 blends as a function of SMA content: (●) $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$; (▲) $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$; (+) $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$

the blend is embrittled. Not clear in this picture is why the 10 wt% SMA1, which is already much more brittle in behaviour than the pure SAN1, has its transition temperature at the same distance from T_g as the pure SAN1. For $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ there is a minimum in the distance between T_g and the transition temperature from mixed-mode to crazing behaviour. The regime where crazing takes place thus becomes smaller and one might say the response becomes tougher with increasing SMA content. The $\dot{\epsilon} = 10^{-5} \text{ s}^{-1}$ curve is rather scattered but it looks as if the difference between the transition temperature and T_g is constant; the blend preserves approximately the same toughness when up to 30 wt% of SMA is added.

It can be concluded from these results that SMA1 is able to suppress the disentanglement crazing behaviour of SAN1. In the regime where SAN1 mostly shears, SMA1 embrittles the blend as expected. Even the low-molecular-weight SMA2, with a molecular weight of only three times the SMA entanglement molecular weight, is able to suppress the disentanglement of SAN1. However, the blends get intrinsically more brittle, which can be concluded from the fact that 50/50 wt% blends with SMA2 show complete brittle tearing at room temperature. It can therefore be concluded that the disentanglement-suppressing mechanism only works under conditions where there are no other disturbing effects, like for instance the tendency of the blend to show scission crazing.

The disentanglement crazing process is governed by molecular weight, strain rate and the monomeric friction coefficient. For the SAN1/SMA1 blends the molecular weights of both components are approximately the same, and hence this parameter cannot be governing the change in response. Potentially either or both of the entanglement molecular weight (which will increase on SMA addition) or the friction coefficient may determine the behaviour. In general, an increase in M_e will favour scission crazing, and it thus seems likely that the addition of SMA, raising

the monomeric friction coefficient in the blend, is the dominant effect. (The variation cannot simply be due to changes in T_g of the blends, or the curve for $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ in Figure 8 would not show a minimum.) The effect of the increase of the monomeric friction coefficient is most significant for combinations of strain rate and temperature where disentanglement crazing is just becoming a viable mechanism. This is because a small rise in the friction coefficient can prevent disentanglement occurring; in regimes either where disentanglement is easy (low $\dot{\epsilon}$) or quite impossible (high $\dot{\epsilon}$, low T) the change in friction coefficient is immaterial. It is for this reason that we see the most significant effect at a strain rate of $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$; the minimum in the curve in Figure 8 can then be explained in terms of the competition between ζ_0 and M_e .

For samples that show mostly shear yielding, the $\zeta_{0,\text{SAN}}$ is not of importance. However, addition of SMA, with the possibility of these chains undergoing scission, leads to embrittlement.

Composto *et al.*¹² report that in a miscible blend of two polymers, both polymers do not necessarily have the same monomeric friction coefficient; in other words the complete response of the blend cannot simply be described by a single value of ζ_0 . The ratio of the two friction coefficients is found to be not even constant as the composition is varied. Since the T_g of SMA lies well above that of SAN, it is tempting to assume that its $\zeta_{0,\text{SMA}}$ is also higher than that of SAN, and that this remains true as the composition is changed, but that $\zeta_{0,\text{SAN}}$ increases when SMA is added to the blend. At $\dot{\epsilon} = 10^{-4}$ and 10^{-5} s^{-1} , this increase in $\zeta_{0,\text{SAN}}$ is sufficient to make disentangling noticeably more difficult so that the *SDO* rises, as does the temperature of the transition from crazing to mixed mode (most pronounced for $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$). However, as the craze interface advances, the SMA chains must be accommodated too, and since their $\zeta_{0,\text{SMA}}$ is high they are likely to undergo scission. The more SMA is added to the blend, the more scission will be occurring and consequently both the *SDO* and the craze stability will drop. This effect will be even more dramatic if the added SMA is of low molecular weight, since only one or two scission events will lead to it no longer being entangled, and hence no longer load-bearing. It is therefore hardly surprising that, at SMA2 additions of greater than 50 wt%, brittle fracture intervenes so rapidly.

At high $\dot{\epsilon}$, it appears that the transition temperature is independent of composition, which at first sight does not suggest that the SMA is having a significant effect. However, as Figure 8 shows, the range of temperature over which crazing dominates is actually increasing owing to the increase in T_g .

CONCLUSIONS

We have investigated the deformation behaviour of thin films of pure SAN. It was found that SAN shows a transition from shear-yielding-dominated behaviour via a mixed-mode mechanism to disentanglement-crazing-dominated behaviour when the temperature at which the deformation is carried out is raised. Lower strain rates and lower molecular weights lead to a drop in the temperature at which the transition to the crazing mechanism takes place. SAN thus equals, as

expected, the deformation behaviour of high-entanglement polymers like polycarbonate and poly(ether sulfone). Addition of SMA to the SAN leads, as expected, in the regime where SAN shows predominantly a shear-yielding behaviour, to a drop in *SDO* and a transition from pure shear yielding to a crazing-dominated mixed-mode mechanism. However, in the regime where SAN shows disentanglement crazing, addition of SMA (up to 50 wt%) leads to a suppression of the disentanglement mechanism. At higher SMA content the films show brittle behaviour. We argue that a small amount of SMA, despite the fact that it is a low-entanglement-density polymer and is therefore expected to embrittle the SAN, can raise the monomeric friction coefficient of SAN owing to its enhanced interactions with the SAN chain. It is therefore able to suppress somewhat the brittle behaviour of SAN at lower strain rates and higher temperatures.

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