Craze microstructure and molecular entanglements in polystyrene–poly(phenylene oxide) blends

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Polystyrene and poly(phenylene oxide) are miscible over the entire range of compositions. Thin films of five blends of high molecular weight polystyrene (PS) with high molecular weight poly(phenylene oxide) (PPO), and four blends of low molecular weight PS (whose molecular weight lies below its entanglement molecular weight M_e) with the same PPO have been prepared. Following bonding of these films to copper grids, crazes were grown by uniaxial straining in air. Suitable crazes were then observed by transmission electron microscopy. From microdensitometry of the image plates it is possible to measure the extension ratio λ_{craze} within crazes in the nine blends. These measured values are compared with predicted values of λ_{max}, computed from $\lambda_{max}=l_e d$, where l_e is the chain contour length between entanglements and d is the root mean square end-to-end distance for a chain of molecular weight M_e. For the high molecular weight PS blends λ_{max} depends on the entanglement properties of both PS and PPO chains. For the low molecular weight PS blends, the PS chains cannot form part of the entanglement network and the correct value of λ_{max} is obtained from appropriate scaling of the pure PPO value. Comparison of λ_{craze} and λ_{max} for both types of blends shows excellent agreement, demonstrating the importance of the entanglement network in determining craze parameters and hence the toughness of a given polymer.

Keywords Polymer blends; structure; microstructure; crazes; polystyrene; (poly(phenylene oxide); entanglements

INTRODUCTION

Although the effect of molecular entanglements on the behaviour of polymer melts has long been recognized[1,2], the importance of the entanglement network for glassy polymers below their glass transition temperature T_g, has received less attention. Recently[3–11], however, evidence demonstrating the profound effect of entanglements upon the mechanical properties of glassy polymers has accumulated.

For high molecular weight polymers, the short term elastic modulus exhibits a rubbery plateau which extends above T_g. The value of the modulus at this plateau can be used to determine the entanglement molecular weight M_e analogous to the molecular weight between chemical crosslinks in a rubber network. Associated with this entanglement molecular weight, two further parameters can be used to characterize the entanglement network; these are the chain contour length between entanglements l_e, and the root mean square end-to-end distance d between the ends of a chain of molecular weight M_e, which will correspond to the length of a straight line between entanglement points.

Experimentally it has been found that stable craze formation can only occur for polymers above a certain critical molecular weight M_c[8,9,12]. For $M_w < M_c$[5,6] there is a dramatic decrease in the fracture toughness of the polymer due to the decrease in plastic work dissipated when significant crazing cannot occur ahead of the crack tip. In this regime below the critical molecular weight, the maximum thickness of a stable craze will be determined by the requirement that the thickness of undeformed polymer which fibrillates (the 'primordial' thickness) must not exceed the root mean square end-to-end distance of the polymer chain, since greater craze thicknesses would require the presence of entanglements for stability. This criterion can be used to predict G_{Ic} values for low molecular weight polymers[10].

If the formation of a craze is determined by the entanglement network, it is logical to expect that the properties of crazes in different glassy polymers will reflect differences in the entanglement networks. The presence of entanglements must set an upper limit for the possible extension of a chain, assuming neither chain scission nor chain slippage (reptation) occurs (i.e. assuming the network behaves as a permanently crosslinked system). In that case the maximum extension ratio λ_{max} will be given by:

$$\lambda_{max} = l_e/d \tag{1}$$

The basic validity of this idea has been demonstrated recently[11] by a transmission electron microscopy study of ten polymers, a strong correlation between the measured extension ratio within the craze, and the maximum draw ratio predicted by equation (1) being found. For those polymers with large l_e's and correspondingly high draw ratios leading to high true stresses within the fibrils, the λ's

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measured lay above the predicted values suggesting a significant contribution of chain scission due to the high stresses. For the lower values of l_e (e.g. polycarbonate and poly(phenylene oxide)) the measured values fell below the predicted maximum.

Satisfying though this correlation is, it is not possible by using such different polymers as polycarbonate and tert-butyl styrene, to study systematically the variation in λ with l_e. In this paper the results of such a systematic study on blends of (a) polydisperse polystyrene (PS), with weight average molecular weight M_w greater than the molecular weight between entanglements M_e, with high molecular weight poly(phenylene oxide) (PPO™) and (b) low molecular weight polystyrene, of average molecular weight $\bar{M}_w = 4000 < M_e$ for PS ($M_e = 19\,100$), with the same PPO, will be described.

The pair of polymers PS and PPO is unusual in that it exhibits complete miscibility over the entire composition range[13–18], as revealed both by a single value of T_g for the mixture, and also by the unchanged coil dimensions measured by small angle neutron scattering (SANS). Furthermore, Prest and Porter[13] have shown that, at least for blends with relatively low PPO contents, a simple relationship holds between the entanglement molecular weight of the blend and the weight fraction* of PPO (χ) in the blend with:

$$M_e(\chi) = \frac{M_e(\text{PS})}{1+3.2\chi} \tag{2}$$

Thus in case (a) the chain contour length between entanglements will vary from the value characteristic of pure PPO to that of pure PS, as the fraction of PS is increased. However, in case (b) the PS chains are too short to form part of the entanglement network and the effect of adding PS to PPO will simply be to 'dilute' the entanglement network characteristic of PPO.

EXPERIMENTAL

The starting materials for this study were (a) polydisperse PS containing no mineral oil, kindly supplied by Dr R. A. Bubeck of the Dow Chemical Company; $\bar{M}_w = 300\,000$, $\bar{M}_n = 113\,000$, (b) monodisperse PS, manufactured by the Pressure Chemical Company, with $\bar{M}_w = 4000$ and $\bar{M}_w/\bar{M}_n \leqslant 1.06$, *and (c) poly(2,6-dimethyl-1,4-phenylene oxide)*, $\bar{M}_w = 35\,000$, $\bar{M}_n = 15000$, kindly suppoied by Dr Roger Kambour of the General Electric Company.

Blends with 10, 25, 50, 75 and 90 wt% PPO with polydisperse PS and 33, 40, 50 and 75 wt% PPO with monodisperse PS were studied. Solutions of these blends were produced by mixing the two polymers in the desired weight ratios, and then dissolving the mixture in chloroform. Glass slides were drawn from the solution to produce uniform thin films with typical thicknesses of 0.7 μm. The films were floated off the slides onto the surface of a water bath, and picked up on annealed copper grids which had been precoated with a solution of the same blend composition. Bonding of the film to the grid was achieved by a short exposure to chloroform vapour.

After drying the film to remove excess vapour, the grids were placed in a strain frame and strained in tension in air until crazes were observed with an optical microscope. Suitable grid squares of interest were then cut from the grid for observation in a Siemens 102 transmission electron microscope (*TEM*). The strain in the film was maintained during microscopy by the copper grid which deforms plastically during straining. This method of specimen preparation has been described in further detail by Lauterwasser and Kramer[19].

To obtain quantitative measurements of the volume fraction v_f of material within the craze, a technique based on analysis of the contrast on an electron image plate has been developed[19,20]. Microdensitometry is used to determine the optical densities on the plate of the craze (φ_{craze}), the film (φ_{film}) and a hole through the film (φ_{hole}). The volume fraction is then given by[13]:

$$v_f = 1 - \frac{\ln(\varphi_{\text{craze}}/\varphi_{\text{film}})}{\ln(\varphi_{\text{hole}}/\varphi_{\text{film}})} \tag{3}$$

Since crazing is a plastic deformation process which takes place at constant polymer volume the extension ratio λ within the craze is then given by:

$$\lambda = 1/v_f \tag{4}$$

For blends of PPO with high $\bar{M}_w$ PS and $\chi > 0.5$ crazing did not occur in as-cast films. Rather, deformation zones (DZ's) were observed, as have been described[11,21] for a range of polymers. These are regions of drawn but unfibrillated polymer. To increase the degree of strain localization, and hence to favour crazing, a physical ageing treatment, annealing of the film below T_g, was carried out prior to straining. For χ in the range 0.5 to 0.9, 1.5 h at 100°C was sufficient to suppress DZ formation and favour crazing, but a 2 h anneal at 132°C was required for pure PPO. For blends of PPO with low molecular weight PS, annealing was necessary for all four blends investigated before craze formation occurred. For these blends an annealing treatment of $\frac{1}{2}$ h at 100°C was chosen.

For those blends where crazes could be obtained in both annealed and unannealed films (i.e. $\chi \leqslant 0.5$) average values for λ_{craze} in both types of specimen are included. They fall together within the error bars of the experiment. Since this agreement exists it is felt that annealing does not alter the response of the polymer to straining, as would be expected if the entanglement network remains fixed upon annealing below T_g. The agreement between λ_{craze} for annealed and unannealed films of PSAN1, a polystyrene–acrylonitrile random copolymer with 76 wt% styrene, has previously been noted[11]. In view of these observations it is felt that even in those blends where crazing does not readily occur without an annealing treatment, λ_{craze} measured in annealed films is a true indicator of the craze microstructure for bulk specimens regardless of their physical ageing treatment.

RESULTS

High molecular weight PS blends

Table 1 lists the average of measured values of λ within the craze, computed from equations (3) and (4), for the series of blends of PPO with high molecular weight polydisperse PS. These measured values of λ_{craze} can be compared with the predicted values of λ_{max}, computed from equation (1), which are also tabulated together with

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* For this system weight fraction and volume fraction differ by less than 2% throughout the range[16]; for the remainder of this paper they will be used interchangeably

Table 1 Parameters for high $\bar{M}_w$ PS/PPO blends

χ (wt fraction PPO)	l_e (Å)	d (Å)	λ_{max}	λ_{craze}
0	400	96	4.2	4
0.1	330	92	3.6	3.6* 3.3
0.25	270	86	3.1	3.2
0.5	220	76	2.9	3.4* 2.8
0.75	190	65	2.9	2.9*
0.90	180	59	3.0	2.7*
1.0	165	55	3.0	2.6*

* = annealed film

their corresponding l_e and d values from which λ_{max} has been calculated.

To evaluate l_e and d for the blends, certain assumptions need to be made. The value of M_e for PS has been taken as 19 100 from melt elasticity measurements[22]. Then l_e can be calculated from:

$$l_e = \frac{M_e}{M_0} l_0 \ , \tag{5}$$

where l_0, the length of a fully extended chain unit of molecular weight M_0, was determined from crystallographic data[23], giving a value of 400 Å. The extrapolated value of $M_e(\chi = 1.00)$ for PPO from equation (2) gives a value of 4300, with corresponding l_e of 165 Å. Assuming equation (5) is valid for all blend compositions with a simple rule of mixtures being adequate to describe the variation in l_0/M_0 for the blends, one obtains the relationship:

$$l_e(\chi) = M_e(\mathrm{PS}) \frac{0.0209 + 0.0175\chi}{1 + 3.2\chi} \tag{6}$$

This equation has been used to evaluate the l_e values listed in *Table 1*.

The entanglement mexh size d can be computed as the root mean square end-to-end distance for a polymer chain of molecular weight M_e. This will yield:

$$d = \kappa (M_e)^{1/2} \ , \tag{7a}$$

where κ is a constant which is polymer dependent. The values of κ can be determined from small angle neutron scattering experiments for PS[24] or from measurements of coil dimensions in a θ solvent[25]. The d values obtained in this way yield $d_{\mathrm{PS}} = 96$ Å and $d_{\mathrm{PPO}} = 55$ Å[11]. Linear interpolation is used to calculate the values of d for the blends, with:

$$d(\chi) = 96 - 41\chi (\text{Å}) \tag{7b}$$

Combining equations (6) and (7b) yields the predicted λ_{max} values listed in *Table 1*.

The validity of these extrapolations needs to be considered, in particular the fundamental assumption that $M_e(\mathrm{PPO}) = 4300$. Seitz[26] has measured the M_e of PPO using the same techniques as described earlier[22], and obtained a value of 7400. However, thermal degradation of PPO is known to occur[13], and this will lead to a greater apparent M_e by reducing the number of effective entanglements. This degradation was the major limitation of extending the work of Prest and Porter[13] to systems with $\chi > 0.4$. Further supporting evidence for using this lower value for M_e is discussed in the appendix.

The validity of calculating l_e and d of the blends by linear interpolation rests on the assumption that the configuration of the two types of polymer chains is unperturbed in the blend from that adopted in the two single component systems. Although the results from SANS[17,18] suggest that this is so, the occurrence of a slight negative excess volume of mixing[16] indicates the two polymers do not behave as ideal θ solvents for each other. However, the interaction is clearly small or the measured radius of gyration R_g obtained from SANS of the blend would not correlate with the R_g of the homopolymer. Thus it is felt that the assumption is justified.

Blends of PPO with PS of $\bar{M}_w = 4000$

As with the high χ blends described in the preceding section, crazing is only observed in these films following an annealing treatment. The average λ_{craze} values are tabulated in *Table 2*. Measurement of λ_{craze} for the $\chi = 0.33$ and $\chi = 0.4$ blends was complicated by the extreme fragility of the crazes. The thermal stresses arising during the annealing treatment were often sufficient to cause cracks to propagate across entire grid squares. When stable crazes did form they were both short and narrow. For $\chi \geqslant 0.5$ craze stability was not a problem.

Since $M_e = 19\,100$ for PS, the molecular weight of the PS used falls well below the entanglement value. Consequently the PS chains cannot form part of the entanglement network, which must be comprised entirely of PPO chains; the value of l_e and d will therefore be determined simply by a dilution of the values in pure PPO. DeGennes[27] has discussed the effect of blending polymers of differing molecular weight on the chain configurations of the two polymers. This discussion related only to cases where the two components had the same chemical form but the simplifying assumption will be made here that they apply equally well to compatible mixtures of different polymers. Since components of only slightly different M_w act as θ solvents for each other, a Gaussian coil configuration will be maintained in the blend. However when, as here, one component is of very different M_w from the other, the short chains act as a good solvent for the long chains. In this case the coil will expand[27,28] with:

$$d_G = d_\theta \chi^{-1/8} \tag{8a}$$

where d_G and d_θ are the d spacings corresponding to the configuration in a good and θ solvent respectively, and:

$$d_\theta = \kappa [M_e(\chi)]^{1/2} \tag{8b}$$

with M_e (and l_e) scaling as $1/\chi$.

Table 2 Parameters for low $\bar{M}_w$ PS/PPO blends

χ (wt fraction PPO)	l_e (Å)	d_G (Å)	λ_{max}	λ_{craze}
0.1	1650	230	7.1	–
0.33	500	110	4.5	4.6
0.4	410	98	4.1	3.85
0.5	330	84	3.9	3.7
0.75	220	76	2.9	3.4

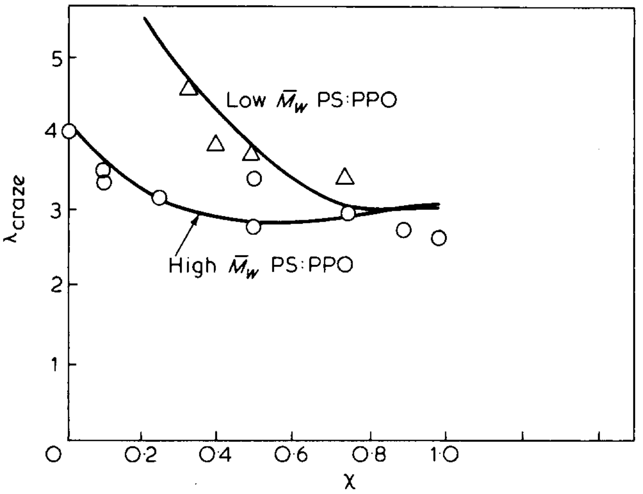

Figure 1 A plot of λ_{craze} vs. weight fraction PPO for the two types of PS/PPO blends. ○, high $\bar{M}_w$ PS blend; △, low $\bar{M}_w$ PS blend. The predicted curves of λ_{max} are also shown as solid lines

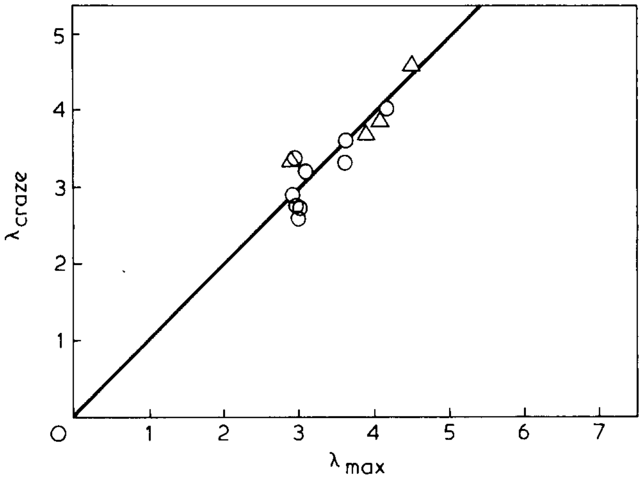

Figure 2 A comparison of λ_{craze} with λ_{max} for all the blends studied. ○, high $\bar{M}_w$ PS blend; △, low $\bar{M}_w$ PS blend. The line $\lambda_{craze} = \lambda_{max}$ is shown

Thus:

$$d_G(\chi) = \frac{d(\chi=1)}{\chi^{5/8}} \tag{8c}$$

and:

$$l_e = \frac{l_e(\chi=1)}{\chi} \tag{8d}$$

Using equations (8c) and (8d), l_e and d values can be computed. These are listed in *Table 2* along with the corresponding values of λ_{max} calculated from them.

DISCUSSION

Comparison of λ_{max} and λ_{craze} in *Tables 1* and *2* shows that the measured values agree closely with λ_{max}. The experimental and predicted values for λ are plotted vs. χ in *Figure 1* for all the blends. It is clear that the measured λ's are very close to those predicted by this simple model, with a significant difference in the observed λ value, at a given χ, for the two types of blends. This demonstrates clearly that chains shorter than M_e cannot be contributing to network properties.

This agreement is more strikingly apparent in *Figure 2* in which λ_{craze} is plotted vs. λ_{max} for the nine blends and the two homopolymers. All the points lie close to the line $\lambda_{craze} = \lambda_{max}$.

The range of λ's which can be investigated in this way is limited by the fragility of the low χ blends with the low molecular weight PS. For instance, an extension ratio of 7.1 is predicted for $\chi = 0.1$ but such crazes cannot be observed. The extreme weakness of such crazes can be rationalized in terms of the high stress which each load bearing PPO chain must support when the number of such chains is low. For blends of PPO with high molecular weight PS, all chains are load bearing and thus the true stress σ_t in the fibrils, given by:

$$\sigma_t = \lambda S_c \tag{9a}$$

increases only slowly as χ decreases.

The behaviour of the low molecular weight blends is in marked contrast to this since only a fraction χ of the chains can support the applied stress. Thus the 'molecular' true stress $(\sigma_t)_m$ which is given by:

$$(\sigma_t)_m = \frac{\lambda}{\chi} S_c, \tag{9b}$$

increases rapidly as χ decreases. *Figure 3* shows the form of $(\sigma_t)_m$ predicted by equations (9a) and (9b), arbitrarily setting $S_c = 1$ for all blends. It is not surprising, therefore, that the low χ/low *MW* PS blend crazes break down very rapidly. The observation that diffuse DZ's appear in unannealed films of $\chi = 0.5$/low *MW* PS blend films, whereas the zones are localized in films of $\chi = 0.5$/high *MW* PS blends, shows also that it is the PPO network alone that determines the plastic deformation behaviour when PS chains with $\bar{M}_w < M_e$ are present.

'Brittle' fracture takes place in most polymers in the following sequence: (1) crazes nucleate and grow, (2) the fibril structure in one or more of these crazes begins to break down to form large voids, (3) those voids grow still larger by rupture of craze fibrils at their edges until they

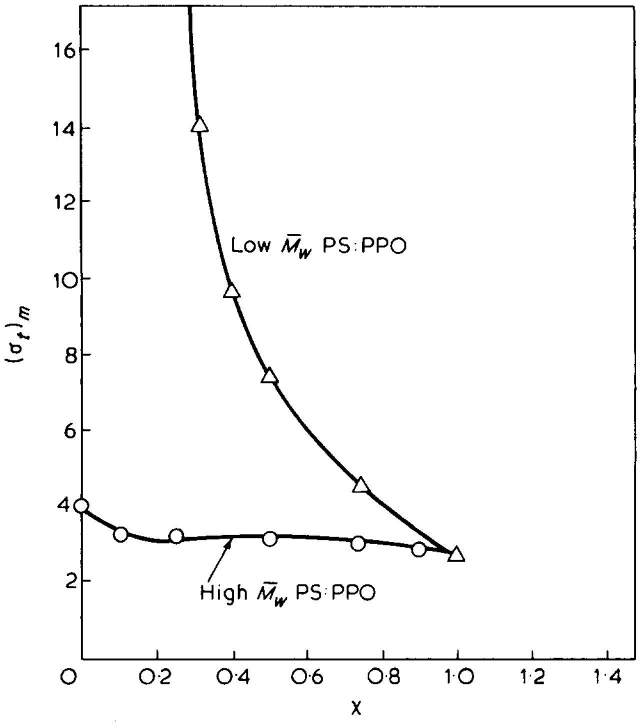

Figure 3 The molecular true stress in the craze fibrils plotted vs. wt fraction PPO for the two types of blends. [S_c has been set to 1.] ○, high $\bar{M}_w$ PS blend; △, low $\bar{M}_w$ PS blend

are large enough to propagate slowly as sub-critical cracks, (4) when one of these cracks reaches critical size, rapid crack propagation begins and fracture results. The 'brittle' fracture stress is thus largely controlled by the fibril breakdown process. As indicated above, the stress which is important in controlling this breakdown is the molecular fibril stress, $(\sigma_t)_m$, the true stress on molecules in the entanglement network of the fibrils.

Clearly decreasing λ_{craze} by decreasing M_e, l_e and thus $\lambda_{\max}$ should have a beneficial effect on craze stability if σ_c and the critical molecular rupture stress remain constant. Molecular blends such as the PPO–PS blends offer an attractive way to achieve this result. It is particularly useful to note that most of the decrease in λ_{craze} and $\lambda_{\max}$ occurs within the first 25% of PPO addition. Relatively small amounts of comparatively expensive PPO are sufficient to produce the bulk of the possible improvement.

The results on the low molecular weight PS–PPO blends have important implications for fracture of polydisperse homopolymers. Since the volume fraction of chains with molecular weight below M_e act essentially as a diluent for the entanglement network, increasing $\lambda_{\max}$ and λ_{craze} approximately as $\frac{(\lambda_{\max})_0}{(1-y)^{1/2}}$ and increasing the molecular fibril stress $(\sigma_t)_m$ as $\frac{(\lambda_{\max})_0}{(1-y)^{3/2}}$, a large volume fraction of low molecular weight tail, which might be desirable to improve processability, can have very significant adverse effects on craze fibril stability, even when the effects on λ_{craze}, through $\lambda_{\max}$, can be barely detectable.

CONCLUSION

The following important conclusions can be drawn:

(1) The fibril extension ratio in crazes in molecular polymer blends is primarily controlled by the $\lambda_{\max}$ of the entanglement network of that particular blend.

(2) Decreases in this extension ratio should improve the fracture properties of the polymer; hence changing the entanglement network of a polymer system by molecular blending offers a systematic way to manipulate fracture properties.

(3) Additions of low molecular weight polymer 'diluent' to the entanglement network lead to modest increases in λ_{craze} but correspondingly much larger increases in the molecular fibril stress. Since breakdown of craze fibrils is normally the slow step in fracture, large additions of low molecular weight material should be especially deleterious to fracture properties.

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APPENDIX

A second reason for suspecting that this measured M_e of 7400 (which would give an $l_e = 280$ Å for pure PPO) is too high comes from analysing the behaviour of unannealed films of pure PPO. In this case only diffuse deformation zones are observed, similar in appearance to those previously described in polycarbonate (PC)[21], whose M_e is known to be 2490[22] and other low M_e polymers[11]. It has been noted[11], that the propensity for DZ formation relative to crazing increases as M_e (or equivalently l_e) decreases. In unannealed PC, crazing in thin films is rarely observed whereas for PSAN1 crazing and DZ growth are competitive processes with DZ growth being favoured at crack tips and short times, whilst crazing may occur at the same level of applied strain but over significantly longer times. For polymers of high M_e and l_e, such as PS, crazing is always observed.

From this correlation between ease of crazing and M_e (or l_e) it is anticipated that M_e for PPO must lie significantly below 7400 since such a high value of M_e would lead to the expectation that PPO should behave similarly to PSAN1 in which both crazing and DZ's do occur without annealing. Since crazing is only observed in annealed PPO films, the behaviour is more consistent with the extrapolated M_e[13] of 4300.