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Microdeformation mechanisms in methyl methacrylate–glutarimide random copolymers

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Transmission electron microscopy (TEM) has been used to investigate the microdeformation mechanisms in thin films ($<1\ \mu$m) of MMA–glutarimide copolymers of various compositions ranging from 36 to 76 mol% glutarimide. These polymers all have an entanglement density of $\sim 5\times 10^{25}\ \mathrm{m}^{-3}$, which is of the same order as that in poly(methyl methacrylate) (PMMA). Crazing is known to be the dominant deformation mechanism in thin films of PMMA tested at room temperature. As the glutarimide content is increased in the copolymers, however, motions associated with formation of shear deformation zones (DZs) are facilitated, and these become increasingly competitive with scission crazing in thin films. The presence of the MMA groups may nevertheless continue to hinder large-scale chain motions associated with high-temperature disentanglement crazing, since it was found that the absolute temperature for the onset of disentanglement in the copolymers remained similar to that in PMMA (ca. 80°C for the strain rates used here), and was essentially independent of the composition and the glass transition temperature (T_g). Copyright © 1996 Elsevier Science Ltd.

(Keywords: microdeformation; PMMA–glutarimide copolymers; transmission electron microscopy)

INTRODUCTION

Methyl methacrylate (MMA)–glutarimide random copolymers[1] offer an attractive alternative to the poly(methyl methacrylate) (PMMA) homopolymer in certain applications, because of their elevated T_gs and improved thermal stability. This present report concerns the use of transmission electron microscopy (TEM) to investigate the microdeformation mechanisms in thin films ($<1\ \mu$m) of a series of MMA–glutarimide copolymers of differing compositions, and is intended to provide an insight into the temperature and rate dependence of the macroscopic fracture toughness of these materials, as will be discussed in more detail in a companion study to be presented elsewhere[2].

Following the work of Lauterwasser and Kramer[3], annealed copper grids were used to support the films and maintain them in tension during deformation and in the electron microscope. This technique has become widespread in the study of amorphous glassy polymers, providing much evidence in favour of the view that the entanglement density, ν_e, is important in the competition between crazing and homogeneous deformation, as will be discussed below. PMMA itself is too sensitive to electron bombardment to be suitable for detailed TEM studies[4], which is unfortunate, since its high transparency, and the existence of a well-defined craze zone at the crack tip in notched samples over a wide range of conditions, have made it a very popular subject for macroscopic fracture toughness investigations[5,6]. MMA–glutarimide copolymers, on the other hand, are relatively stable in the electron microscope, and this present investigation of a homologous series of such polymers provides an interesting comparison with such direct observations as exist for PMMA.

The role of entanglement in microdeformation has been extensively discussed elsewhere[7,8], and will only be outlined briefly here. Polymers such as polystyrene (PS), which craze readily over a wide temperature range, are generally characterized by a low ν_e. Assuming the existence of a permanent entanglement network in the glassy state, the surface density of strands linking entanglement points which must break to accommodate void formation during crazing is relatively low, and so there is a correspondingly low cost in energy associated with fibrillation[7]. Such materials are macroscopically brittle because the low starting ν_e, coupled with entanglement loss during crazing, means that few entanglements remain to stabilize the craze fibrils, and there is little resistance to crack nucleation and propagation via craze breakdown[7,9]. Polymers with high ν_e values, such as polycarbonate (PC) and poly-(ether sulfone) (PES),

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on the other hand, craze less readily at ambient temperature and macroscopically they show much tougher behaviour[7,8,10]. However, although thin films of PC and PES normally show homogeneous shear deformation zones (DZs) at ambient temperature, they do craze at temperatures close to the T_g. In this temperature range, the polymer chains at the craze void tops are thought to become sufficiently mobile to disentangle by 'forced reptation', a mechanism which is argued to be essentially frictional, and hence also favoured by low molecular weights and low strain rates[7,8,10–14]. The chain motions necessary for disentanglement are widely held to be frozen out in the glassy state, but recent T_g measurements in PS[15] appear to bear out earlier suggestions[13] that chain mobility may be greatly enhanced within a surface layer of thickness ξ at the polymer–air interface. Since ξ is argued to diverge as the temperature approaches T_g from below, but remains independent of the chain size[15], it may be possible to formulate criteria for disentanglement crazing based on some critical thickness $\xi_c(M)$ for the mobile layer at the craze void tips as an alternative to current models which assume some intrinsic temperature dependence for the monomeric friction coefficients[8,10,13,14].

Scission crazing is expected to be favoured over both disentanglement crazing and DZs by low temperatures and high strain rates, since unlike disentanglement, the kinetics of chain scission are not strongly temperature dependent and are associated with small time constants. Evidence of this is the observation of a transition from DZs to scission crazing in thin films of PC when the temperature falls below ca. −120°C[16]. Comparison of a range of glassy polymers indicates that the threshold of ν_e above which scission crazing will be replaced by homogeneous deformation zones (DZs) in thin films at ambient temperature is of the order of $5 \times 10^{25}\,\mathrm{m}^{-3}$[7]. One therefore expects thin films of PMMA and different compositions of PMMA–glutarimide copolymers, all of which have $\nu_e \sim 5 \times 10^{25}\,\mathrm{m}^{-3}$ (see below), to show mixed shear and crazing close to room temperature and to be particularly sensitive to changes in thermal history (physical ageing), strain rate and temperature, and also to structural modifications, through their influence on chain stiffness and mobility. Studies of styrene–acrylonitrile random copolymers (SAN) and fully miscible blends of PS and poly(phenylene oxide) (PPO) support this idea, and indeed the variation in effective strain rate may be sufficient to cause scission crazing, DZs and disentanglement crazing during a single test when ν_e is close to the threshold value[17].

Bulk PMMA is well known from macroscopic tests to craze at room temperature, but there is a relatively severe constraint on homogeneous shear yielding in bulk samples, particularly in the presence of notches, so that thin-film observations need not reflect this. It is nevertheless found that PMMA thin films also readily undergo scission crazing at room temperature[18], presumably reflecting the intrinsically high yield stress of PMMA well below the T_g, which may be understood in terms of the presence of a very marked β-peak in the loss modulus, extending from below room temperature to more than 50°C at $1\,\mathrm{Hz}^2$. The dominant effect of the individual MMA units on the yielding kinetics in styrene-based random copolymers containing various proportions of MMA has been demonstrated from the direct investigation of the plastic flow processes[19], and our own results indicate this also to be the case in glutarimide–MMA random copolymers[2]. Thus, by varying the MMA content one has a means of systematically influencing the yielding behaviour, with increased MMA contents tending to hinder the cooperative motions involved in yielding. This may in turn provide an insight into the competition between scission crazing, DZ formation and disentanglement crazing in these materials.

EXPERIMENTAL

The proprietary designations and some physical characteristics of the polymers chosen for this study, which were supplied by Röhm and Haas Ltd, are given in *Table 1*, and their generic chemical formula is shown in *Figure 1*. Thin films of these polymers (ca. 0.5 μm thick) were cast on to glass slides from chloroform solution. Drying was carried out for 20 min in a vacuum oven at $T_g + 20\,\mathrm{K}$. Following the method of ref. 3, the films were floated off the glass slides on to distilled water and picked up on annealed copper grids. The films were further dried at ambient temperature for 60 h under vacuum, and were finally bonded to the grids by heating to $T_g + 15\,\mathrm{K}$ for 30 s. The grids were then strained in tension using the Polymer Labs Minimat miniature tensile test apparatus at a strain rate of $2 \times 10^{-3}\,\mathrm{s}^{-1}$ (unless otherwise stated) and at various temperatures. The tests were monitored using an Olympus SZH10 stereo microscope (in reflected light) and certain tests were also recorded on videotape, thus allowing an estimation of the strains associated with the onset of microdeformation in the polymer films. After straining, individual grid squares were removed for observation in a Phillips EM300 transmission electron microscope operating at 100 kV. The films were not subjected to any form of physical ageing treatment in order to make comparison of the different grades as meaningful as possible. (No systematic studies of the effects of physical ageing have so far been carried out on these materials.)

Table 1 Proprietary names and physical characteristics of the copolymers used in this study; polydisperisity in each case was 2.1

Trade name	Designation	T_g (°C)	Imide (wt%)	Imide (mol%)	M_w
Paraloid HT510	GIM36	134	49	36	76 000
Kamax T240	GIM58	147	70	58	110 000
Kamax T260	GIM76	158	84	76	101 000

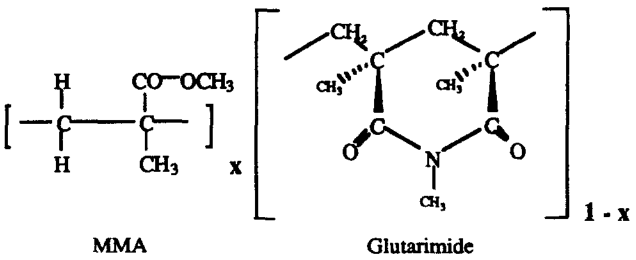

Figure 1 Chemical structure of MMA-*co*-glutarimide polymers

Values of ν_e were determined in each case from the value of the plateau modulus G_0^N at the minimum in tan δ associated with the rubbery plateau above T_g [20,21]. This was carried out by using a Rheometrics Dynamic Analyser (RDA) to carry out torsion measurements on 25 mm diameter circular plaques. The entanglement density ν_e was then estimated by using the following:

$$\nu_e = \frac{N_A G_0^N}{RT} \qquad (1)$$

where N_A is the Avogadro constant. All of the polymers were found to have values of ν_e of the order of $5 \times 10^{25}\,\mathrm{m^{-3}}$ (GIM76, 4.78–5.22; GIM58, 4.3; GIM36, $4.59\text{–}5.25 \times 10^{25}\,\mathrm{m^{-3}}$).

RESULTS AND DISCUSSION

Basic phenomenology

Considering a range of temperatures both above and below the ambient temperature, we observed the following five regimes of behaviour in thin films, as shown schematically in *Figure 2*:

(1) At low temperatures (typically $T < 10°\mathrm{C}$), long, high-aspect-ratio crazes were observed, spanning most of the width of a given grid square (0.4 mm). An example is shown in *Figure 3* for GIM76; crazes formed under these conditions in GIM36 proved too beam sensitive for satisfactory electron micrographs to be obtained.

(2) At intermediate temperatures (between 10°C and $T_l \sim 80°\mathrm{C}$ for all of the copolymers) two types of

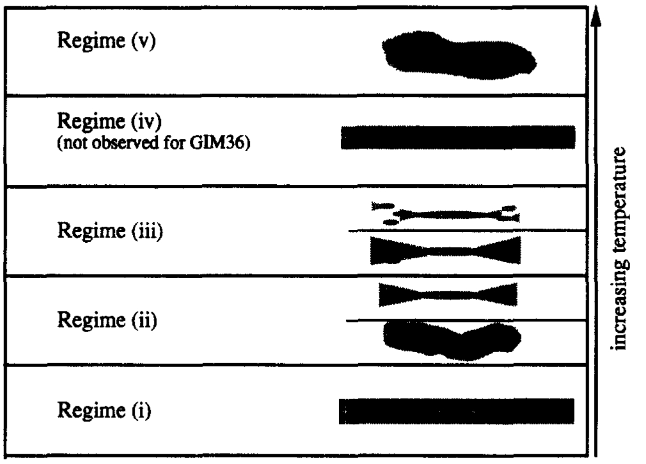

Figure 2 The various regimes of behaviour of MMA-*co*-glutarimide polymers

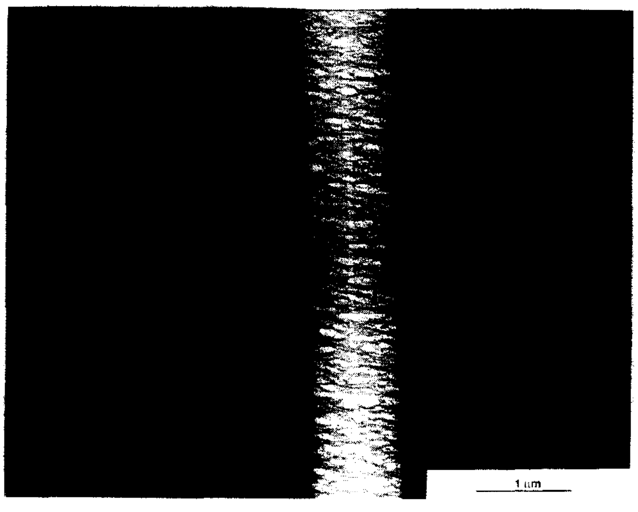

Figure 3 Low-temperature crazing in GIM76 at 0°C

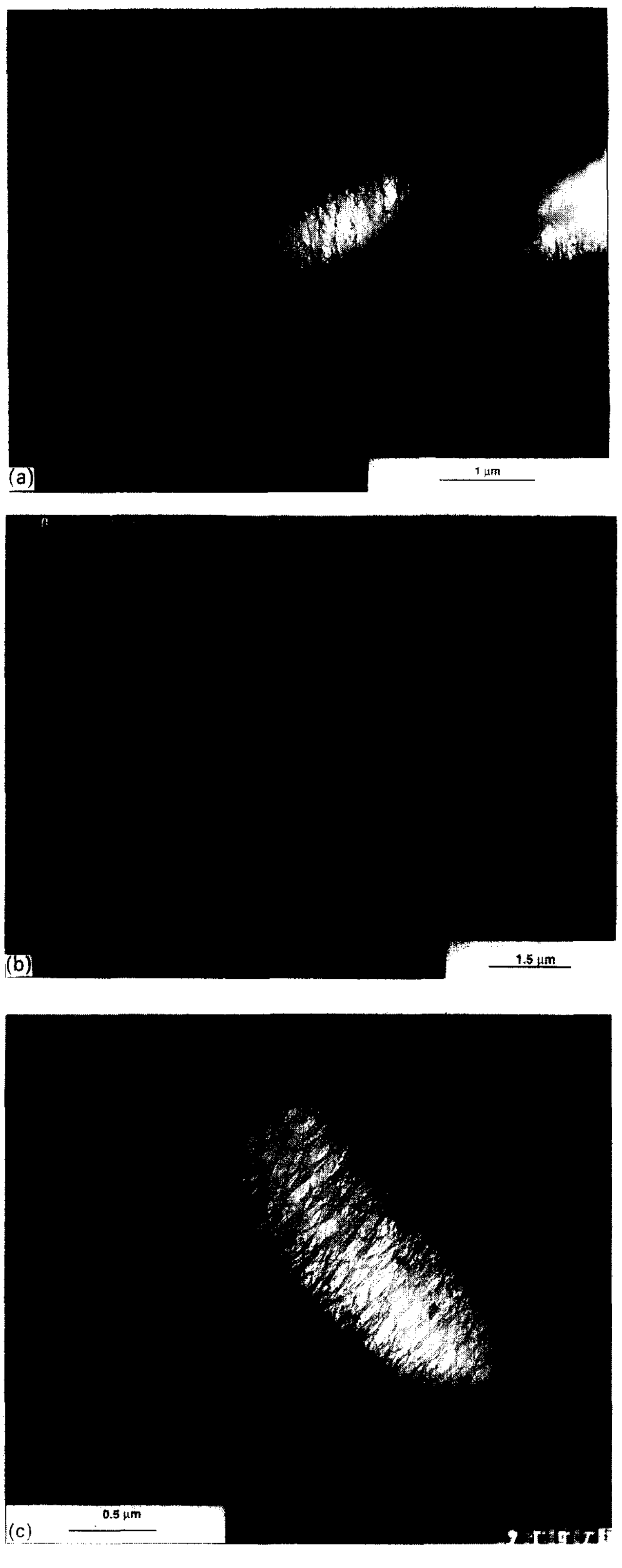

Figure 4 Deformation behaviour at intermediate temperatures: (a) craze with diffuse edges in GIM76 at 21°C; (b) diffuse DZ in GIM58 at 21°C; (c) shear blunting at craze tips in GIM76 at 50°C

deformation were observed to coexist, i.e. crazes (fibrillar deformation) and diffuse DZs. At temperatures just above the transition from scission crazing to mixed deformation, the crazes were of a high aspect ratio, and the diffuse DZ was generally restricted to the craze–bulk interfaces (*Figure 4a*), although some large isolated DZs were seen (*Figure 4b*). As the temperature was raised further, the DZs became more widespread and were also observed at craze tips. The crazes took on relatively low aspect ratios, i.e. similar to the 'short fat' crazes referred to previously by Donald and Kramer[17] (*Figure 4c*).

(3) Above $T_1 \sim 80°\mathrm{C}$, the deformation remained mixed, but crazing was dominant, and the DZs became less widespread and tended to be accompanied at the tips of the main crazes by regions of multiple crazing (*Figure 5*).

(4) Above ca. 125 and 120°C in GIM76 and GIM58, respectively, long, high-aspect-ratio crazes were observed, and the diffuse DZ were no longer visible in the micrographs (*Figure 6*). This regime was absent in the case of GIM36.

(5) Close to the T_g (GIM76, $T > 145$; GIM58, $T > 130$; GIM36, $T > 110°\mathrm{C}$), the films deformed homogeneously.

This behaviour is summarized in *Figure 7*, where the transition temperatures are mapped as a function of the glutarimide content. In the following section we will focus on the phenomenology of deformation in the copolymer films in more detail.

Fibril coalescence in the mixed regimes

In regimes (2) and (3), individual features often occurred which were difficult to identify unambiguously with any of the mechanisms described in the Introduction. Those features (*Figure 8*) identified as crazes had a well-defined mid-rib, which is ascribed to the stress concentration at the craze tip as it propagates, resulting in slightly higher fibrillar extension ratios than in the craze bulk[7]. Although this mid-rib is assumed to be characteristic of crazes rather than DZs, the structure of the crazes in the regions immediately adjacent to the mid-rib was often homogeneous.

It is reasonable to assume the mid-rib and the central regions of the craze to have formed earlier than the outer regions, and at relatively high stresses and strain rates, which are expected to favour scission crazing. It might therefore be argued that there is a transition from

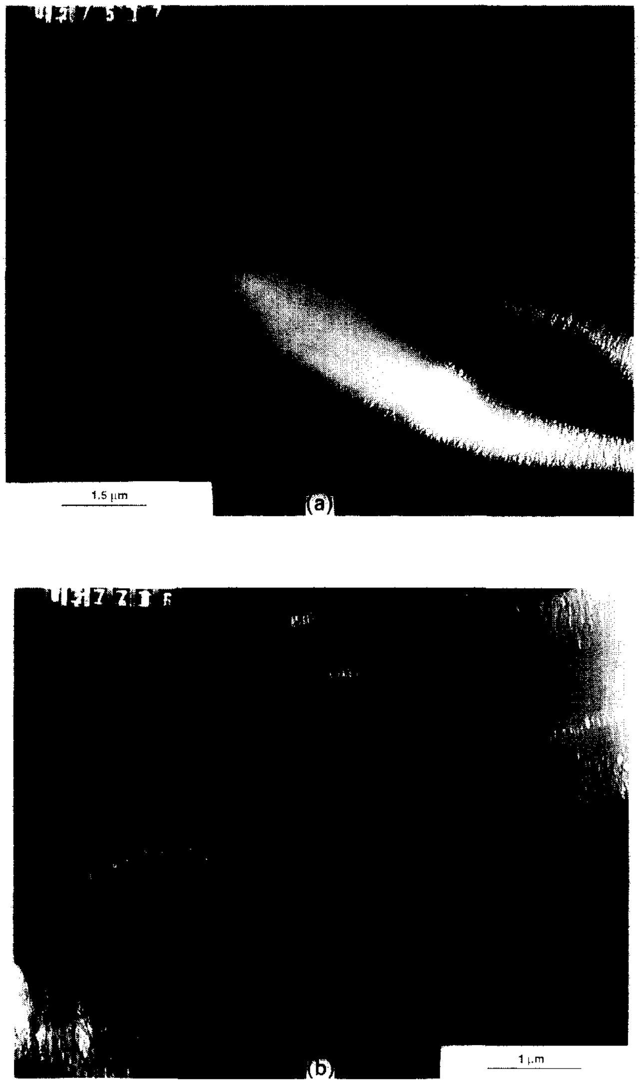

Figure 5 Multiple crazing at a craze tip in GIM76 at: (a) 90°C; (b) 130°C

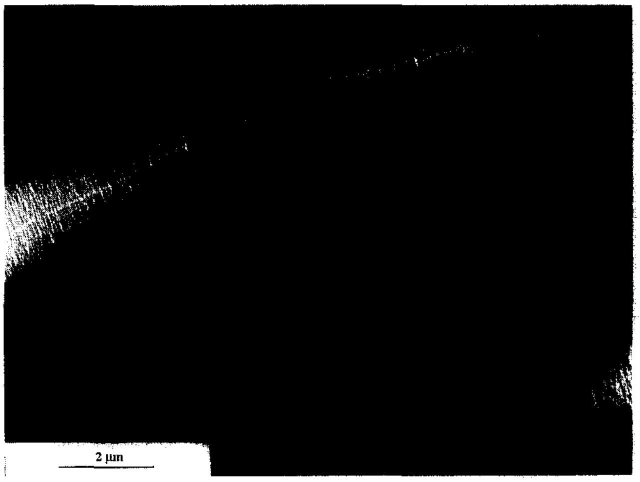

Figure 6 Crazing in GIM76 at 140°C

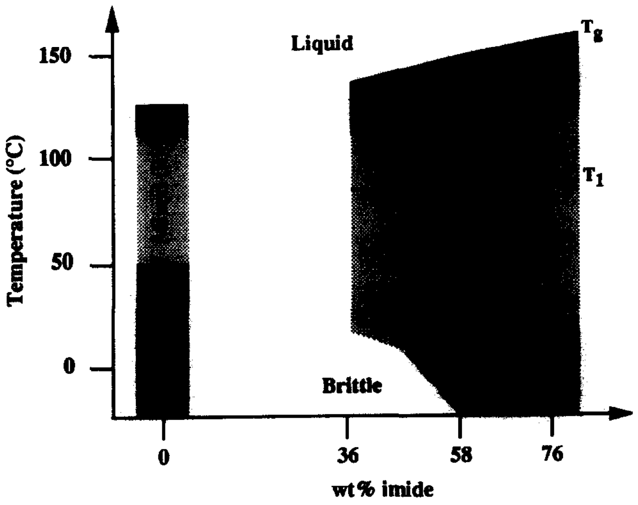

Figure 7 Deformation map for different imide contents of the copolymers and for PMMA (from refs 18 and 19)

scission crazing to homogeneous deformation as the local strain rates at the craze-tips and craze-bulk interfaces falls (owing to the multiplication of crazes/DZs in the film). At much later times or after cessation of straining, as the strain rate drops further, conditions may become favourable for disentanglement, accounting for the well developed fibrillation at the craze edges. This is essentially the explanation given by Donald and Kramer in their studies of SAN, and PS/PPO blends[17].

However, according to the above reasoning, the regions of deformation should be composed of three distinct regions, and one expects to see some fibrillation both in and around the mid-rib. Here, in the mixed regime, there was often no apparent fibrillation in the central part of the crazes; the craze resembled a homogeneous DZ with a mid-rib. Moreover, closer examination of the homogeneous regions occasionally revealed faint striations perpendicular to the craze length (*Figure 8*), suggestive of a collapsed fibrillar structure on a similar scale to that at the craze edges. This is in turn strongly suggestive of fibril coalescence, as discussed by Yang and coworkers[22,23]. These authors reported the central regions of wide crazes to be thinner than the undeformed films, as shown in *Figure 9*, implying the fibrils to be very densely packed. Thus must be a consequence of cross-tie fibrils. One may thus infer that zones containing a mid-rib, an inner homogeneous region of relatively high extension ratio, an outer region of lower extension ratio, and finally, fibrillation at the edges, which were occasionally observed in the mixed regime, resulted from mixed deformation of the type observed by Donald and Kramer[17] with additional coalescence.

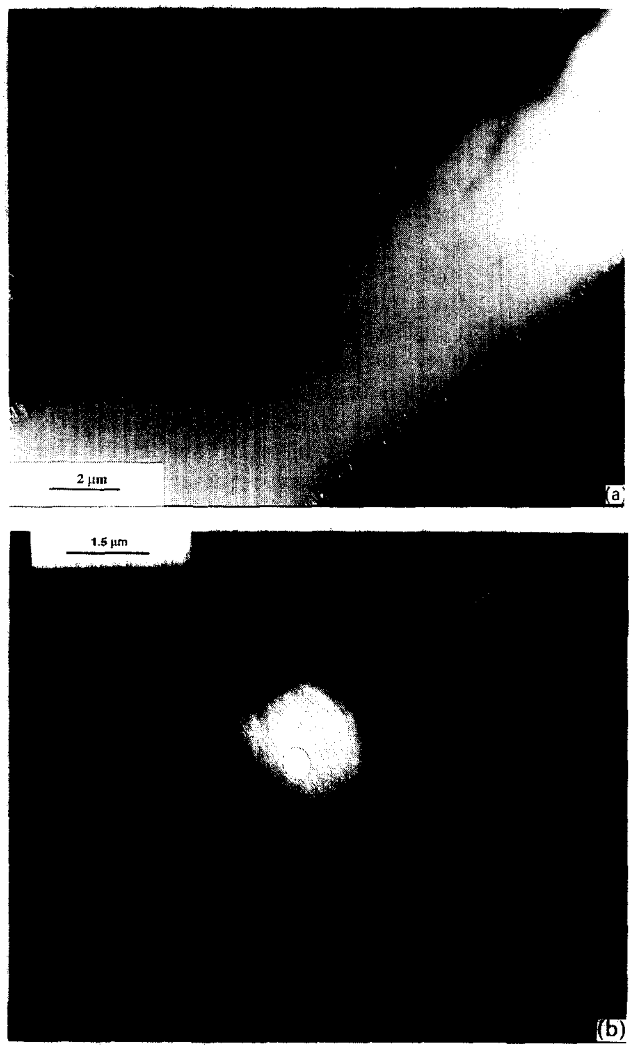

Figure 8 Features of regimes (2) and (3): (a) typical coalesced craze in GIM76 at 100°C; (b) coalesced short fat craze in GIM36 at 100°C, showing striations perpendicular to the craze length

The important factors for coalescence will be temperature, the presence of cross-tie fibrils, the initial craze fibril separation and the fibrillar molecular weight. These will in turn depend on the test temperature. In the temperature range corresponding to regime (2) (up to T_1), crazing mainly occurs by chain scission, the craze fibrils are in close physical contact and the relatively high mobility of chain fragments at the fibril surfaces in scission crazes may allow coalescence of the craze fibrils in the central regions of the craze on time-scales comparable with those of the tests. Indeed some degree of coalescence has been observed in the centres of low-molecular-weight PS crazes at ambient temperature[24]. This should not greatly affect the relative extension ratios of the craze body and the mid-rib as deduced from the optical density of the micrographs, hence the persistence of the mid-rib even in apparently homogeneous structures.

In the temperature range above T_1, corresponding to regimes (3) and (4), the well-defined fibrillar structures characteristic of low-temperature crazes reappeared and the DZs eventually disappeared altogether. Furthermore, as the temperature was raised above T_1, the craze extension ratios as measured by densitometry of the electron micrograph plates[7] were found to increase both with increasing temperature and decreasing strain rate (*Figure 10*), which has been widely cited as evidence for disentanglement[8,10,13]. Another piece of evidence is the sharp drop in the strain for the onset of deformation at T_1 (*Figure 11*), as was associated previously with shear to disentanglement crazing in PES and PC[10]. Possibly the most convincing test of disentanglement, however, would be the demonstration of a molecular-weight dependence of the craze stress, since this immediately implies the participation of whole chains in the crazing process. This was not possible in this present case since polymers with different molecular-weight distributions were not available.

As regards coalescence, two competing processes may

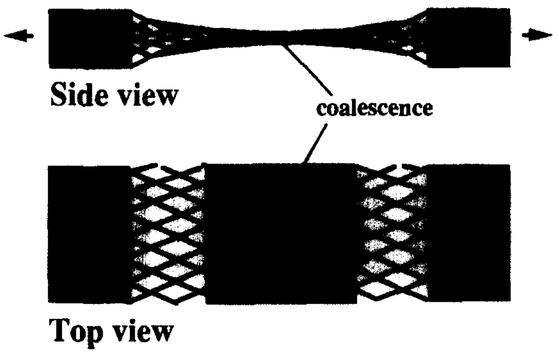

Figure 9 Schematic representation of the through-thickness contraction of a craze which may promote fibril coalescence (viewed from the side and from the top)

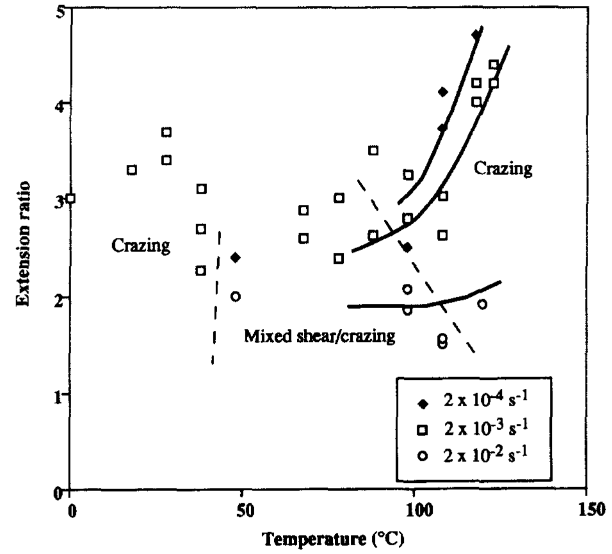

Figure 10 Deformation ratios in crazes in GIM76 at different strain rates and temperatures

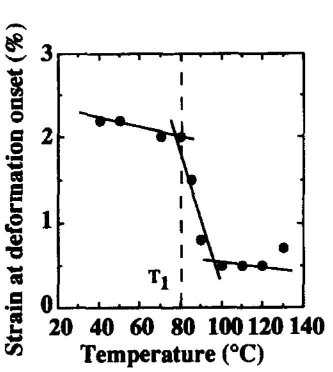

Figure 11 Strain for deformation onset as a function of temperature in GIM76

be operating. The increase in temperature will increase chain mobility and favour the coalescence process. On the other hand, fibril formation through disentanglement, as opposed to chain scission, will result in increased fibrillar molecular weights, which may act to reduce the effective chain mobility in the fibrils. This may account for the observation of a decrease of coalescence and its occurrence at a larger critical craze width as we pass from regime (2) to regime (3). For example, at 50°C and at a strain rate of ca. $2 \times 10^{-3}\,s^{-1}$, coalescence is visible in crazes wider than 1.1 μm, whereas the critical width rises to ca. 1.6 μm in tests carried out at 100°C and $4.6 \times 10^{-5}\,s^{-1}$.

Transition from short fat crazes in regime (2) to other types of instabilities

In unaged thin films of certain high-ν_e polymers and also in certain crosslinked polymers[7,16], regimes of temperature exist well below the T_g in which only diffuse DZs are observed, generally associated with holes or dust particles. Unlike the highly localized DZs seen in aged films, in which the extension ratio λ_{DZ} is approximately equal to λ_{max} (the natural draw ratio) everywhere within the DZ and falls abruptly to 1 at the zone edges, in the diffuse DZs there is no well-defined zone edge, and λ_{DZ} varies considerably, only tending to λ_{max} in the mid-part of the DZ. As discussed by Haward[25], in the absence of an intrinsic yield drop, highly entangled or crosslinked polymers may work-harden too rapidly for the Considère criterion for localized deformation to be satisfied. In the copolymers investigated here, isolated diffuse DZs were never observed alone. Instead, they tended to be associated with localised deformation in the form of crazes. Thus, even if the Considère criterion were not satisfied for shear deformation, the presence of local stress concentrations meant that shear deformation did not occur uniformly throughout the whole film, but manifested itself in the form of diffuse DZs.

At the highest temperatures in regime (2), short fat crazes with diffuse zones at their tips were observed (*Figure 4c*). This phenomenon has already been discussed by Donald and Kramer in their study of SAN, and PS/PPO blends. Scission crazes are the first type of instabilities to develop in response to the high level of stress caused by the applied strain. The onset of crazing will be associated with a drop in the local stress and strain rate at the craze tips. This shifts the balance in favour of the molecular motions and chain orientation associated with the formation of diffuse DZs[17]. The ensuing stress relaxation and orientation in turn blocks further progress of the craze tips[26]. However, since in general the stress at the craze–bulk interface well away from the craze tip remains close to the global stress, there will be little additional orientation arising from diffuse deformation in these regions, and the craze widening mechanism can still operate, thus resulting in a 'short fat' craze.

As the temperature is raised further (regimes (3) and (4)), the molecular mobility increases. Therefore, unlike at lower temperatures, where entanglement prevents relaxation of orientation under stress[27], the chains begin to slide through even the severest of topological constraints[28], thus making shear blunting less effective and favouring disentanglement crazing. If the chain relaxation rate is of the same order as the work hardening rate, crazes begin to appear inside the diffuse DZs present at the tips of primary crazes (*Figure 5a*–regime (3)). On the other hand, if the temperature is sufficiently high to enable chain relaxation to dominate, there is no craze blunting, and the observed crazes regain the high aspect ratios characteristic of the low-temperature scission crazes (*Figure 6*–regime (4)). Finally, very close to the T_g (regime (5)), stress relaxation will be too rapid to allow any form of localized deformation and the films deform uniformly.

Comparison of the different polymers

The different MMA–glutarimide copolymers considered in this study show certain similarities in their micromechanical behaviour, but also display certain differences.

The apparent fragility of GIM36 at temperatures below ca 40°C (regimes (1) and (2)) compares with the copolymers with higher glutarimide contents may be due to two factors. First, this copolymer has a relatively low molecular weight, which may contribute to craze fragility, since the higher chain-end density will lower the effective ν_e in the craze fibrils, and hence their load bearing capacity. Secondly, when the MMA content exceeds a certain level, the MMA linkages may begin to prevent the co-operative molecular motions involved in

DZ formation and limit stress relaxation in the films. Certainly, PMMA shows predominantly scission crazing up to much higher temperatures than the glutarimide-rich copolymers, with DZs not appearing until ca. 50°C. (They are already present at 20°C in GIM58 and GIM76.) Moreover, the variations in the relative ease of scission crazing and DZ formation cannot be accounted for in terms of a variation in the chain scission contribution to scission craze stress with ν_e, since ν_e was not found to vary with glutarimide content. This contrasts with the results of a recent study of MMA–maleimide copolymers[29], where a strong correlation is seen between the maleimide content, ν_e, and the temperature ranges in which diffuse DZs were observed in the samples. Further consideration of the role of MMA content in DZ formation and its effect on toughness is deferred to ref. 2, in which the macroscopic fracture is discussed in terms of secondary relaxation processes and the competition between shear and crazing at the crack tip.

Beyond 80°C, as we have seen, crazing became dominant as the temperature was raised and finally, for temperatures above ca. $T_g - 10\,\mathrm{K}$, there was a transition to uniform homogeneous deformation of the films. Since the transition at 80°C was associated with disentanglement in both the copolymers and in the PMMA homopolymer, it follows from this that disentanglement crazes were observed over the widest range of temperatures in the polymers with the highest T_g values, i.e. those with the highest glutarimide contents (GIM76). One therefore infers that the MMA linkages hinder disentanglement as well as DZ formation, so that disentanglement crazing is limited to a progressively narrower range of temperatures below the T_g as the MMA content increases.

CONCLUSIONS

The MMA–glutarimide copolymers discussed here all have an entanglement density of $\sim 5 \times 10^{25}\,\mathrm{m}^{-3}$, which is similar to that in the PMMA homopolymer, and is expected to be characterized by mixed crazing and homogeneous deformation in thin films of glassy polymers at ambient temperature. PMMA is an exception to this in that at room temperature crazing dominates, which suggests suppression of the molecular motions that are associated with yielding. As the glutarimide content is increased above 36 mol% in the copolymers and yielding is facilitated, the DZs become increasingly competitive with scission crazing in this temperature range. This is likely to have benefits for the macroscopic fracture toughness.

Disentanglement in PMMA occurs at relatively high temperatures, and the temperature for the onset of disentanglement in the copolymers remains similar to that in PMMA (ca. 80°C for the strain rates used here), and approximately independent of composition and T_g. Thus, the temperature range in which disentanglement crazing appears to occur, increases with glutarimide content. This may be due to persistent blocking of the disentanglement by the MMA groups.

More generally, this present work demonstrates that in addition to the entanglement density, which is considered to be a fixed parameter for the polymers studied, changes in the yielding behaviour arising from chemical modification can influence the competition between shear and crazing in thin films, and by implication, the macroscopic behaviour. This is likely to be of particular practical significance for systems based on polymers such as PMMA which exhibit both high-temperature secondary relaxations and intermediate entanglement densities.

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