The effect of thermal ageing on impact-modified engineering resins

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The effects of sub-T_g ageing on the impact properties of neat *versus* impact-modified poly(ethylene terephthalate) (PET), polycarbonate (PC) and a glycol-substituted PET polyester (PETG) were studied. Notched Izod bars of unaged neat PC fail in a ductile manner at room temperature whereas PET and PETG bars fail in a brittle (craze-initiated) mode. When PC is aged or tested at −20°C, however, the PC fails by the same brittle mode as the polyesters. This behaviour is attributed to an increase in yield stress and the subsequent change in the stress state during impact from more of a plane stress to plane strain state. At the strain rates employed, this causes the failure mechanism to switch from shear yielding to crazing. The embrittlement that accompanies ageing is greatly suppressed by the addition of impact modifiers to neat resins. Toughness in the impact-modified materials is believed to derive from both an increase in the number of deformation sites as well as the promotion of shear yielding in the matrix phase even after ageing or during low-temperature impact.

(Keywords: fracture; impact; polycarbonate; poly(ethylene terephthalate); ageing)

INTRODUCTION

Impact modifiers are typically used to improve the impact behaviour of brittle polymers such as poly(methyl methacrylate) (PMMA) and polystyrene (PS). Engineering resins such as polycarbonate (PC) are often considered sufficiently tough to preclude the use of additional modifiers. However, such glassy polymers undergo embrittlement over time or are brittle at low temperatures. Ageing-induced embrittlement is particularly noticeable in materials that are used/stored at temperatures less than but approaching the glass transition temperature (T_g). In the present set of experiments, physical ageing in glassy polyesters, which have relatively low glass transition temperatures (~75°C), and polycarbonate, which is used in extended-lifetime applications, was studied.

Physical ageing arises from the non-equilibrium state of rapidly vitrified glasses. The changes in physical, mechanical and thermal properties that accompany physical ageing have been well documented[1–6]. Ageing can bring about an increase in density, yield stress and modulus, and a reduction in the enthalpy of the glass, impact strength, ultimate elongation, creep rate, stress relaxation rate, equilibrium sorption of gases and absorption of liquids. These effects are usually attributed to segmental rearrangement and concomitant reduction in free volume[3,6–10] or alternatively an increase in the energy barrier to molecular flow[11], which occurs with ageing. Such effects can be 'erased' by thermal or mechanical treatment[1]. In the present set of experiments, the impact behaviour of polycarbonate (PC), poly(ethylene terephthalate) (PET) and a glycol-substituted PET polyester (PETG) was monitored as a function of thermal ageing, impact modification and (PC only) test temperature.

EXPERIMENTAL

Materials

The PET used was ICI America's Carodel® 5122C, a bottle-grade resin with an intrinsic viscosity of 0.72 dl g^{-1} and a glass transition temperature of ~75°C. The PETG used was Eastman's Kodar® 6763. The composition of this copolyester is equivalent to PET in which 33 mol% of the ethylene glycol is replaced by cyclohexanedimethanol. The resultant lack of regularity in the chain inhibits crystallization. The intrinsic viscosity of this resin is 0.75 dl g^{-1} and the glass transition temperature is ~80°C. The PC used was General Electric's Lexan® 141, with $M_w = 7.05 \times 10^4$, $M_n = 3.12 \times 10^4$ and a glass transition temperature of ~140°C.

The above materials were compounded with 15% and 30% (w/w) loadings of Rohm and Haas' stabilized core–shell all-acrylic impact modifier (AIM) Paraloid® EXL-3373 and methacrylate–butadiene–styrene (MBS) modifier Paraloid EXL-3647. These modifiers and loading levels were not chosen based on optimization studies, but were selected for scouting purposes.

Processing

Drying. Because of the hygroscopic nature of PET and PETG, and the deleterious effect of water on polymer molecular weight, all base resins were dried overnight in a vacuum oven at 100°C. Impact modifiers were dried at 60°C.

Compounding. Samples were compounded on a 2.5 cm Killion extruder using a high-shear screw at 1.7 Hz. Maximum barrel temperatures were about 260, 246 and 282°C for PET, PETG and PC, respectively.

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Injection moulding. All pelletized samples were dried in a vacuum oven at 60°C overnight and moulded on a 445 kN injection moulder using 40°C moulds to retard crystallization in the PET and to quench cool all of the resins. A very slight amount of hazing was seen in some PET parts owing to low levels of crystallinity. Izod bars (0.3 cm thick) and tensile testing dogbones were moulded. Dart drop plaques that were 0.25 cm thick were moulded as well.

Ageing

All resins were aged for 0, 5, 10, 20 and 31 days in air ovens set at 60°C for PET and PETG and 130°C for PC. After ageing, samples were removed from the ovens and allowed to cool at ambient temperature. The MBS modifiers used here were not sufficiently thermally stable to be aged at 130°C for extended amounts of time. Thus, most of the PC work will involve all-acrylic impact modifiers. Ageing had no measurable effect on PET crystallinity, as measured by differential scanning calorimetry.

Testing

All samples were tested by notched Izod (ASTM D256 with 0.25 mm notch radius, milled edgewise, 5.6 J pendulum capacity), by dart drop ('Dynatup' tup velocity of 3.0 m s^{-1}, tup weight of 141 N and tup energy at impact of ~0.47 J) and by uniaxial tensile drawing (ASTM D638, 0.76 cm gauge length, 1.3×10^{-4} m s^{-1} jaw separation speed). The impact tests were conducted at both 23°C and −20°C, whereas tensile testing was conducted at room temperature. Owing to a shortage of samples, low-temperature impact data are in places missing for 5 and 10 day ageing times. Generally, five samples were used in each impact test and four to ten samples for each tensile test. After testing, the Izod samples were retrieved, mounted on stubs, sputter coated with Au/Pd (and in a few cases pure Au), and then viewed by a scanning electron microscope operated at 10 kV.

RESULTS AND DISCUSSION

Tensile testing

The most prominent changes in tensile properties for all compounded samples are that the Young's modulus and yield stress of all neat resins are lowered by the addition of impact modifiers. Upon ageing, yield stress increases for all samples and then remains essentially constant at long ageing times. This behaviour corroborates with previous work done in this area[4–6]. Recall that ageing phenomena have been associated with a 'densification' process in which the free volume of the polymer is reduced as chains relax towards a more equilibrium state[3,6,10,12,13]. Greater energy (higher stresses) would thus be required to initiate the chain slippage associated with yielding in these densified samples[11,13].

Both break stress and elongation at break either remain constant or decrease with ageing, as would be expected for embrittlement. For instance, the elongation at break of PETG drops very suddenly upon ageing. This is accompanied by a drop in break stress. This effect is not seen in impact-modified PETG. Elongation at break remains relatively constant as a function of ageing for both neat and impact-modified PET.

Impact testing

Polyesters. The room-temperature Izod impact strength of PET and PETG is quite low (27 and 64 J m^{-1}, respectively). By adding impact modifier, not only is the impact strength greatly increased (710 and 1040 J m^{-1}, respectively), but is relatively insensitive to ageing (*Figures 1* and *2*). At −20°C, the Izod impact strengths of PET and PETG are again quite low (~27 J m^{-1}). Impact modification yields marginal toughening in PET (<110 J m^{-1}) and excellent toughening in PETG (720 J m^{-1}). (This difference in behaviour may be attributable to modifier dispersion effects.) The impact-modified PETG essentially retains impact strength with ageing (660 J m^{-1} at 30 days ageing).

Both PET and PETG are subject to a serious loss of room-temperature impact strength with ageing, as

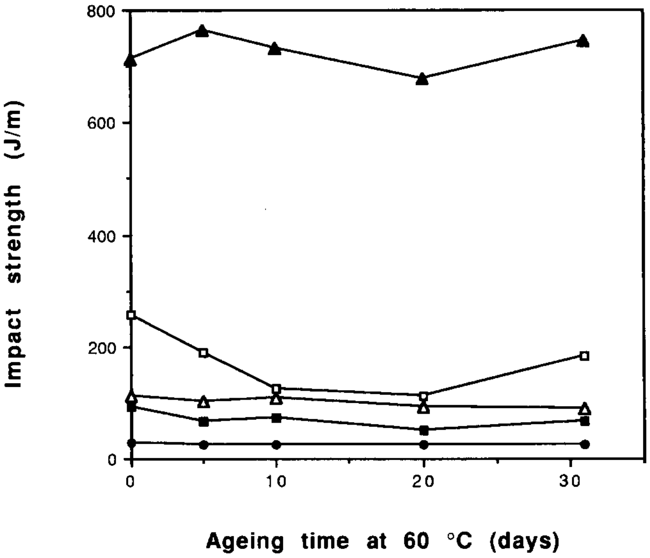

Figure 1 PET notched Izod impact strength at 23°C *versus* time aged at 60°C: (●) PET; (□) PET + 15% Paraloid EXL-3373; (■) PET + 30% Paraloid EXL-3373; (△) PET + 15% Paraloid EXL-3647; (▲) PET + 30% Paraloid EXL-3647

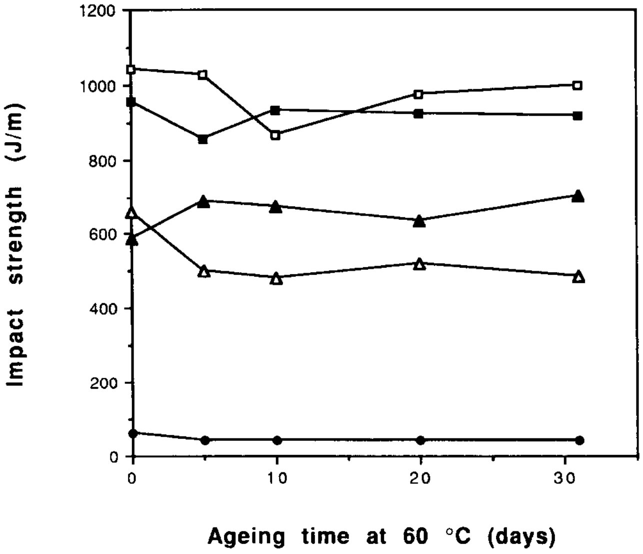

Figure 2 PETG notched Izod impact strength at 23°C *versus* time aged at 60°C: (●) PETG; (□) PETG + 15% Paraloid EXL-3373; (■) PETG + 30% Paraloid EXL-3373; (△) PETG + 15% Paraloid EXL-3647; (▲) PETG + 30% Paraloid EXL-3647

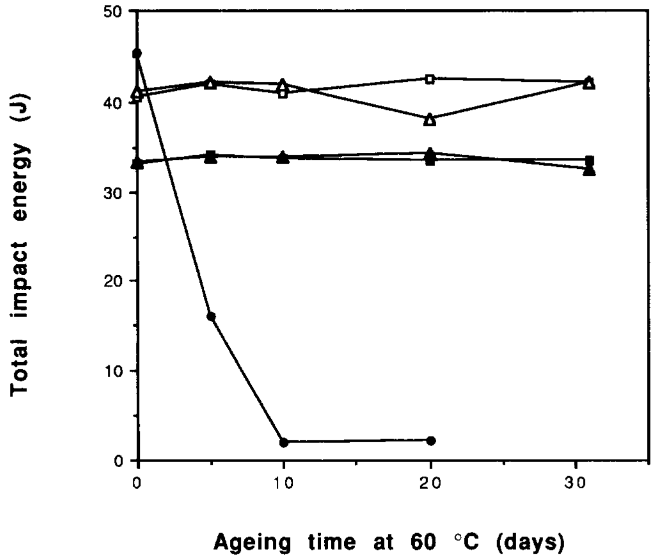

Figure 3 PET dart drop total impact energy at 23°C *versus* time aged at 60°C: (●) PET; (□) PET + 15% Paraloid EXL-3373; (■) PET + 30% Paraloid EXL-3373; (△) PET + 15% Paraloid EXL-3647; (▲) PET + 30% Paraloid EXL-3647

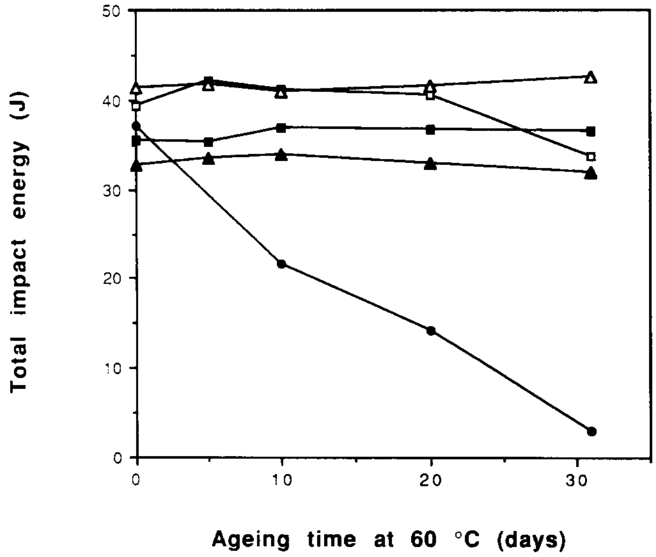

Figure 4 PETG dart drop total impact energy at 23°C *versus* time aged at 60°C: (●) PETG; (□) PETG + 15% Paraloid EXL-3373; (■) PETG + 30% Paraloid EXL-3373; (△) PETG + 15% Paraloid EXL-3647; (▲) PETG + 30% Paraloid EXL-3647

evidenced by dart drop data (*Figures 3* and *4*). Unaged base resins have impact strengths equivalent to or greater than those of their modified counterparts (~41 J total energy absorbed by base resins). However, ageing at 60°C reduces impact strength of unmodified material to ~3 J within 30 days, whereas impact-modified materials retain their impact strength with ageing.

At −20°C, the dart drop impact strength of unaged PET is already very low (3 J), though it can be boosted to 34 J by the addition of impact modifiers. PETG, on the other hand, is initially quite tough (46 J), though toughness is gradually lost with ageing. In contrast, impact-modified PETG remains ductile (~34 J) even with ageing.

Polycarbonate. The Izod impact strength of PC varies substantially with temperature. At room temperature, impact strength is high (890 J m^{-1}) but drops precipitously with ageing (64 J m^{-1} within 31 days at 130°C). The addition of impact modifier reduces impact strength somewhat (probably due to uncharacteristically high impact modifier loadings used) but also greatly suppresses ageing effects, such that at ageing times of 5 days or more the impact-modified PC is much tougher than the neat resin (*Figure 5*). At −20°C, unaged neat PC is not very tough (< 160 J m^{-1}). The addition of 15% AIM raises impact strength to ~640 J m^{-1}. After 30 days of ageing, the impact-modified PC still retains an impact strength of 540 J m^{-1}.

In contrast to Izod data, room-temperature dart drop data for PC suggest that PC derives much less benefit from the addition of impact modifiers, since the impact strength of neat PC was reduced only from ~53 to 48 J after 30 days of ageing at 130°C.

A comparison of dart drop and Izod impact behaviour for unaged PET and PETG suggests that these resins are particularly notch-sensitive (*Figures 1–3*). Likewise, although PC is tough by both the Izod and dart drop evaluation prior to ageing, retention of impact strength with ageing appears to be very different for the two tests. The apparent difference between impact toughness retention with ageing as measured by Izod and dart drop testing is due to the different test geometries and thus stress fields that arise during impact.

The dependence of stress state on sample geometry is well established[4–6,14]. For instance, at sufficiently high strain rates, thick samples (or sharply notched samples) fail in a relatively brittle manner when compared to thinner (or bluntly notched) samples owing to the greater plane strain *versus* plane stress character which develops during deformation in the thicker (or sharply notched) parts. In thinner parts, drawdown (yielding) along the thickness direction can preclude the development of triaxial stresses during deformation. The above observed thickness effects have in fact given rise to geometrical criteria that are used as guidelines to ensure the attainment of plane strain (triaxial stress) conditions in test parts[15]. An increase in yield stress (such as that which

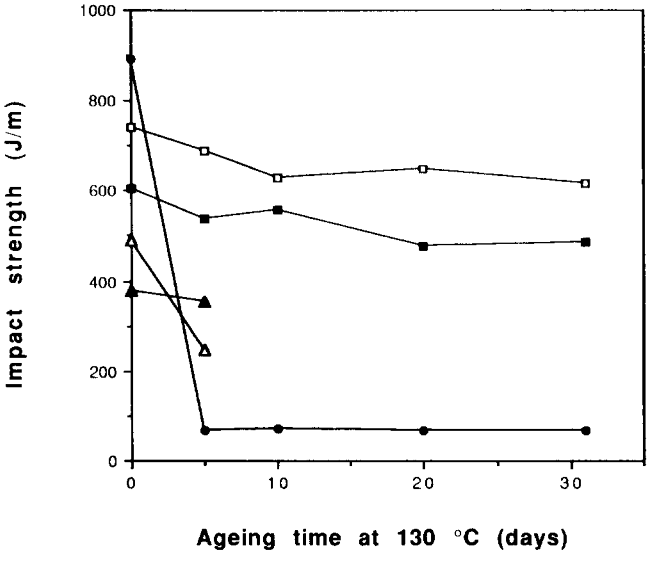

Figure 5 PC notched Izod impact strength at 23°C *versus* time aged at 130°C: (●) PC; (□) PC + 15% Paraloid EXL-3373; (■) PC + 30% Paraloid EXL-3373; (△) PC + 15% Paraloid EXL-3647; (▲) PC + 30% Paraloid EXL-3647

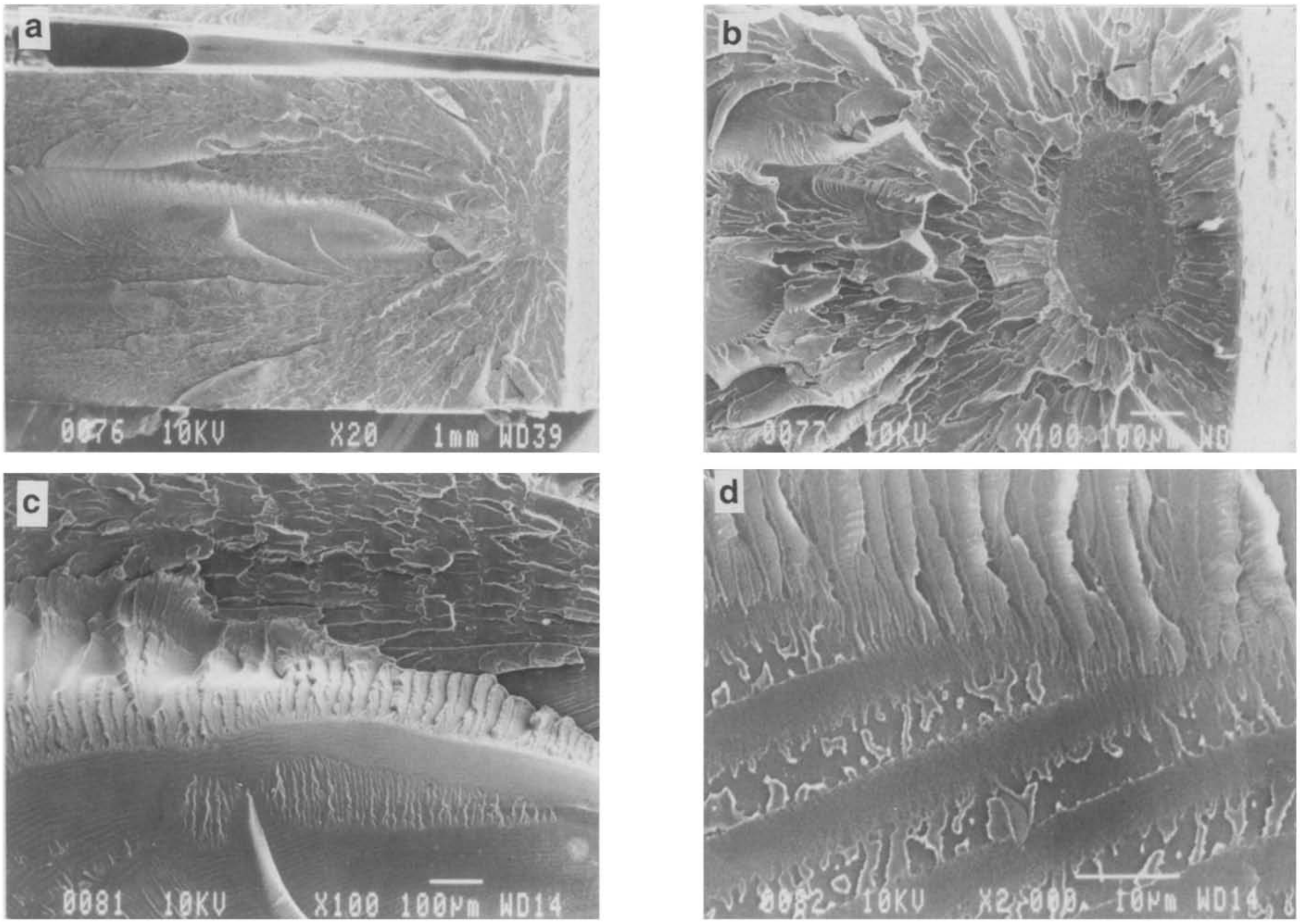

Figure 6 SEM micrographs of PETG notched Izod bar fracture surface, 23°C failure: (a) × 20, notch at right; (b) × 100, oval region near notch; (c) × 100, fracture bands and Wallner lines away from notch; (d) × 2000, Wallner lines (all micrographs are reduced to ~70% for reproduction)

occurs during ageing) reduces the part thickness needed to attain plane strain conditions during impact.

In the present Izod experiments on PC, drawdown occurs in unaged specimens only. It appears that the increase in yield stress with ageing hinders drawdown and results in the generation of triaxial stresses (more of a plane strain state) during impact[5]. This causes crazing and brittle failure rather than shear yielding and ductile failure to occur during impact[6,16]. Izod bars apparently fail in a brittle manner while dart drop plaques do not, because of the high stresses present at/near the notch tip, where craze initiation takes place.

Morphological studies

Unaged resins. In order to understand the notch sensitivity of PET and PETG, fracture surfaces of these materials were analysed by SEM. The fracture surfaces of unaged PET and PETG Izod bars look very similar, revealing a craze-initiated brittle failure morphology (*Figure 6*) similar to that seen by others[5,6,16]. Apparently, a predominantly triaxial stress state develops at/near the Izod bar notch, which effectively increases the shear yield stress, causing it to exceed the craze stress, and leading to craze-initiated failure. In dart drop plaques, stress concentrators such as notches are not present. Thus, the effective yield stress is lower[17] and shear yielding may well prevail as the deformation mode prior to failure.

The morphological features that typify brittle craze-initiated failure are essentially the same as those outlined by Hull and Owen[16]. They include a well defined oval initiation site from which hackles radiate. Initiation does not always occur exactly at the notch, but rather may be somewhat away from the notch, depending on the brittleness of the sample[5]. The initiation site typically either contains an inhomogeneity or is geometrically predisposed to be the region of high stress concentration. The region just surrounding the initiation site (crack origin) is often smooth in appearance. It is called the 'mirror' zone, and is associated with slow crack velocity. The mirror zone may result from the rupture of craze fibrils from a single craze. As the crack velocity increases, the surface 'roughens', and one progresses into the 'mist' zone. The mist zone is characterized by non-coplanar failure, though the crack planes are much closer to one another than in the hackle region. Indeed, the non-coplanar appearance may be due to oscillation of the crack front from one bulk/craze interface to the other interface of a given craze as opposed to failure of two different non-coplanar crazes. Often the mist region looks patchy in appearance owing to this non-coplanar failure. Such a morphology was observed here at initiation sites of both PET and PETG. The crack front propagates along the length of hackles, away from the initiation site. Hackles arise from localized plastic deformation on the fracture surface and form by the failure of non-coplanar crazes, giving the surface a very rough appearance. Hackles are typically associated with high crack velocities.

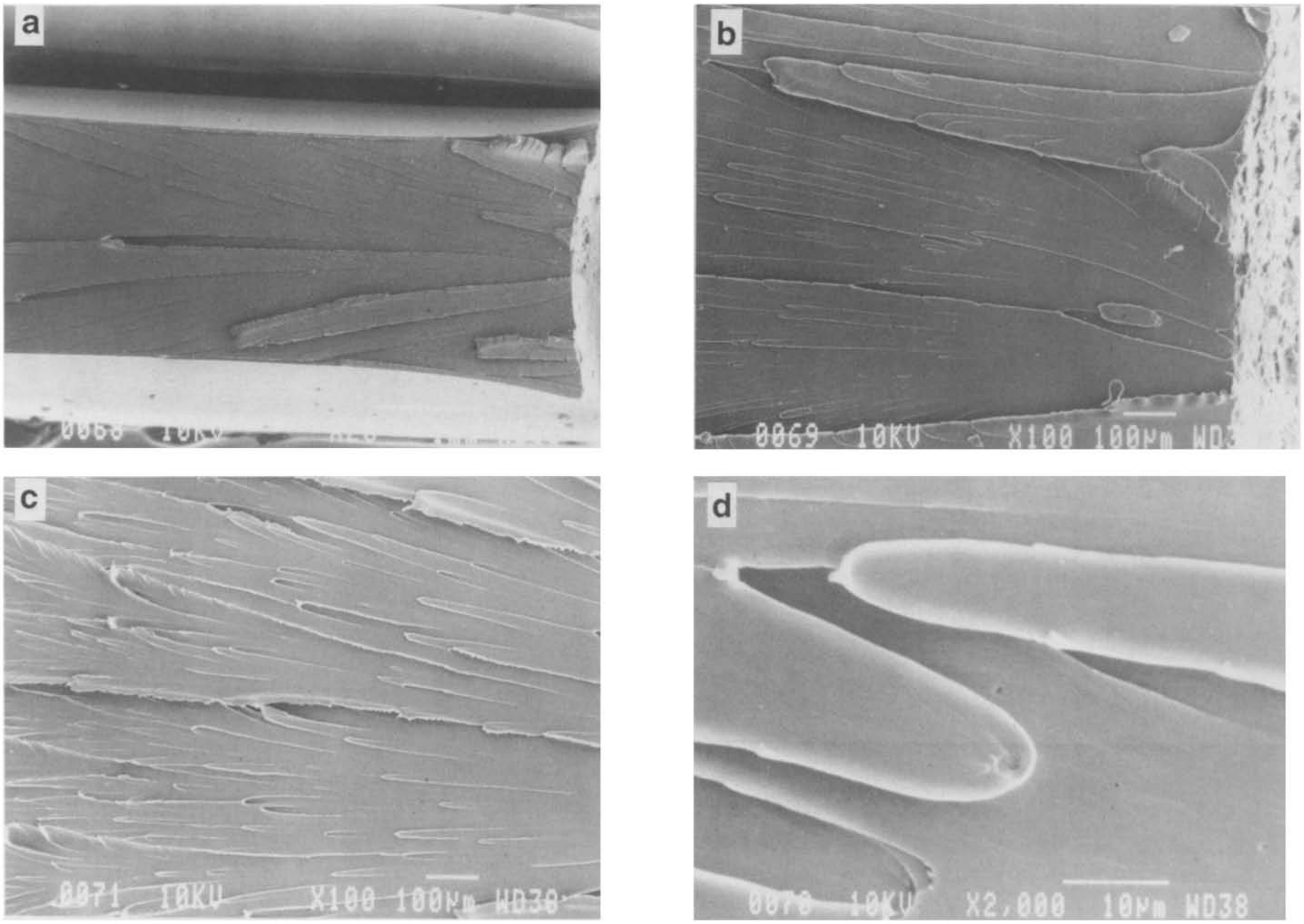

Figure 7 SEM micrographs of non-coplanar failure in PC notched Izod bar fracture surface, 23°C failure: (a) ×20, notch at right; (b) ×100, notch at right; (c) ×100; (d) ×2000 (all micrographs are reduced to ~70% for reproduction)

Progressing along the crack growth direction, there is a cyclic (period of ~100 µm) increase and decrease in surface roughness, which will be termed ribbing. This may be attributed to the periodic branching of crazes that precede the crack front. Other features of interest are Wallner lines. These lines are periodically spaced (10 µm). In *Figure 6c* they can be seen running perpendicular to the ribbing, which suggests that they arise from the interaction of the crack-front stress field and a stress wave reflected off the side of the Izod bar[16,18]. Wallner lines, like ribbing, can be attributed to a periodic oscillation between planar and non-coplanar failure.

The fracture morphology of the PC Izod bar is in stark contrast to that of PET and PETG. This is not surprising, since unaged, unmodified PC fails in a ductile manner and is quite tough in both room-temperature Izod and dart drop tests. Although the fracture surface (*Figure 7*) is non-coplanar it is relatively smooth at high magnification (10000×). Even though failure occurs on a couple of planes, the multitude of failure planes seen in PET and PETG are absent. In addition, there is no oval initiation site. Clearly PC fails by a different mechanism than PET and PETG. In light of these morphological features, it is probable that PC deformation involves a significant amount of shear yielding[16].

Impact-modified resins. PET and PETG impact modified with 30% MBS impact modifier both fail in a ductile manner and have high Izod impact strength provided the impact modifier is adequately dispersed (*Figures 1* and *2*). Observation of Izod fracture surfaces of both impact-modified PET and PETG reveals that deformation takes place at numerous sites during impact, the impact modifiers acting as local stress concentrators (*Figure 8*). Some ductile fibrils of matrix are evident. In addition, very small holes are present in the fracture surface. Visual observation of tested PET dart drop plaques reveals that impact-modified PET forms shear bands during impact whereas unmodified PET shows no evidence of stress whitening at all. Apparently, shear yielding of the impact-modified matrix at multiple sites enables much energy to be absorbed and dissipated prior to failure, thus toughening the polyester.

When PC is impact modified with 15% AIM, the Izod impact strength decreases slightly (*Figure 5*). This is a result of the overly high loadings used. Typically, loadings of <8% are recommended, and in those cases the addition of impact modifier has been known to increase impact strength. The Izod impact morphology of impact-modified PC (*Figure 9*) differs significantly from that of unmodified PC (*Figure 7*). The parabolic hackles, as seen in neat PC, are no longer present. Moreover, a close-up of the fracture surface (*Figures 9c* and *9d*) reveals a surface full of small holes (~500 nm in diameter), which are approximately the same size as the impact modifier. The surface also gives evidence of ductile fibrils pulled from the matrix.

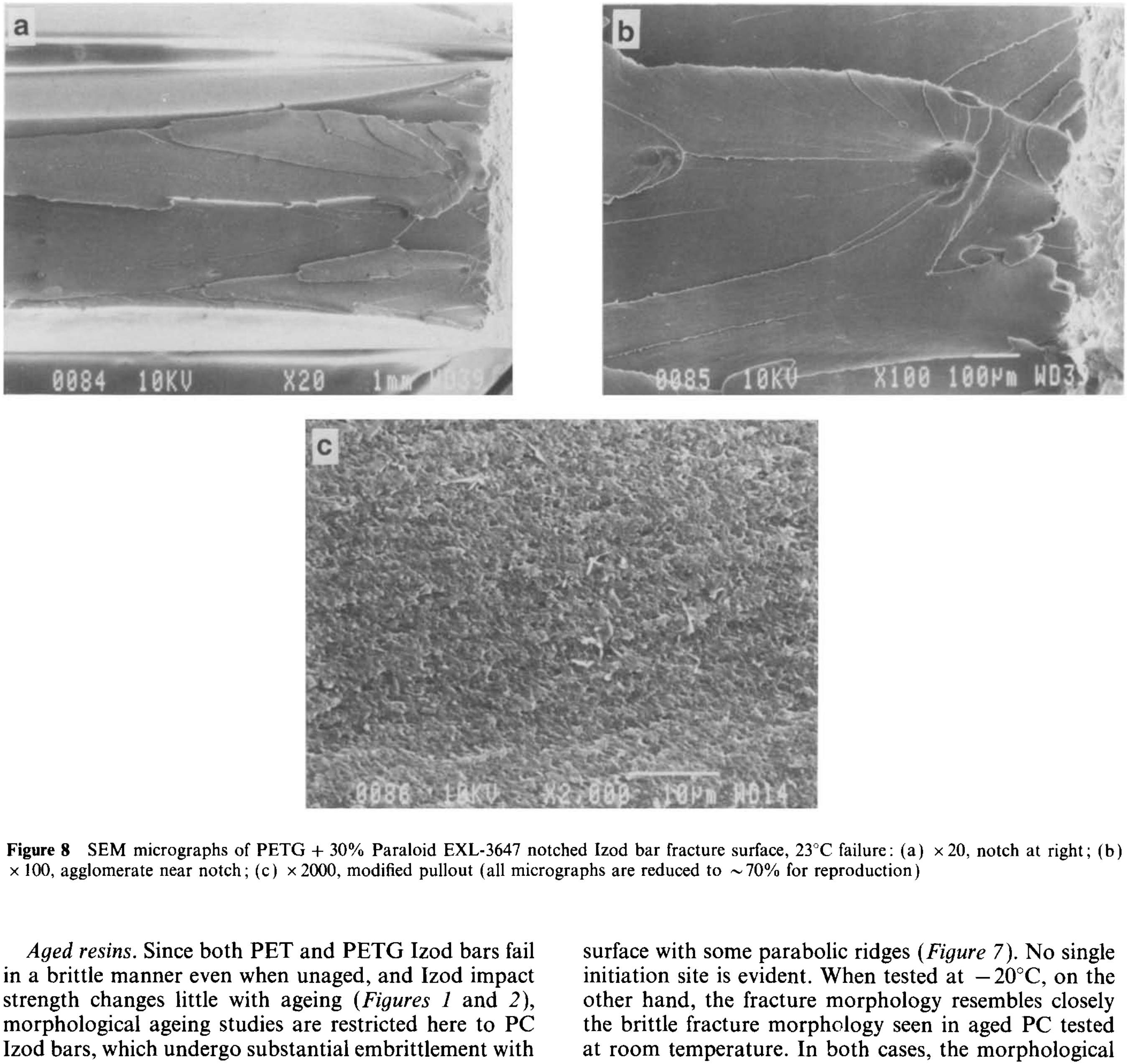

Figure 8 SEM micrographs of PETG + 30% Paraloid EXL-3647 notched Izod bar fracture surface, 23°C failure: (a) ×20, notch at right; (b) ×100, agglomerate near notch; (c) ×2000, modified pullout (all micrographs are reduced to ~70% for reproduction)

Aged resins. Since both PET and PETG Izod bars fail in a brittle manner even when unaged, and Izod impact strength changes little with ageing (*Figures 1* and *2*), morphological ageing studies are restricted here to PC Izod bars, which undergo substantial embrittlement with ageing (*Figure 5*).

PC aged for five days at 130°C fails very differently than unaged PC. In fact, the aged PC fracture surface morphology is essentially equivalent to that seen for unaged PET and PETG, indicating a craze-initiated mode of brittle failure.

Impact-modified polycarbonate. As with unaged modified PC, the fracture surface of 15% AIM modified and aged (5 days at 130°C) PC is full of 'holes'. The holes are approximately the same size as the impact modifier. The similarity between aged and unaged impact-modified PC fracture surface morphologies is consistent with the negligible difference in impact strength of the two Izod sets (*Figure 5*). It is evident that ageing effects on failure mode are very much minimized by the presence of impact modifier.

Effect of impact temperature. PC Izod bars undergo a ductile to brittle transition as impact temperature decreases from 23 to −20°C. A comparison of fracture morphologies bears this out. As shown previously, neat PC tested at room temperature shows a relatively smooth surface with some parabolic ridges (*Figure 7*). No single initiation site is evident. When tested at −20°C, on the other hand, the fracture morphology resembles closely the brittle fracture morphology seen in aged PC tested at room temperature. In both cases, the morphological features of fractured Izod bars clearly indicate brittle failure by a craze-initiated mechanism. Thus, aged PC (tested at 23°C) fails by essentially the same mechanism as unaged PC tested at −20°C.

Impact modifier cavitation versus *debonding*

SEM micrographs reveal holes in fracture surfaces that are approximately the same size as modifier particles. Such holes can arise in several different ways. The most obvious way is that the modifier particles debond from the matrix, leaving behind a hole. A second possibility is that the modifier particles cavitate and the fracture crack then splits the cavitated particle open, leaving behind a hole. Thirdly, it is possible that the fracture crack proceeds through the modifier particle, forming a free (fracture) surface. This would enable the rubber to relax and be drawn into the bulk of the material, away from the surface, thus forming a depression. (The rubber particles may be under tensile stress prior to impact owing to the difference in thermal expansion coefficients between the rubber and the matrix.) Although all of these scenarios are possible, the immiscibility of the acrylic-based outer shell of the modifier with PET and

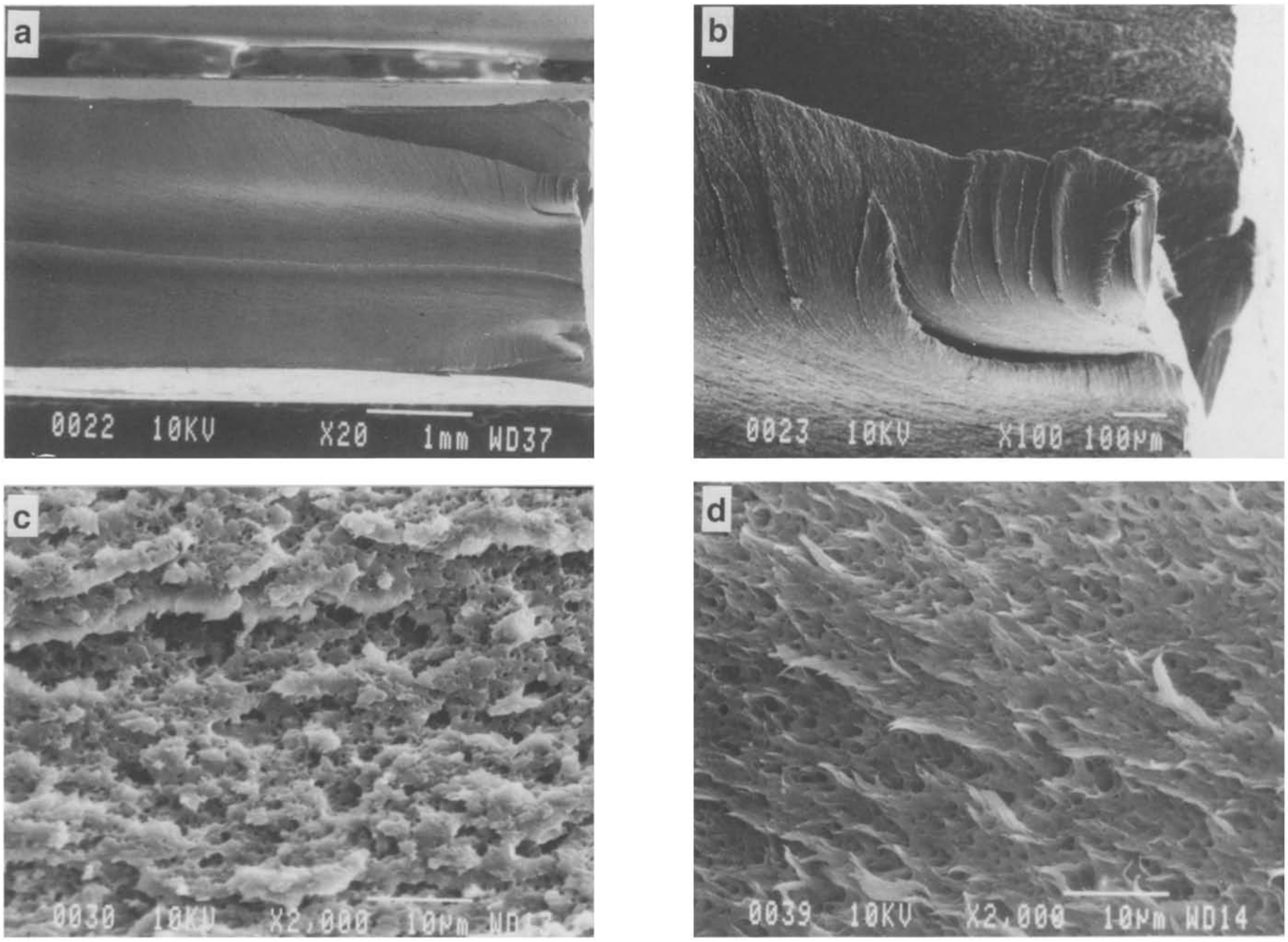

Figure 9 SEM micrographs of PC + 15% Paraloid EXL-3373 notched Izod bar fracture surface, 23°C failure: (a) × 20, notch at right; (b) × 100, notch at right; (c) and (d) × 2000, close-ups of deformation (all micrographs are reduced to ~70% for reproduction)

PETG matrices causes one to expect debonding to occur. Impact modifiers in PC, on the other hand, have recently been shown to cavitate and then promote shear yielding[19]. The cavitation rather than debonding is consistent with the apparent compatibility of PC and PMMA[20]. The consequences of debonding or cavitation are that they produce a stress state in the matrix near the particle, which is very biaxial in nature (owing to the free surface). This in turn promotes shear yielding rather than crazing as a deformation mechanism since yield stress is lower in a biaxial than triaxial stress state[17]. Shear bands, which are seen in impact-modified PET dart drop plaques while none are seen in neat PET, provide further evidence of a shear yielding mode of deformation.

CONCLUSIONS

This work was conducted to determine the effect of commercially available MBS and AIM impact modifiers on ageing-induced embrittlement in non-crystalline polymers such as PC and polyesters. Results demonstrate that the presence of impact modifiers enables such materials to retain impact strength with ageing. The ageing-induced ductile to brittle transition in PC is attributed to an increase in shear yield stress with ageing, thus reducing the likelihood of shear yielding as a deformation mechanism. A reduction in test temperature has the same effect on yield stress and appears to affect the deformation mechanism in a similar way, bringing about brittle craze-initiated cracking.

Whether a material is brittle due to ageing, low test temperature, or the nature of the resin itself, the addition of impact modifier to the material can increase toughness by changing the deformation mechanism. One main effect of impact modifiers on deformation is to promote simultaneous deformation at numerous sites. During impact, the matrix around modifier particles yields, as evidenced by the generation of shear bands. Moreover, the modifier particles themselves may deform. Cavitation of modifier particles, or debonding of modifier from the matrix, are believed to foster shear yielding by generating more of a biaxial stress state in the matrix near the particle and reducing the yield stress locally.

Clearly, ageing-induced embrittlement of PC, PET and PETG can be reduced to a great extent by the judicious use of impact modifiers. Such modifiers not only enable a material to attain high impact strength at the outset, but to retain it as well.

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