Structural changes during the deformation of thermoplastics in relation to impact resistance

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Plain and rubber-modified polymers deform by shearing, crazing, and voiding. The structural changes during deformation were studied by density measurements, small-angle X-ray scattering (SAXS), and electron microscopy (EM). The consequences of these deformation processes for impact resistance are briefly discussed.

INTRODUCTION

Besides elastically stored energy, energy-dissipating large-scale plastic deformation processes which occur by crazing[1,2] and/or shearing[3] determine the impact strength of plastics. Void formation is very often superimposed on both processes. This complex deformation behaviour is not completely understood at the present time and led us to study these structural changes and their consequences on ductility.

EXPERIMENTAL

For measuring the ductility the Charpy impact flexural test (DIN 53453) was applied. All test pieces were injection-moulded, unless another method is explicitly mentioned. The test apparatus is equipped with a force and displacement transducer for recording the force–deflection diagrams during testing.

The structural changes during tensile deformation were observed by

(i) measuring the density in a dilatometer filled with water in which the deforming test piece was immersed

(ii) SAXS from specimens in the stressed or unloaded state

(iii) electron microscopy (EM) of ultramicrotomed sections cut preferentially in the tensile direction of the sample.

RESULTS AND DISCUSSION

The preferred deformation process inherent in the various polymers in tension can very often already be deduced from the appearance of deformed specimens: necking and reduction of the cross-section of the test piece indicate shear processes; stress whitening is mainly caused by crazes and voids. These deformation mechanisms are not only influenced by the chemical nature of the polymers, physical ageing effects, and the thickness of the specimens (the latter influence prohibits transferring results from thin samples to thick ones), but also by the test temperature and strain rate.

Figure 1 presents as an example the force–deflection diagrams of various plain polymers at different test temperatures. Each of these products is highly deformable near room temperature (right column of *Figure 1*) and consequently ductile. At the temperature of liquid nitrogen (left column) the same products are brittle and they are only able to store elastic energy. In the middle column of *Figure 1* the force–deflection diagrams are given for these products at those temperatures at which the molecules are starting to

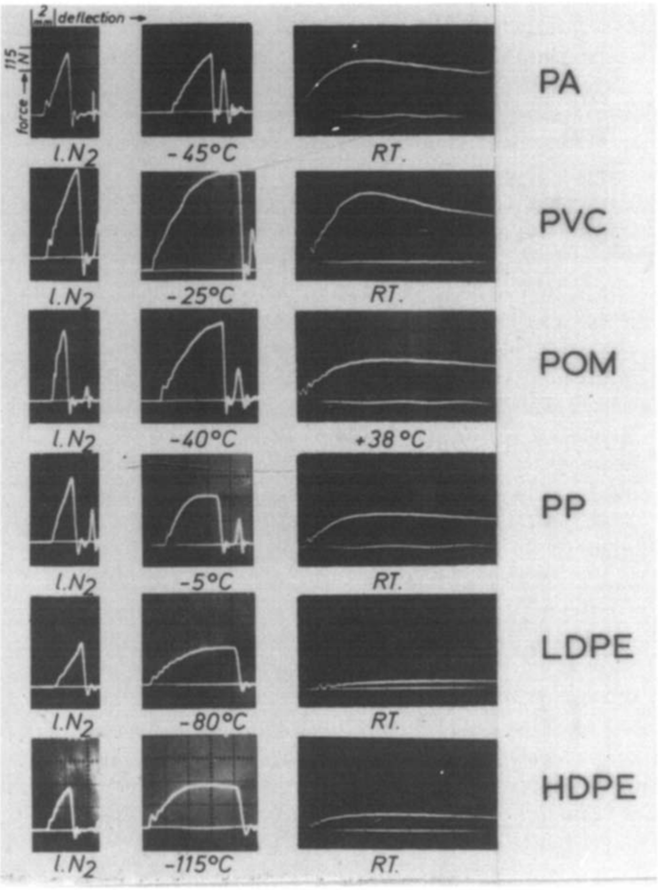

Figure 1 Force–deflection diagrams recorded during impact strength tests (unnotched specimens)

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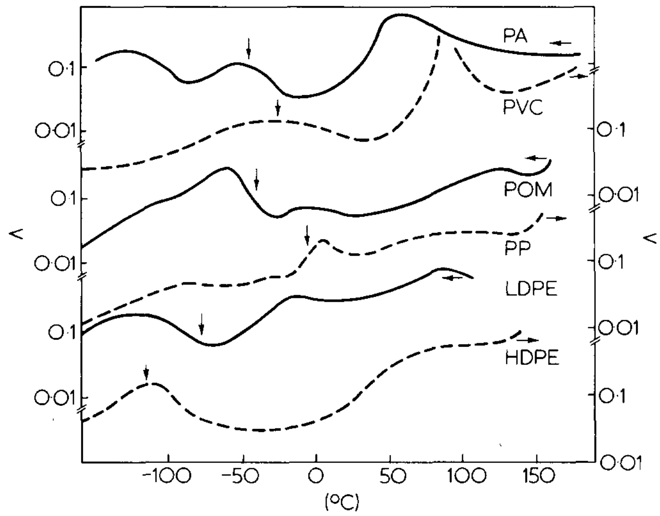

Figure 2 Logarithmic decrement of various thermoplastics measured by the torsion pendulum method (DIN 53445)

become mobile enough to enable onset of plastic deformation processes, but at which they are not mobile enough to avoid crack formation and consequently fracture.

The temperatures at which the molecules begin to be sufficiently mobile for plastic deformation to occur is also reflected in torsion pendulum measurements (DIN 53445). In *Figure 2* the temperatures at which the products mentioned in *Figure 1* (middle column) begin to be deformable are indicated by arrows on the log (decrement) curves. The onset of large scale plastic (shear) deformation processes coincides with a region of pronounced relaxation transition. In comparing the temperatures for impact strength and relaxation processes we must pay attention to the different strain rates in both tests since temperatures in impact test correspond (according to the higher strain rate and accepting a time–temperature equivalence) to lower temperatures in torsion pendulum measurements. The temperature difference depends on the activation energy of the decisive relaxation process. Apart from this temperature shift the impact test does not allow us to locate precisely the temperature for the elastic–plastic transition because the onset of plastic deformation is not very sharp and its detection depends also on molecular weight and orientation of the molecules. But anyway, the temperature dependence of the internal friction proves instructive for finding the temperature region for the beginning of mobility of molecules and large scale plastic deformation. A quantitative correlation between the log (decrement) peak and impact strength is not to be expected because pendulum measurements are performed in the linear viscoelastic range, whereas impact strength is a highly non-linear phenomenon, including fracture processes. Products like PS and SAN which do not show any pronounced relaxation process below room temperature deform at ambient temperature primarily by the craze mechanism. Materials in which relaxation processes take place near (test) room temperature, e.g. PMMA and to some extent PVC play a less precise role. These materials deform at ambient temperature by both crazing and shearing.

A well-established way of improving the impact strength is to incorporate rubber particles into thermoplastics. By this method additional sites for initiation of extensive deformation processes inherent to the matrix material are introduced into the material. Examples are rubber-modified PS(HIPS), SAN(ABS) and PVC.

Dilatometer measurements have proved helpful[4] in separating quantitatively dilatant processes (crazing, voiding outside crazes) from shear processes, because shear processes are believed not to change the density of the material whereas dilatant processes are known to do so. It has very often been overlooked in the literature that dilatometer measurements, however, do not distinguish craze formation from other dilatant processes (voiding). Therefore, additional test methods must be applied.

Figure 3 shows transmission electron micrographs of ultramicrotomed sections cut parallel to the tensile direction of a deformed HIPS. As expected for this material and in accordance with density measurements on the same material[5], a number of crazes perpendicular to the tensile direction are seen between the rubber particles. This enhanced crazing is believed to dissipate the impact energy. In the material shown here, crazing is accompanied by void formation inside the rubber particles, especially near the sites where crazes contact the particles. From this result we learn that in a non-shearing material dilatant stress is not only relaxed by forming crazes and voids in the matrix, but also by voiding inside the rubber particles. This effect has not found extensive attention in the past (a few exceptions are, e.g. the work of Haaf, Stabenow and Breuer[6] on rubber-modified PVC, the work of Hagerman[7] to whom void formation appears a general response of materials to local high stresses at stress concentrations, and the work of Beahan and Bevis[8] on rubber-modified styrene polymers).

The disadvantage of transmission electron microscopy in studying structural changes relevant in deformation is the need for unloading the test piece and sample preparation during which crazes can disappear[9] and rearrangements can take place. *Figure 4* shows the volume change during deformation of HIPS and ABS. If the strain is sustained after deformation, the density of the specimen remains nearly constant; the stress, of course, relaxes to some extent If, however, the stress is fully relaxed by unloading the specimen, the density increases again, thereby annealing in our case nearly half the volume increase caused by the initial deformation. Therefore it proved instructive to study the materials also in the stressed state.

Figure 5 shows SAXS from HIPS test pieces in the stressed and (unloaded) fractured state, respectively. The diagrams of the deformed specimens show club-shaped scattering in the tensile direction, superimposed by an elliptical or circular halo. In the stressed state scattering is higher than in fractured specimens but shows the same components. The halo represents scattering from voids, elliptically shaped in

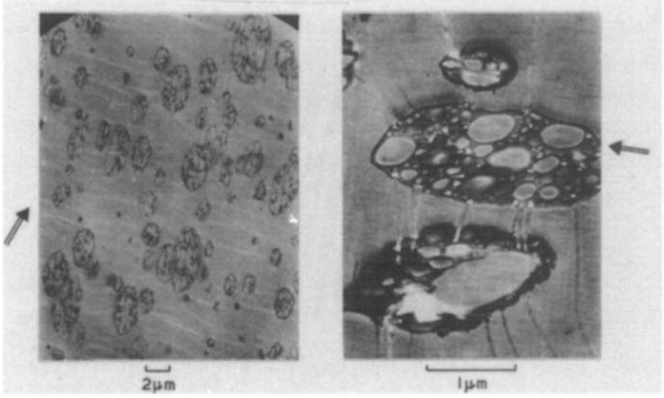

Figure 3 Transmission electron micrographs of ultramicrotomed sections cut in tensile direction of a HIPS sample. (Arrows indicate tensile direction)

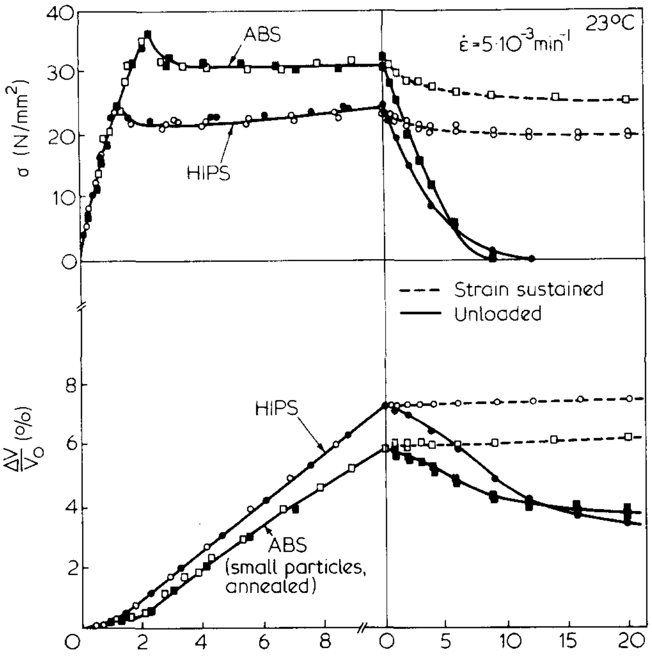

Figure 4 Volume changes of HIPS and ABS (small particles, unoriented) specimens during and after tensile deformation

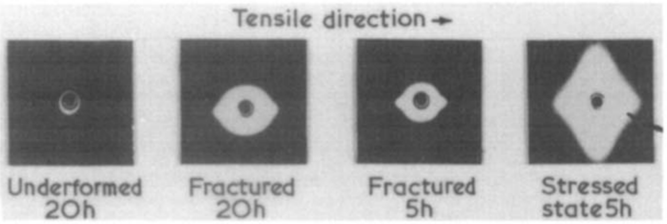

Figure 5 SAXS from deformed HIPS specimens in the deformed and relaxed state (exposure times: 5 or 20 h)

the tensile direction when specimens are stressed, and more spherically shaped in unloaded test-pieces. The club-shaped scattering is caused by minute openings spread out perpendicular to the tensile direction. These openings are probably the crazes visible in *Figure 3.* The halo in the undeformed control sample can be attributed to the scattering from the rubber particles. This result confirms the suggestion that voiding is indeed superimposed on crazing during the deformation and that changes take place during unloading but without producing in principle a new element of structure. We are still working to establish a quantitative correspondence between the EM and SAXS. The difficulty arises in analysing the diffraction pattern of such a complicated arrangement of scattering particles as present in deformed HIPS.

As was shown in a former paper[5], ABS with exclusively small rubber particles ($d \leqslant 0.08$ μm) is only ductile in impact test, if the molecular orientation in the tensile direction is not too high; otherwise, this product is rather brittle. As has been further shown, in the highly oriented state this product does not change its volume during low rate deformation and scarcely shows any stress whitening except near the fracture surface. Consequently, no crazes could have been created on a large scale and only shearing has occurred. In less oriented specimens, however, extensive stress whitening and volume increase during deformation was observed. Further details and explanations of this size- and orientation-dependent effect are given in the above-cited paper[5]. EM (*Figure 6*) now confirms our formerly mentioned suggestion that in this highly oriented ABS material (injection-moulded) even near the fracture surface (*Figure 6a*) no crazes are formed, whereas in annealed (1/2 h at 190°C) and deformed specimens crazes are discernible all over the specimen (*Figure 6b*). In both cases, small voids are formed inside the rubber particles; in oriented testpieces, however, this occurs only near the fracture surface from which *Figure 6a* is taken. The result that rubber-modified styrene polymers are only ductile in impact test when stress whitening occurs and crazes are formed strengthens us in believing crazes to be mainly responsible for the high impact strength in this type of product.

In PVC which in principle is able to craze and shear, Haaf, Breuer and Stabenow[6] have found that after rubber-modification only matrix-shearing and voiding inside the rubber particles occur, but no crazing. The authors claim, therefore, that stress whitening and volume increases are caused by voiding in the rubber particles, but impact strength is due to shearing in this product.

To study deformation processes in rubber-modified thermoplastics with a tough parent polymer in more detail, we included PC with incorporated rubber particles in our measurements. The parent polymer PC is believed to deform under normal conditions (avoiding physical ageing, flaws, craze agent, high temperatures, etc.) only by shearing. Indeed, the volume of the injection-moulded rubber-modified PC only slightly increases (*Figure 7*) beyond the

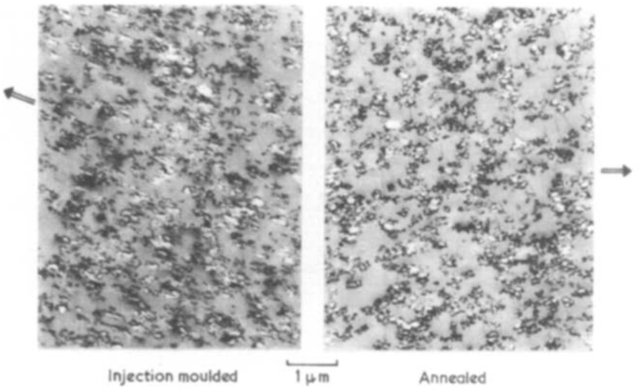

Figure 6 Transmission electron micrographs of ultramicrotomed sections cut in tensile direction of ABA (small particles) specimens which are injection-moulded (left picture) and additionally annealed (right) before deformation. Arrows indicate tensile direction

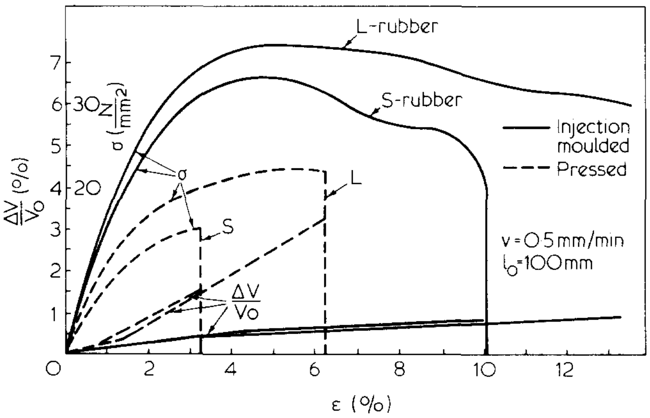

Figure 7 Volume change of rubber-modified (S = small particles, L = large particles) PC, specimens injection-moulded (———) or moulded (— — —)

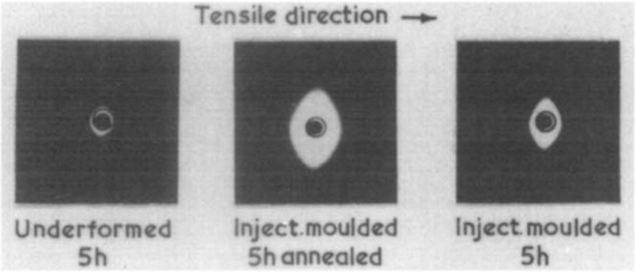

Figure 8 SAXS from rubber-modified PC (L-rubber) (stressed state)

yield stress, dilatant processes are unimportant. But surprisingly the behaviour changes by testing annealed (1/2 h at 200°C) specimens, the volume increases drastically during deformation. From SAXS diagrams (*Figure 8*) void formation (void elongated in the tensile direction) is concluded, but no crazes are discernible. According to our measurements the impact strength of the annealed samples is less than half the value of injection-moulded test pieces. Probably, in this rubber-modified product, voiding occurs not inefficiently for crack initiation inside the rubber particles, like in PVC and styrene polymers, but rather at the rubber/matrix interface. Accordingly, yield stress and fracture strain are small in annealed samples (*Figure 7*). A corresponding situation was described by Yee[10] for polyethylene modified PC.

CONCLUSIONS

The onset of deformation processes inherent to polymers and important for impact strength takes place already below the glass transition temperature near a relaxation transition.

Very often voiding in the matrix or in the rubber particles of modified polymers is superposed on the well-known shear and craze deformation processes.

The superposition of voiding on deformation processes prohibits the separation of crazing from shearing only by dilatometric measurements.

By unloading specimens of crazing-and/or voiding materials the density of the specimen increases again, thereby indicating rearrangements in the deformation structure. This effect limits the application of EM and forces the inclusion of other methods such as SAXS in studies of structural changes during deformation.

In the stressed or strained state the deformation structure is more anisotropic than in the unloaded state.

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