Brittle Fracture in PBT

Cause and Remedies. Injection moulded PBT parts suffer brittle fracture on a sporadic basis in practice, with generally only a few parts being affected. Nevertheless, the damage suffered by the processor may be immense. The latest studies show that a key initiator of this quality impairment is thermal overheating, both during polymerisation and during processing.

Degradation at High Temperatures

Although PBT has proved successful as a solid, dimensionally stable material, it does display a certain notch sensitivity, and hard, sharp-edged inclusions in an injection moulding lead to stress peaks which then cause cracks and brittle fracture. Earlier studies [1 to 3] have shown that highly crystalline structures in PBT are the cause. As with all plastics, other potential causes include pigments, pigment agglomerates and foreign particles. In what follows, it will be shown that cracked PBT particles (specks) are the chief cause of brittle fracture.

Thermal damage (cracking) in PBT has been investigated by different working...
groups [4 to 6]. In general, PBT can undergo thermal, thermo-oxidative or hydrolytic degradation at processing temperatures of between 240 and 280°C. The degradation of the PBT can be tracked via its reduced molecular weight, its viscosity number or its increasing carboxyl number. With pyrolytic degradation, in particular, CO, CO$_2$ and butene are released as gaseous degradation products. Figure 1 shows the thermo-oxidative degradation of PBT 

![Fig. 1. Thermo-oxidative degradation of PBT](image)

Back in 1976 already, Passalacqua et al. demonstrated the degradation mechanism of PBT at temperatures of between 240 and 280°C [4]. As with PET, it is the ester function that constitutes the weak point. The chain is split through a cyclic transitional state, and a new acid end group develops, along with an unstable butadiene end group. This is split off as the next step, and butadiene is released [5]. Figure 2 shows the thermal degradation of PBT at temperatures of between 240 and 280°C with the release of butadiene.

![Fig. 2. Thermal degradation of PBT at temperatures of between 240°C and 280°C with the release of butadiene](image)

**No Influence of Structure and Pigmentation**

The homogeneity and quantity of the colour batch employed plays a key role in respect of brittle fracture. The fracture frequency of a plug made of black-pigmented, non-reinforced PBT was considerably reduced through a more homogeneous distribution of the colour batch. Material that is coloured on compounding units by the raw material producer has a lesser tendency to brittle fracture than material coloured at the injection moulder’s. It still reveals damaged spots at times, however.

The molecular weight distributions measured by means of gel permeation chromatography (GPC) do not indicate any differences between parts suffering tough fracture and those suffering brittle fracture. There is similarly no evident correlation between pigment concentration and the frequency of brittle fracture. On account of pointers in the literature, the investigation also focussed on the crystallinity and structure of the plugs studied. However, neither DSC nor structural investigations based on wide angle X-ray scattering provided any indication as to why the different brittle-fracture be-

![Fig. 3. Optical investigation of inclusions that have developed through the part being stored overnight in the injection mould; the inclusions stand out clearly from the crystalline surroundings](image)

![Fig. 4. Scanning electron micrograph of the inclusions in the part which was left in the injection moulding machine overnight](image)
haviour should occur. Big crystalline superstructures (spherulites) in PBT ought, theoretically, to increase the tendency towards brittle fracture on account of the stress concentration at the spherulite edges. By way of an experiment, it proved possible to suppress the formation of big crystalline superstructures by means of nucleation. No change was seen in brittle-fracture behaviour, however. This means that fluctuations, within the standard range, in colour batch concentration, molecular weight distribution and crystallinity cannot be the cause of brittle fracture.

Inclusions through Thermal Degradation

The results of tests with cracked inclusions provide a completely different picture. In black PBT plugs that had undergone brittle fracture, it proved possible to optically detect hard, black inclusions in thin sections. To allow these inclusions to be clearly allocated to a cause, parts in non-reinforced PBT were injection moulded on an E8 test mould at BASF, with the injection moulding machine being run overnight until it was empty and then switched off without being purged. The next morning, the first parts were taken out of the test mould for testing. The inclusions in these parts stand out clearly against the crystalline surroundings (optical: Fig. 3; X-ray electron micrograph: Fig. 4). When the inclusions in the fractured plugs were compared with the inclusions in the part produced in the test mould by means of Atomic Force Microscopy (AFM), identical structures were clearly evident (Figs. 5 and 6).

In parallel to this, it proved possible to precisely reproduce the brittle fracture in injection mouldings that had fractured in practice by selectively adding approxi-
of the original value. In the second case (Fig. 7, right) the molecular weight falls right down to 5 % of the starting value. One percent of the PBT damaged in this way was mixed with original granules and made into test specimens. Interestingly enough, adding this material does not lead to either a fall in the tensile strength or the elongation at fracture, or to a reduction in impact strength. One explanation could be the good solubility of the thermally shortened, but not oxidised, molecule chains in the PBT.

Thermal or thermo-oxidative degradation is a general phenomenon associated with PBT and thus affects the majority of polymer producers, even if the chain length of the PBT and its glass fibre content or additives vary as a function of the producer and the type of PBT involved. The investigations would, however, suggest that brittle fracture is not attributable to differences in the chain length or in the molecular weight.

Local Overheating causes Specks

The results obtained show that hot points surrounded by oxygen (local overheating) during compounding and injection moulding can be the reason behind damage due to cracking. Cracked particles (specks) can develop in all plastics during either polymerisation or compounding, or indeed during injection moulding proper. In practice, both the raw materials producers and the injection moulders generally take care to keep the concentration and size of cracked particles to a minimum. As was shown through the investigations conducted on PBT, it is particularly important to avoid contact with oxygen at elevated temperatures – as can happen if melt residues remain at the nozzle tip, for instance.

REFERENCES

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