Notes

Observation of “Black” and “White” Crazes in High-Impact Polystyrene under Transmission Electron Microscopy

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Deformation behavior in rubber-toughened polymers has long been studied. It is now well-known that their deformation mechanisms are crazing and shear yielding in the matrix and cavitation and debonding of the rubber particles. When crazing is the dominant deformation mechanism, increase in the craze density is a well-accepted means to increase polymer toughness.[1] Therefore, it is desirable to quantify the craze deformation in order to estimate the polymer toughness.

Transmission electron microscopy (TEM) is commonly used to observe crazes. To observe crazes in bulk specimens, thin slices are prepared using a technique named microtoming. Before the microtoming, the specimens are required to be stained. For polymers containing butadiene rubber, osmium tetraoxide (OsO_4) is the most popular staining agent. OsO_4 reacts with double bonds in the rubber, resulting in increase of brittleness of the rubber particles and contrast between the rubber and matrix.[2,3]

It is known that TEM micrographs from the stained specimens show not only dark rubber particles but also dark crazes (named “black crazes” here),[4−6] in contrast to the surrounding matrix. Kambour and Russell[7] reported that OsO_4 also reacts with craze fibrils, which increases contrast between the craze structure and the surrounding matrix. However, it was not clear about the reaction that enhances contrast of the crazes.

Gebizlioglu et al.[8] examined crazes in high-impact polystyrene stained by OsO_4 using scanning transmission electron microscopy with X-ray fluorescence analysis. They reported that the black crazes contained high concentrations of osmium metal, and by giving sodium metaperiodate treatment, osmium existed in the lower oxide form. They also suggested that the lower oxide of osmium is osmate ester or its mixture with osmium dioxide that was precipitated on craze fibrils.

Brown et al.[9] and Gebizlioglu et al.[10] reported that polystyrene could be toughened by blending it with a small amount (less than 10 wt %) of low-molecular-weight polybutadiene. Their proposed toughening mechanism by the polybutadiene, which was later adopted in a toughening model,[11] is that low-molecular-weight polybutadiene, dispersed in the matrix in spherical shape, is absorbed into crazes under the deformation-induced negative pressure in the crazes. The absorbed polybutadiene plasticizes the craze fibrils and contributes to the toughness increase.

On the two possibilities for the lower oxide of osmium (osmate ester and osmium dioxide) in the crazes that Gebizlioglu et al.[8] proposed, Brown et al.[9] argued that the formation of osmate ester did not explain why the crazes stained in the polybutadine-modified polystyrene had a much stronger contrast than that of crazes in pure polystyrene. Brown et al. suggested that dark crazes might be the result of staining the low-molecular-weight unsaturated rubber molecules that diffused into the crazes during the craze growth.

This paper presents further evidence to clarify the cause of black crazes and provides evidence to show that the rubber molecules are not necessarily diffused into the entire crazes. In other words, crazes that do not contain the rubber molecules can exist in the stained rubber-toughened polymers. Material used for the study was high-impact polystyrene (HIPS). The HIPS contained butadiene of 8 wt %. Weight-average molecular weight of the polystyrene matrix was 225 300. The average diameter of rubber particles was 0.8 μm. HIPS pellets were injection-molded to form dumbbell specimens with a cross section of 6×3 mm^2 in the gauge section.

Mechanical tests were carried out using a falling weight type impact tensile test machine.[12] The specimens underwent low impact tensile loading with a strain rate of 18 s^{-1}. A significant whitening zone was generated by the test, within which fracture occurred. The whitening zone near the fracture surface was then selected for the TEM study.

The morphology and deformation behavior of the fractured specimens were observed using TEM. The specimens were first stained in the vapor of an OsO_4 solution of 2 wt % for 48 h before the microtoming. An ultra-microtome (Reichert Jung Ultracut) with a Diatome diamond knife was used to obtain thin sections of approximately 100 nm in thickness. A Hitachi H7100 TEM, operated at 75 kV, was used for the observation.

A TEM micrograph of an undeformed specimen is given in Figure 1 which shows well-dispersed rubber particles of salami structure with polystyrene (PS) occlusions. The micrograph shows uniform brightness in the PS matrix, with no evidence of crazes.

The deformation behavior of a fractured specimen in a whitening region is shown in Figure 2. The arrow in the micrograph indicates the direction of tensile loading.

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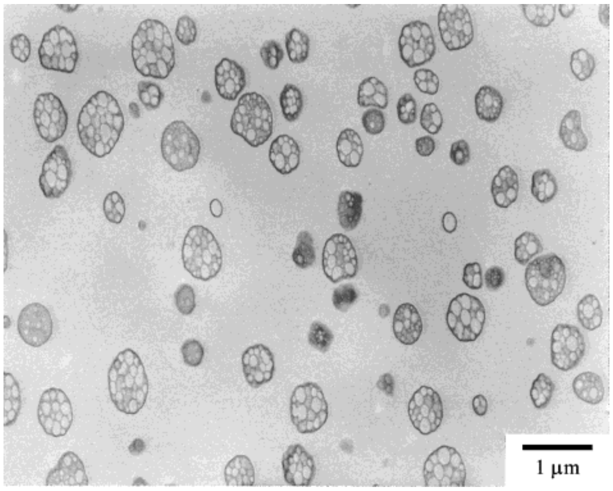

Figure 1. TEM micrograph of an undeformed HIPS specimen.

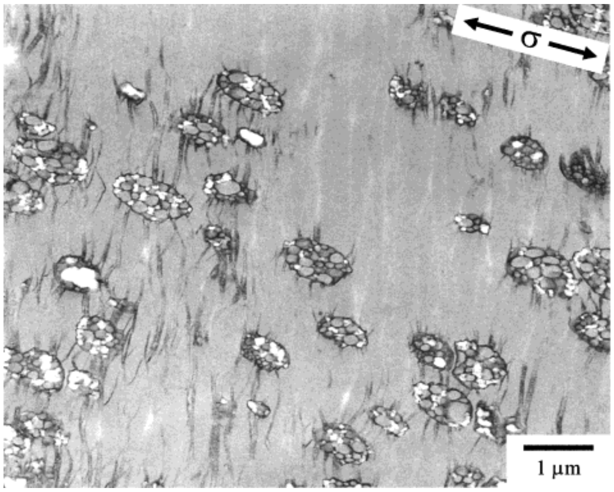

Figure 2. TEM micrograph of a fractured HIPS specimen in a whitening region. The arrow represents the direction of tensile loading.

The micrograph shows many long bright and dark lines in the matrix in a direction nearly perpendicular to the loading. Most of the dark lines are adjacent to the rubber particles, with the bright lines as their extension into the matrix. There is no doubt that the dark lines are crazes (black crazes), but the bright lines were never reported from the stained HIPS in the past. It should be pointed out that the bright lines are not completely white, which suggests the lines do not represent cracks.

Figure 3 shows a micrograph at high magnification at an interface between rubber particles and matrix. The micrograph shows that the bright lines are well connected with the "black crazes", sharing the same boundary line with the undeformed matrix. This suggests that the bright lines are continuations of the black crazes, therefore also representing craze deformation (named "white crazes" in the rest of the text). The existence of the white crazes excludes the above possibility that OsO_4 reacts with the radicals that were created during the chain scission process for the craze formation.

The results show that crazes of different contrast (black and white crazes) can be generated from the stained HIPS. The observation supports the suggestion from Brown et al.[9] as this is the only rational explanation for the coexistence of black and white crazes, depending on whether the crazes are covered or not covered by low-molecular-weight polybutadiene molecules.

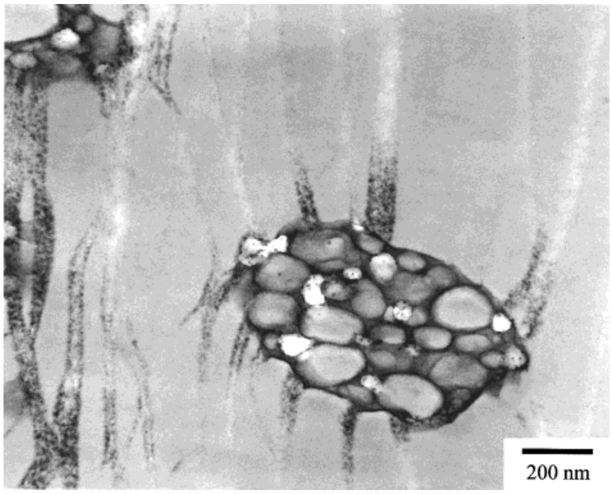

Figure 3. TEM micrograph of a fractured HIPS specimen at an interface between rubber particles and a matrix in a whitening region.

However, there are two features in Figure 2 that require further explanation. The first is that some of the black crazes are not connected with rubber particles; the second is that the length of the black crazes varies before they turned to white, and in some cases only white crazes were generated from the rubber particles. For the first feature, it was probably caused by the sectional view of the TEM micrographs on the two-dimensional growth of the crazes. When the craze growth direction is out of the plane of the TEM sample, the sample only shows part of the craze growth path which may appear to be isolated from the particles but is in fact connected to the rubber particles that are not included in the TEM samples.

For the second feature (the different lengths of the black crazes), we believe that this is caused by difference in molecular weight of the polybutadiene molecules. As the mobility of the polybutadiene molecules strongly depends on their molecular weight, the low-molecular-weight molecules can diffuse further into the crazes, compared to the high-molecular-weight molecules. This results in a relatively long black craze after staining. It should be noted that mobility of the molecules also depends on the strain rate. The highest strain rate used in the study, 18 s^{-1}, is expected to have a strong restriction on the molecular movement, thus significantly shortening the black craze length. However, at this stage, we could not assess molecular weight variation of polybutadiene in the rubber particles.

The results also indicate that black crazes do not represent all of the crazes that can be generated in the specimen. Considering only the black crazes for the deformation mechanism may underestimate the energy absorption capability of the material. Therefore, TEM should be used with caution in examining stained rubber toughened polymers, to make sure that all crazes, including the white crazes, are considered for evaluating the extent of the deformation behavior.

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