NOTES

Spherulite Cracking During Oxidative Aging of Polypropylene

In our research on polypropylene some observations were made which are believed to be of interest to those concerned with oxidative degradation of polyolefins.

When polypropylene sheets are aged at 135°C. in air, a rather sudden change of the tough sheet into a grainy powder is observed after a certain heating time. In order to gain an impression of these structural changes during heat aging we have aged thin films of a polypropylene fraction ($[\eta] = 2.53$) pressed on microscope slides and crystallized at 135°C.

Figure 1 shows a sample in polarized light after 5 days at 135°C. The structure is still identical with that after 1 day at 135°C. The film consists of well-shaped spherulites, showing mixed positive and negative birefringence.

The temperature was then raised to 140°C., and the sample was investigated daily. After 14 days at 140°C., a large number of cracks was observed in part of the sample (see Figs. 2 and 3). The whole sample was cracked after 17 days.

Nearly all cracks lie along the spherulite radii and pass through the centers of the spherulites. In Figure 4 is shown a part of the sample which has just started to crack.

Fig. 1. Polypropylene film of fraction crystallized at 135°C. after aging in air for 5 days at 135°C.; as viewed through crossed nicols, 48×.

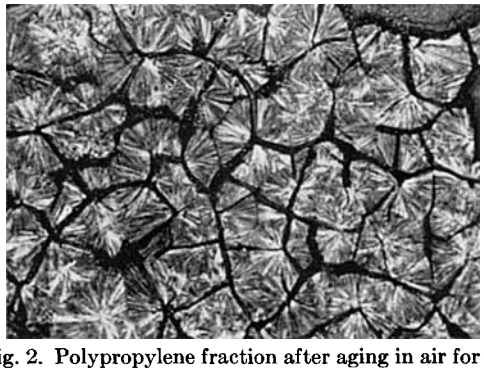

Fig. 2. Polypropylene fraction after aging in air for 5 days at 135°C. and 14 days at 140°C.; as viewed through crossed nicols, 48×.

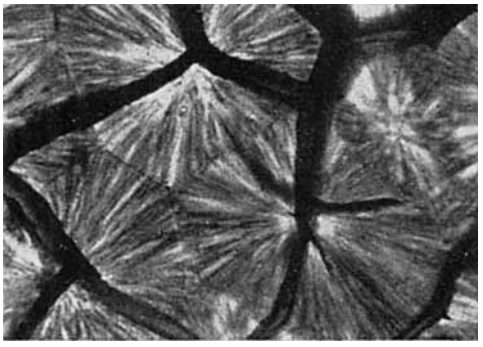

Fig. 3. Detail from Fig. 2; 190×.

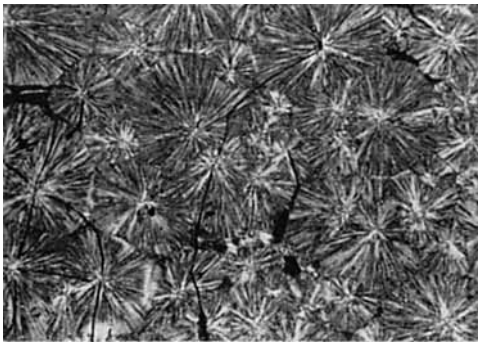

Fig. 4. Polypropylene sheet showing initial crack formation after aging in air at 135 and 140°C.; as viewed through crossed nicols, 48×.

A similar radial crack formation was observed by Reding and co-workers[1,2] during thermal degradation of polychlorotrifluoroethylene and during stress cracking and heat embrittlement of high-density polyethylene.

Apparently, in all three polymers the radii of the spherulites are weaker than the boundaries, contrary to the hypothesis of Kafavian,[3] who assumed that during heat-aging the spherulites would be left intact, whereas the amorphous boundaries would be readily attacked by oxygen.

References

1. Reding, F. P., and A. Brown, *Ind. Eng. Chem.*, **46**, 1962 (1954).
2. Reding, F. P., and E. R. Walter, *J. Polymer Sci.*, **38**, 141 (1959).
3. Kafavian, G., *J. Polymer Sci.*, **24**, 499 (1957).

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