Morphology of ethylene–propylene copolymers

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A separated phase has been observed in ethylene–propylene block copolymers. However, the morphology of this separated phase, identified by Differential Interference Contrast Microscopy (d.i.c.), depends on the method of manufacture and it has been suggested that the difference in morphology arises from the formation of an amount of true AB-type block copolymer manufactured in the gas-phase process. This component is not thought to be present in copolymers so far examined, produced by means of the diluent process.

Keywords Morphology; microscopy; polyolefin; copolymers; phase separation

INTRODUCTION

Polyolefine development in recent years has concentrated mainly on improving the performance of existing materials. Two areas of research that have been investigated are the production of physical blends of proportions of homopolymers with various types and amounts of thermoplastic rubbers, and the development of the copolymers in which the two monomers are present in the same reaction vessel. In this paper the sole consideration will be the ethylene–propylene copolymers.

Two types of copolymer are available commercially, the random or statistical type in which, as their name implies, the ethylene is incorporated in a purely random manner; this type includes the thermoplastic rubbers manufactured at high ethylene contents using a vanadium catalyst system. The second group of copolymers are the so called 'block' copolymers where the copolymerized ethylene is thought to reside in distinct regions of the polymer chain. Until recently little or no data was available regarding the nature of the block segments of these materials. Cogswell and Hanson[1] arrived at the conclusion that in certain ethylene–propylene end block copolymers the material consisted of a physical blend of two homopolymers, a high molecular weight polyethylene dissolved in polypropylene of a lower molecular weight. In the light of subsequent evidence it is felt that in the copolymerization process it is unlikely that the product would be a simple two component system comprising two homopolymers, since the change from one monomer feedstock to the other is not a clean one and that for a short time at least the reaction vessel will contain competing monomers, giving rise to a material with variable composition. The copolymers investigated by Cogswell and Hanson were presumably manufactured using a diluent process. In this process one monomer after the other is passed into a hydrocarbon diluent containing a Ziegler type coordination catalyst in suspension. More recently a series of papers by Prabhu *et al.*[2–4] describe an investigation into block copolymers manufactured using a Gas Phase Process, that is, using a dry Ziegler type catalyst and gaseous monomers in a two stage reaction. By preparing multiblock AB type copolymers up to $(AB)_{200}$ and identifying the carbon–carbon links between the constituent blocks using a number of techniques, they concluded that this manufacturing technique yields predominantly true $(AB)_n$ type block copolymers in which the ethylene rich segment of the chain is chemically linked to the homopolymer preblock. This gas phase process is also used commercially; in the first stage polymerization takes place in a propylene atmosphere, then after a predetermined time the polypropylene preblock, along with the living catalyst and some unreacted monomer, is transferred to a second vessel containing a mixture of ethylene and propylene.

The occurrence of phase separation in ethylene–propylene block copolymers was reported recently by Curson and Louden[5] in a paper describing the combined use of Differential Interference Contrast Microscopy (d.i.c.) and Laser Raman Spectroscopy. In that paper they described the identification of a separated phase within the polypropylene matrix by means of d.i.c. then, using the microscope to direct a beam of laser light at the separated phase, they analysed the Raman scatter. Using this technique they were able to show that the separated phase had the composition of an ethylene–propylene rubber. Again it is assumed that the material used by these workers was manufactured by the diluent process.

The aim of the present work is to show that phase separation occurs in block copolymers manufactured by both the diluent and gas-phase processes, but that the morphology of the separated phase is different for the two materials so far studied, and it is hoped to show that the different morphologies may originate in the method used for manufacture.

EXPERIMENTAL

Materials

Two block copolymers were used in this study, both commercially available materials. The first contained

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Figure 1 (a) Diluent block copolymer between crossed polars. (b) Diluent block copolymer in Differential Interference Contrast

approximately 3% ethylene and was manufactured by the diluent process; this will be designated diluent block. The second material was a 6% ethylene copolymer manufactured by the gas phase process, this will be referred to as gas phase block. These two materials were compared microscopically with a homopolymer and a random copolymer containing 3% ethylene.

Microscopy

5 μm sections of each of the materials were cut with a glass knife microtome from compression moulded plaques. The plaques were moulded at 190°C in an electrically heated press then cooled to 120°C at which temperature they were held for at least one hour. This procedure resulted in specimens displaying large, well formed spherulites. The sections were viewed in transmitted light on a Nikon Optiphot Universal Microscope. Two illumination modes were employed, plane polarized light by which the spherulitic structure, typical of the polyolefines, is evident and secondly, Differential Interference Contrast, a mode that is very sensitive to microscopic differences in either specimen thickness or refractive index; contrast being created by the difference in light paths of adjacent beams generated by the Nomarski prism[6].

RESULTS

The same field of view is evident in the photomicrographs in *Figures 1a* and *b*. In *Figure 1a* the diluent block is viewed between crossed polars while in *Figure 1b* the illumination is d.i.c. In *Figure 1b*, within the bulk of the spherulite, small circular inclusions can be seen. Since it is unlikely that the specimen thickness will vary in such a way, it seems reasonable to assume that these inclusions indicate a separated phase. The shape of the inclusions in this case are regular with dimensions ranging from 0.7 to ~ 3 μm. The size of this phase is variable and dependent on the thermal history of the sample and may be altered by repeated melting and recrystallization processes.

Figures 2a and *b*, however, are photomicrographs of the gas phase block viewed between crossed polars and in d.i.c. respectively. Although the spherulitic structure seen in *Figure 2a* is not too dissimilar from that in *Figure 1a*, the shape and size of the inclusions in *Figure 2b* are significantly different to those in *Figure 1b*, in this case the shape is much less regular and smaller in size, the maximum dimension being in the order of 1 μm.

Figures 3 and *4* show the same features of the diluent block and the gas phase block in d.i.c., but this time at a higher magnification to emphasize the difference in shape.

The photomicrographs in *Figures 5* and *6* show sections of the hompolymer and the random copolymer viewed in d.i.c. and it is evident that the separated phase is absent in both cases. No separated phase is to be expected in the homopolymer since, apart from very small quantities of stabilizer and atactic polypropylene, this material is essentially a one component system. At the low ethylene concentrations, present in the reactor during the manufacture of the random copolymer, the comonomer enters the chain at isolated intervals and as such is unable

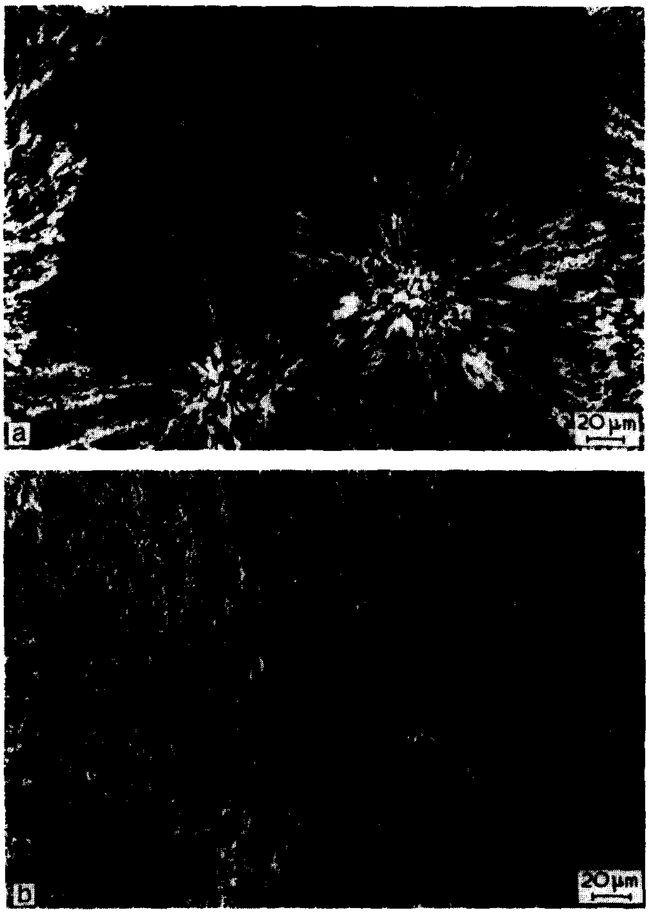

Figure 2 (a) Gas phase block copolymer between crossed polars. (b) Gas phase block copolymer in Differential Interference Contrast

Figure 3 Diluent block copolymer in Differential Interference Contrast

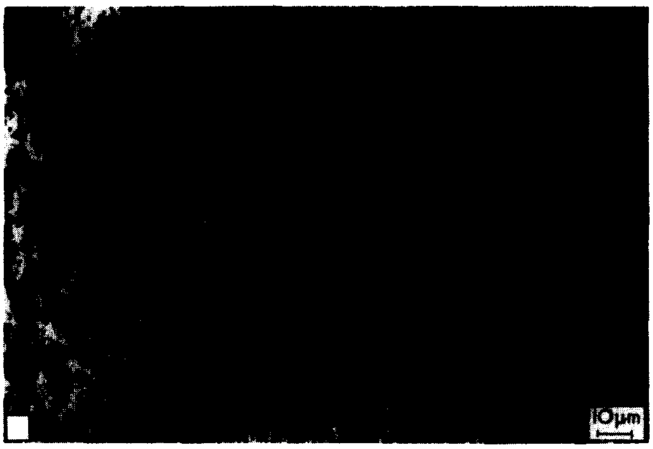

Figure 4 Gas phase block copolymer in Differential Interference Contrast

Figure 5 Homopolymer in Differential Interference Contrast

Figure 6 Random copolymer in Differential Interference Contrast

to separate and form a second phase. Because of its small size, with respect to the propylene repeat units, it is able to enter the crystalline matrix of the polypropylene during chain folding.

DISCUSSION

The differences in morphology highlighted here, between copolymers manufactured by the different processes, result from the formation of the separated phase. This second phase is a consequence of the formation of an ethylene–propylene rubber-like transition region occurring during the change from one monomer supply to another. The rubber regions, once formed, coalesce during the first melting stage after polymerization because of their incompatibility with the homopolymer melt and are fixed by subsequent cooling and crystallization processes to produce the inclusions visible in the microscope. The ethylene rich regions in the diluent block copolymers, if it is assumed that they are not chemically linked to the homopolymer preblock, may be expected to coalesce with a greater ease to produce the larger well formed spheres.

The size of the separated phase in the gas-phase block copolymer, although smaller than in the diluent block, is too large to be accounted for solely by the presence of the ethylene-rich end blocks of a true copolymer. It may be explained by assuming that even in the commercial gas-phase process a certain amount of free rubber will be produced. It is possible, because of the smaller size and the higher reactivity of the ethylene molecule, that some new chains will initiate in the second stage of the reactor. However, the tendency for this process to yield significantly greater amounts of true AB-type block copolymer manifests itself as the smaller irregular shapes of the separated phase. The block copolymer chains act as an emulsifier between the separated phase and the polypropylene matrix decreasing the size of the inclusions in a similar fashion to that described by Heikens and Barentsen[7] in their study of polystyrene/polyethylene blends with added graft copolymer. Participation of the polypropylene preblock in the crystallization process on cooling acts to deform the particles, resulting in their irregular shape.

CONCLUSION

For the limited number of samples so far examined it has been shown that a separated phase is present in ethylene–propylene block copolymers, the morphology of which appears to differ depending on the method of manufacture. The results obtained may be interpreted as evidence for the presence of an amount of true ethylene–propylene block copolymer produced in the gas-phase process. It is possible that the presence of this component will influence the properties of the copolymer and it may be that this will need to be considered when selecting materials for particular applications.

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