Dynamic Orientation Studies of Polymers

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Static and dynamic x-ray diffraction, small angle x-ray scattering, light scattering, small angle neutron scattering, birefringence, infrared dichroism, crystalline polymers, polyethylene.

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DYNAMIC ORIENTATION STUDIES OF POLYMERS

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INTRODUCTION

The purpose of this investigation was to carry out dynamic wide angle x-ray diffraction (WAXD), small angle x-ray scattering (SAXS), dynamic birefringence, dynamic small angle light scattering (SALS), and dynamic infrared dichroism (IRD) on various types of polyethylene and their blends. These goals were accomplished and have led to several important research publications, as described below.

SUMMARY

The technique of dynamic small angle x-ray scattering was developed in which the x-ray scattering could be observed as a sample was subjected to oscillatory strain. This was done, using a stroboscopic signal averaging type technique, at the National Center for Small Angle Scattering Research at the Oak Ridge National Laboratory. It was possible to observe the dynamic opening and closing of voids as well as the orientation of crystalline lamellae.

Wide angle x-ray diffraction was used to study crystal orientation of radiation crosslinked polyethylene samples which were crystallized from the oriented melt. At low melt orientations, the a-crystal axis was found to orient parallel to the stretch direction, whereas with increasing melt orientation, one progressed to a state of c-axis orientation. A degree of crosslinking - melt orientation superposition principle was discovered in which corresponding states of crystal orientation occurred at corresponding states of melt orientation. Morphological transitions of these samples were studied using the small angle light scattering technique.

The use of the two-dimensional optical multichannel analyzer (OMA) was developed for the quantitative studies of SALS during crystallization and deformation. Techniques for calibration and for data processing were developed. A principal use for this device was in the study of blends of linear low density polyethylene (LLDPE) with high density polyethylene (HDPE) and with conventional low density polyethylene (LDPE). The SALS studies were accompanied by WAXD, SAXS and raman longitudinal acoustic mode (LAM) spectroscopy. It was concluded that LLDPE co-crystallized with HDPE but not with LDPE. However, in the latter case, both species reside in the same spherulites. A two-step crystallization occurs where the LLDPE crystallizes first, forming volume filling spherulites. The LDPE crystallizes by a secondary process within the already formed spherulites. These two stages may be readily followed with the OMA.

Dynamic mechanical properties and dynamic birefringence studies were carried out on the above blends. Because of the differing morphological role of the two components of the LLDPE/LDPE blends, they were found to contribute to these measurements in a non-equivalent manner. The properties were dominated by the LLDPE component which formed the "backbone" of the spherulites. It is notable that this reinforcing effect of the LLDPE occurs even when it is present at only 10% concentration. This illustrates a relatively new and important concept in the understanding of polymer morphology - where a small amount of a crystallizable component in a blend can influence the morphology of a major component, and thus have a major influence on properties.

Another application of this principle deals with the use of nucleating agents to
control crystal morphology. The SALS technique, using the OMA, was applied to the study of the nucleation of polypropylene (PP) and LLDPE by the soluble organic nucleant, dibenzyl sorbitol (DBS). It was found that the DBS not only served to nucleate more spherulites and hence, decrease their size, but also changed the internal arrangement of crystals within the spherulites. This observation indicates the possibility of inducing major property changes with small amounts of nucleant.

The OMA was also used to study the spherulite deformation process. Quantitative HV, VV, and Hh polarized light scattering data were obtained for uniaxially deformed PE and PP samples. Data revealed not only information about the change in spherulite shape, but also details about the way in which the crystals within the spherulites rearranged. Results were fitted to parameters in models involving such parameters was shown that the deformation modes of PE and PP were quite different. An affine model for internal spherulite deformation was shown to be inadequate, and good progress was made in developing a non-affine model.

The above technique has the advantage that data acquisition is fast, so that measurements may be extended to dynamic studies. Thus, the completed work "opens doors" for new studies for which alternative support is being sought.

Another novel technique pioneered during this study was the use of small angle neutron scattering (SANS) for the study of chain deformation. Such studies were carried out on polystyrene (PS) and PE, where it was found that the molecular extension of high MW PS is affine but that for PE is not. A paper is being prepared considering proposed models for the latter situation. These measurements also are leading to appreciable additional studies of chain extension in crystalline polymers for which support (ONR) has been approved. They also point the way to future dynamic studies which will permit "molecular level" rheology of crystalline polymers.


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