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Effect of Absorbed Chemicals on the Local Mode Relaxation in Aliphatic Hydrocarbon Polymers

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ABSTRACT: Samples of low-density polyethylene, ethylene/propylene rubber, and 66 nylon were allowed to absorb various amounts of low molecular weight compounds, and their dynamic mechanical properties were measured. In several cases, the strength of the local mode relaxation was reduced, and the glass transition was shifted to markedly lower temperatures.

Introduction

In an earlier study,[1] it was found that the presence of up to 6.8% of various chemicals did not affect the temperature or strength of the γ-relaxation in poly(tetrafluoroethylene) (PTFE). Other relaxations which occur in the amorphous regions at higher temperatures were affected by the presence of absorbed chemicals. It was concluded that the γ-relaxation, which has been associated with the motion of short chain segments, in the amorphous regions[2] is entirely intramolecular.

The behavior of the γ-relaxation in PTFE is in sharp contrast with the effect of water or methanol on the γ-relaxation in 66 nylon.[3] In nylon, the γ-relaxation is reduced in strength and is shifted to slightly lower temperatures.[4] Water and methanol are antiplasticizers for nylon and increase its modulus at temperatures below the α-relaxation.[3] Dielectric studies[5] showed that absorbed water narrowed the γ-relaxation of nylon in the frequency domain, causing it eventually to approach the Debye model for a single relaxation time. It was concluded that at low temperatures water forms mechanically stable bridges between amide groups in adjacent chains, thus increasing the modulus and restricting the γ-relaxation to the motion of isolated polymethylene sequences between amide groups. Of course, the remaining dielectric activity indicates involvement of at least a few amide groups.

In view of the contrasting effects of absorbed chemicals on the local mode relaxations in PTFE and nylon, it was decided to investigate similar phenomena in polymers of ethylene and to study the effect of additional chemicals on nylon.

Experimental Section

Compression-molded bars of a low-density polyethylene (LDPE) having a density of 0.919 g/cm^3 after a standard cooling cycle were immersed in various solvents until the weight no longer increased. Other specimens were placed in closed jars with fixed amounts of solvents and equilibrated for times longer than those required to reach saturation. Similar experiments were performed on specimens of cured ethylene/propylene rubber (EPDM) having an ethylene/propylene mole ratio of 3.9. While this material was largely amorphous, it had an endothermal DSC peak at 54 °C, with a latent heat of 6.3 cal/g, corresponding to about 9% polyethylene-type crystallinity. Nylon studies were done on the oriented tape which had been used in earlier work.[3]

All samples were tested on the Du Pont 982 dynamic mechanical analyzer (DMA) coupled to the 1090 thermal analyzer.

Polymers of Ethylene

Initially, samples of low-density polyethylene were saturated with toluene, *n*-hexane, and isooctane, respectively. The dependence of the loss modulus on temperature is shown in Figure 1. The γ-relaxation at −115 °C was unaffected by the presence of 8.4% isooctane but largely suppressed in samples which had absorbed 14.9% toluene or 16.6% *n*-hexane. In all three cases, the β-relaxation was shifted to markedly lower temperatures.

Samples of LDPE were then allowed to absorb various amounts of toluene from 3.4% up to saturation. As shown in Figure 2, increasing levels of toluene progressively reduced the maximum in the loss modulus for the γ-relaxation with little change in temperature. The temperature of the β-relaxation shifted to lower temperatures as the amount of absorbed toluene was increased. A similar series with isooctane also showed a shift in the β-relaxation but no significant change in the γ-relaxation.

Because cross-linked ethylene/propylene rubber (EPDM) is highly amorphous, it is possible to study higher levels of absorbed toluene. The plots of loss modulus in Figure 3 show that as in LDPE, toluene lowered the peak height for the γ-relaxation and shifted the β-relaxation to lower temperatures. The pattern seems to change somewhat beyond 8% toluene.

Actually, the data for LDPE and EPDM fit together quite well. The maxima in loss modulus for the γ-relaxation follow the same relationship (Figure 4). The peak height decreases up to 8–10% toluene (dry basis) and then

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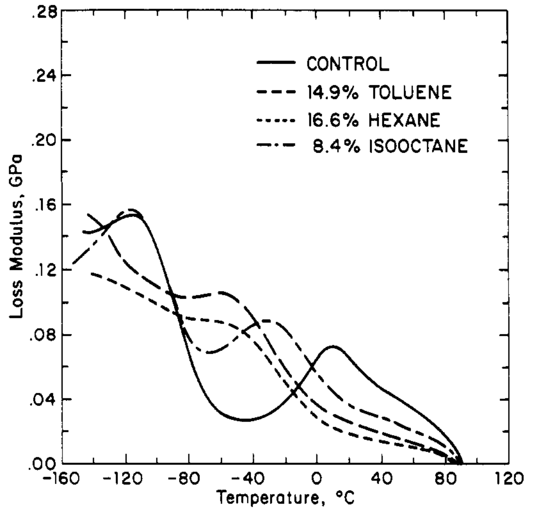

Figure 1. Loss modulus of LDPE saturated with various solvents.

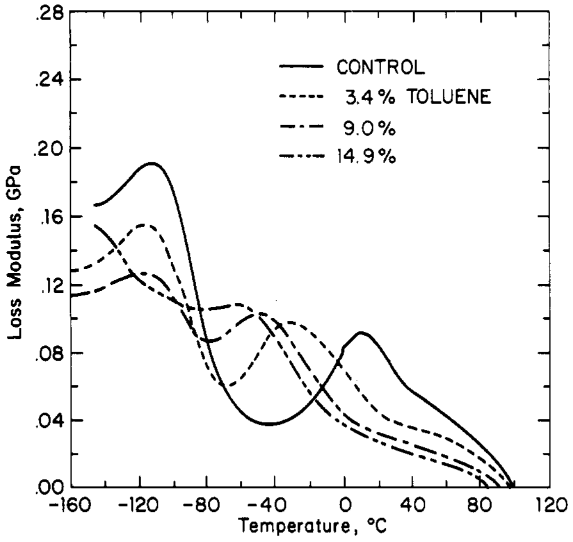

Figure 2. Loss modulus of LDPE containing various amounts of toluene.

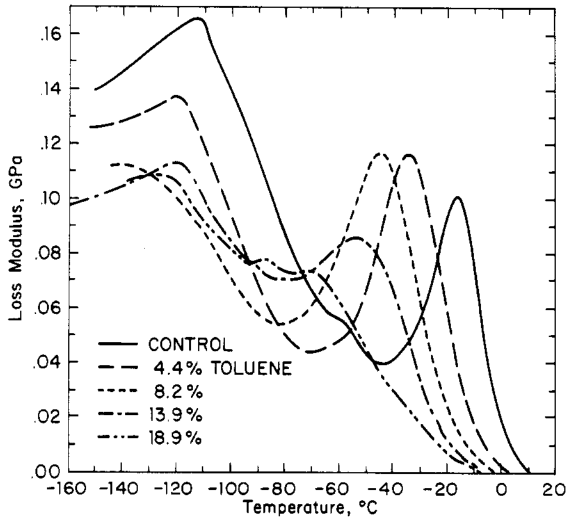

Figure 3. Loss modulus of EPDM containing various amounts of toluene.

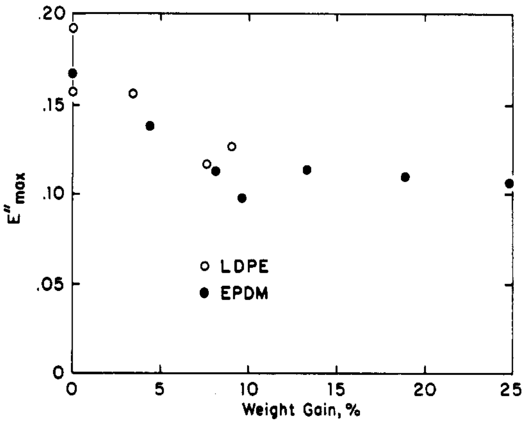

Figure 4. Effect of toluene on the maximum in loss modulus for the γ-relaxation in polymers of ethylene.

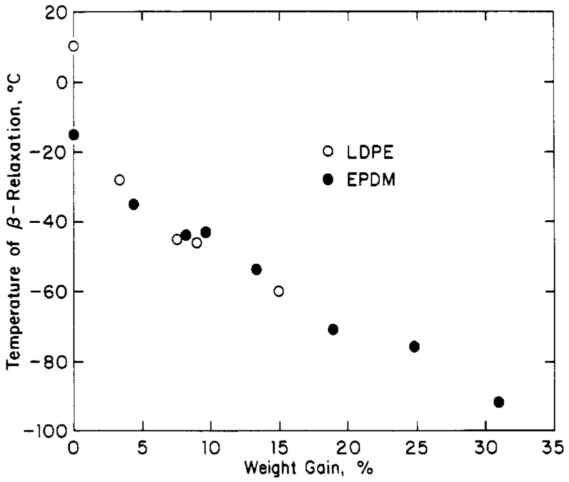

Figure 5. Effect of toluene on the temperature of the β-relaxation in polymers of ethylene.

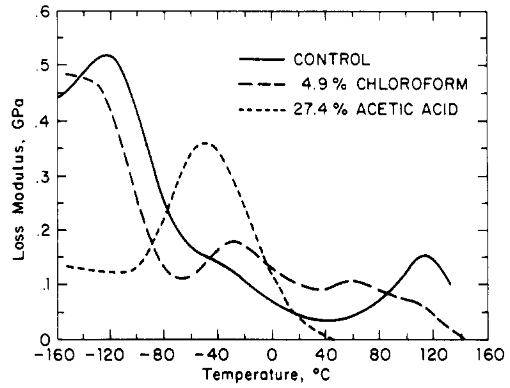

Figure 6. Loss modulus of 66 nylon saturated with chloroform and acetic acid.

remains essentially constant up to 25% toluene. The decrease in the temperature of the peak for the β-relaxation with increasing levels of toluene also follows a common relationship (Figure 5). An exception is the dry state where the relaxation occurs at a higher temperature in LDPE. In earlier work,[6] it was found that the temperature of the β-relaxation moves smoothly through intermediate temperatures in blends of LDPE and EPDM.

66 Nylon

Samples of the oriented nylon tape which had been used in earlier studies[3] of the effect of water and methanol were saturated with chloroform (weight gain 4.9%) and acetic acid (weight gain 27.4%), respectively. As shown in Figure 6, the γ-relaxation was slightly reduced by the presence of the relatively low level of chloroform and essentially eliminated in the sample saturated with acetic acid. These compounds do not have the strong antiplasticizing action which has been seen with water.[3,4]

Discussion

It is clear that the lack of dependence of the γ-relaxation of PTFE on the presence of absorbed chemicals does not represent a general pattern. The behavior of isooctane in LDPE is similar to that of perfluorocarbons, Freons, carbon tetrachloride, or chloroform in PTFE. In all of these cases, the weight gain at saturation is about 8% or less. Toluene and *n*-hexane interact more favorably with LDPE and are absorbed more strongly. These compounds reduce the strength of the γ-relaxation even at low concentrations. Actually, the incremental effect of toluene is smaller above 8–10%. Unlike water or methanol in nylon, they are not antiplasticizers. Clearly, the local mode relaxation in polymers of ethylene is not entirely intramolecular. It does depend on the composition of the environment of the polymethylene sequences in the amorphous phase.

In nylon, the γ-relaxation can be suppressed by compounds such as acetic acid which are not antiplasticizers and presumably do not have the same ability as water to form bridges between amide groups. While this relaxation seems to be similar to the γ-relaxation in polyethylene and is thought to reflect local motions in polymethylene sequences, its dielectric activity suggests some involvement of the polar amide groups. This is supported by the fact that it has been observed in nylon 3 and nylon 4 which contain sequences of only two and three methylenes, respectively.[7] A weight gain of 27.4% acetic acid corresponds to about one molecule of acetic acid per amide group in the amorphous regions, assuming about 50% crystallinity. If the acid molecules are bonded firmly to the amide groups at low temperatures, they may well inhibit local chain motions.

It is interesting to find that toluene lowers the temperature of the β-relaxation in LDPE and EPDM in the same way. In EPDM, the β-relaxation clearly has the properties of the glass transition.[8] This is reflected in the mechanical properties and in the increments in the heat capacity and the coefficient of thermal expansion. The present data add weight to the view that the β-relaxation is the glass transition in polyethylene.[9] Support is also found in the blends of LDPE and EPDM.[6] Increasing crystallinity broadens the β-relaxation and shifts it to higher temperatures. The data in Figure 5 indicate that this effect is largely overcome by the sorption of toluene.

Attention is also directed to the recent studies of Popli and co-workers,[10] who concluded that the β-relaxation in polyethylene is associated with chain units in the interfacial regions between crystalline and amorphous domains.

This work combined with the earlier study on PTFE[1] shows that there can be considerable variation in the effect of absorbed chemicals on the local mode relaxations in polymers. In several cases, the strength of the relaxation is reduced, indicating that the corresponding molecular motion is at least partially inhibited. This may reflect any of several kinds of interactions between the small molecules and the polymer. It is generally found that the glass transition or a similar relaxation attributed to the motion of longer chain segments in the amorphous regions is shifted to lower temperatures, frequently by a large amount.

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Dielectric Relaxation of Liquid Crystalline Polyacrylates and Polymethacrylates

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ABSTRACT: A series of liquid crystalline polyacrylates and polymethacrylates was studied by frequency- and temperature-dependent dielectric measurements. Depending on the molecular structure, between two and five different relaxation processes were observed. Three of them are active below the glass transition. They can be attributed to reorientations of dipoles located at the center of the mesogenic group (β-relaxation), at the ends of the spacer group (γ_1-relaxation), and at the end group (γ_2-relaxation). At the glass transition the centers of gravity of the mesogenic groups and the polymer main chain become mobile. Dipole reorientations associated with this motion contribute to the dielectric relaxation (α-relaxation). At higher temperatures the reorientation of the long axis of the mesogenic groups can be observed (δ-relaxation). For the polyacrylates it passes continuously through all phases; in the case of the polymethacrylates it sets in together with a phase transition.

Introduction

Polymeric liquid crystals are complex systems,[1-3] which combine the properties of polymers with those of liquid crystals.[4] For an understanding of the thermal behavior of these systems investigations on the molecular dynamics are necessary.[5-10] Dielectric relaxation measurements are a suitable method for these investigations.[11] The various dipole moments in the molecule act as probes for motions in all its parts. Measurements can be performed over a large frequency and temperature range. This is important because different relaxation processes may become active. One can expect the occurrence of relaxations of local

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