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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Polymeric dielectrics have applications in energy storage devices but their potential utility can be compromised by the presence of loss processes. The present project was concerned with identifying the

molecular mechanisms underlying and responsible for losses. The program and results involved a two-fold approach to understanding loss processes occurring below the glass transition. This is an important regime since the polymers have structural integrity in the glassy state. One of the two approaches was experimental and the other involved molecular modelling. The ester group was taken a chemical structural model for loss processes originating as the result of flexible side group motion in an otherwise glassy polymer. Extensive experimental results were obtained on two series of polymers. One concerned vinyl acetate/ ethylene copolymers, the other, methyl acrylate/ ethylene copolymers. They both contain flexible ester side groups but differ in the direction of attachment. On the basis of this data, a detailed model for the intramolecular environment effects on the loss process was worked out. It was successful in explaining the main features of the experimental behavior. Understanding the intermolecular contribution will also be necessary but is more difficult. Progress was made however. A method for generating realistically packed amorphous polymers was developed. It is hoped that this method will allow modelling of the effect of the intermolecular environment on loss processes.

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PROBLEM STATEMENT

Polymeric dielectrics find application in storage devices for rapid delivery of electrical energy. However their performance can be compromised by the presence of losses. The present research was directed toward understanding the mechanism of loss processes on a molecular basis. The approach involved studies on polymers possessing a common source of loss, namely, a molecular motion in an otherwise structurally rigid material below the glass transition. The polymers studied were selected on the basis of being model systems by virtue of having a flexible polar side group of well understood molecular structure. The side group acts as a source of molecular motion that in turn leads to dielectric loss. The studies involved not only extensive experimental measurements but also detailed molecular modelling.

SUMMARY OF IMPORTANT RESULTS

It was found that a pendant (and polar) ester group attached to a non-polar polymer chain was an excellent choice as a model for subglass relaxation processes. Two series of polymers were studied. One of them was a series of vinyl acetate / ethylene copolymers and the other was a series of methyl acrylate / ethylene copolymers. The flexible ester side groups in the two series are chemically isomeric but differ in the direction of attachment. Dielectric measurements were made over a wide range of both temperature and frequency on series of samples of varying polar side group content. The data was then analyzed and reduced via phenomenological equations including the Cole-Cole and Havriliak-Negami equations. The effect of the polar comonomer composition and temperature on the strength of both the primary glass transition process and the subglass process was determined. The loss in a polymer is directly related to the magnitude of the relaxation strength. The effects of these variables on the shape (relaxation width parameter) and the location of the loss process (activation energy and entropy of the central relaxation time) were also determined. It was found that the parameters for the subglass processes in the two types of polymers were significantly different, and, in preliminary molecular interpretation, that the differences could be correlated with the molecular structure of the ester group and the bonds attaching it to the chain. This work formed the basis of two publications to appear shortly in *Macromolecules* and also the Ph. D. thesis of Douglas Buerger.

Much more detailed molecular modelling was then carried out. It dealt with isolated chains and concentrated on relaxation strengths. We believe

that the most diagnostic indicator of the correctness of a molecular mechnism is the ability to explain strengths and their dependence on the molecular architecture of the relaxing polar groups. Furthermore, there is reason to believe that the strengths will respond mainly to the intramolecular environment and will be less sensitive to the intermolecular one. Thus isolated chain modelling is likely to be useful in this context.

The modelling involved extensive conformational energy calculations on ester groups attached to polyethylene chains. As a preliminary to these, it was necessary to develop a more carefully calibrated set of empirical force field functions for compounds containing ester groups. After this was accomplished, the energetics of molecular segments with both the ester group and the polymer chain in various conformations was explored. The results of these calculations were then fit to a summarizing model in terms of parameters based on a few specific types of nearby molecular interactions.

The molecular interaction parameters were used as the basis of statistical weight matrices in a rotational isomeric state model of isolated copolymer chains. By calculating the average molecular dipole moment, a connection with the experimentally measured total relaxation strengths was established. Agreement for calculated and experimental values for both types of copolymers was found. Then the relaxation strength of just the subglass processes was was separated out from the total strength. This was done by generating ensembles of chains each with the main chain locked into various conformations and calculating via a site model the relaxation strengths of the side group in various nearby environments. The calculated strengths of the subglass loss processes were in satisfactory agreement with the experimental ones.

The agreement obtained between the molecular model and the experimental behavior for the strengths lends considerable confidence to the heretofore unconfirmed conceptual postulate that the subglass loss is actually due to rotation of flexible side groups. The confidence is increased by the fact that there is considerable difference in experimental behavior between the two types of copolymers studied experimentally and modelled and considerable differences between the polar homopolymers and their dilute copolymers with ethylene. This degree of molecular mechanism development has not been achieved before.

The actual location of the loss processes with respect to frequency and temperature is also an important question and no doubt depends heavily on intermolecular packing through barriers to dipole reorientation. However it may well be that the *variations* in activation energies and thus loss locations with changes in molecular composition are primarily intramolecularly dependent. Activation barriers were calculated for

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various relaxation environments and a correlation between these and the experimental loss locations was apparent. It appears that the picture of an overall barrier made up of a structurally sensitive intramolecular contribution plus a intermolecular packing contribution mayturn out to be useful.

The above modelling work forms the basis for the Ph. D. thesis of Grant Smith. The thesis is being written now and publications will be based on it. The first one, presenting the conformational energy force field, has been submitted for publication.

The mechanism of subglass loss in polymeric dielectrics, even for the restricted case of flexible side group rotation, will not be fully understood until the effects of intermolecular packing are successfully modelled. An important step in this direction was made by means of developing a Monte Carlo simulation that allowed the packing of an amorphous polymer to be calculated with sufficient realism that comparison of properties of the resultant bulk material with experiment could be made. Now that simple realistically packed bulk polymers can be prepared by modelling it should be possible to investigate molecular motions that give rise to loss, such as the side group jumps discussed above, in a packed intermolecular environment. We are looking forward to doing this. The Monte Carlo simulation was carried out by the principal investigator and a publication based on it wil appear soon in *Macromolecules*.

Another study that was undertaken was to study the dielectric relaxation in chloromethyl styrene/ styrene copolymers. This system was selected for study because the pendant chloromethyl is expected to have a very low barrier to rotation about the attaching bond and thus provide a probe for a subglass loss process where the barriers to rotation are largely intermolecular rather than intramolecular. The study is still underway but the results seem to indicate the presence of a loss process that is so extremely broad that it doesn't resemble a conventional dipolar reorientation process and therefore could be the result of variations in packing environments.

PUBLICATIONS

"Sub-glass Relaxation Processes. Dielectric Relaxation in Vinyl Acetate/ Ethylene Copolymers". D. E. Buerger and R. H. Boyd *Macromolecules*, in press.

"Sub-glass Relaxation Processes. Dielectric Relaxation in Methyl Acrylate/ Ethylene Copolymers". D. E. Buerger and R. H. Boyd *Macromolecules*, in press.

"An Off-LatticeConstant-Pressure Simulation of Liquid Polymethylene". R. H. Boyd *Macromolecules*, in press.

"A Force Field for Conformational Energy Calculations on Polymers Containing Ester Groups". G. D. Smith and R. H. Boyd, *Macromolecules*, submitted.

PARTICIPATING SCIENTIFIC PERSONNEL

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