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The requirement in underwater acoustics that a structure be acoustically transparent demands that the sound speed and density of the material match those of water. In general, a material that has this low a sound speed and density is found to be flexible. If it is additionally required that the structure be rigid, the only material that has been shown to be usable is a partially fluorinated epoxy containing mixed microsphere fillers. The epoxy resin used has a partially fluorinated backbone with a perfluorooctyl side chain. This work is an attempt to explain its unique properties.

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Papers presented at the Boston, Massachusetts Meeting

BULK MODULUS OF PARTIALLY FLUORINATED EPOXIES

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INTRODUCTION

The requirement in underwater acoustics that a structure be acoustically transparent demands that the sound speed and density of the material match those of water. In general, a material that has this low a sound speed and density is found to be flexible. If it is additionally required that the structure be rigid, the only material that has been shown to be useable is a partially fluorinated epoxy containing mixed microsphere fillers[1]. The epoxy resin used has a partially fluorinated backbone with a perfluorooctyl side chain. This work is an attempt to explain its unique properties.

RESULTS AND DISCUSSION

Neat Fluoroepoxies

Sound speed and density are important parameters for acoustical applications of polymers and are easily measured in the laboratory. Sound speed may be most readily understood conceptually when discussed in terms of the dilatational modulus, which is the product of density and sound speed squared. The dilatational modulus includes contributions from both the bulk and shear moduli. However, the bulk modulus is the predominant contributor.

Density (at 25°) and sound speed (at 25° and 1.5 MHz) were measured for fluoroepoxy samples containing perfluorinated alkyl side chains ranging in length from no side chain (C0) to eight carbons (C8). Figure 1 gives the relationship between the computed dilatational modulus and the length of the side chain for samples cured with an adduct between ethylene diamine and the resin. These show an increase in the dilatational modulus with increasing length of the side chain. Such a change suggests that the bulk modulus of this material decreases as the free volume of the polymer matrix increases with increasing length of the pendant side chain. Data collected on samples cured with bis(3-aminopropyl)tetramethyldisiloxane were similar to the above except that each sample had a dilatational modulus that was ca. 0.3 GPa lower. In the absence of precise shear modulus data on these samples, one cannot conclude that this decrease in dilatational modulus is not a result of a decrease in shear modulus. A more likely explanation is that the reduced backbone rigidity produced by the silicone amine allows greater deformational freedom, thus imparting greater free volume which contributes to a reduction in the bulk modulus. For both data sets, the relationship cannot be described as linear. If one similarly plots these as the reciprocal of the dilatational modulus (an approximation to compressibility), the plots are also not linear. The dilatational modulus and compressibility cannot be considered to be additive quantities for these materials.

Other fluoroepoxy samples were made using a mixture of C0 and C8 resins mixed in equi-molar quantities and cured with silicone amine. Although the density of these were the same as the C4, the mixed chain-length samples had a higher sound speed and consequently a higher dilatational modulus. Such a difference suggests that perhaps the free volume is a function of a fractional root of the chain length.

Composite Fluoroepoxies

Composite samples were fabricated using "Expancel" (50-μm vinylidene chloride-acrylonitrile shell) and "Carbosphere" (30-μm carbon shell) microspheres. Figure 2 shows the dilatational modulus calculated from the measured sound speeds and densities. As the volume percent of "Expancel" increases, the dilatational modulus decreases rapidly. Because of their soft plastic shell these microspheres have a bulk modulus that is much lower than the resin. As the volume percent of "Carbospheres" increases the dilatational modulus increases. "Carbospheres" have a very hard graphitic carbon outer shell and consequently a high bulk modulus. If each component contributes additively to the bulk modulus of the composite, these plots should be straight lines describing an average of the components.

The chain length data are also not linear when plotted against compressibility, the reciprocal of bulk modulus. Perhaps these simple bulk models do not account for the shear stiffness of the microsphere shells when the resin is compressed in bulk. Such a model is indeed very interesting but is beyond the scope of this paper.

Explanation of Neat Fluoroepoxy Bulk Modulus

The curvature of the data plots implied that neither the bulk modulus nor the compressibility is proportional to the length of the side chain in the neat fluoroepoxy samples. As an alternate model, it might be considered that the free volume occupied by the side chain is a solid with a fixed base. The volume of such a solid is proportional to its height. As a first approximation, the average length of the perfluorinated alkyl side chain might be taken as proportional to the square root of the number of carbons in the chain, in analogy to the end-to-end distance calculated for polymer chains. Thus the free volume and the compressibility of the fluoroepoxy polymer might be expected to be proportional to the square root of the number of carbon atoms in the side chain. When this is tested, indeed the calculated compressibilities of the fluoroepoxies are nearly linear with the square root of the number of carbons in the side chain. This provides a suggestion of the validity of this model, but is certainly inadequate to conclude that this model completely represents this system.

CONCLUSIONS

The dilatational modulus calculated for a series of partially fluorinated epoxies is partially explained in terms of the free volume produced by the pendant side chain. The change in modulus observed for samples containing microsphere fillers is only qualitatively explained by assuming that the bulk moduli of the components are additive. Differential scanning calorimeter and dynamic mechanical studies are underway to validate the models proposed herein.

REFERENCES

1. Corley M. Thompson, "Development of a Structurally Rigid, Acoustically Transparent Plastic", J. Acous. Soc. Am., accepted.

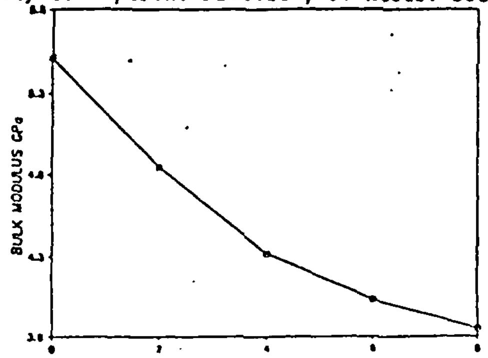

Figure 1. Dilatational modulus as a function of the length of the perfluorinated side chain for adduct-cured samples.

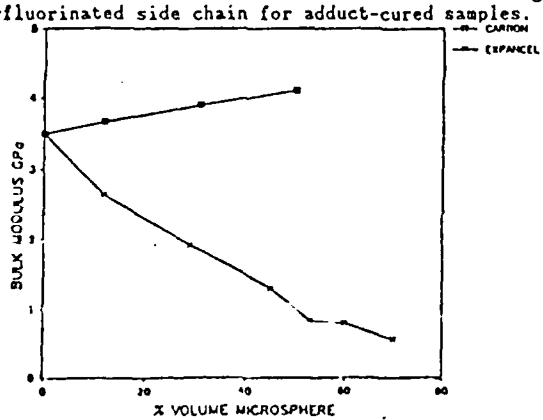

Figure 2. Calculated dilatational modulus as a function of the volume percent of microspheres.