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Isotropic Kevlar and PBA (Poly 1,4-benzamide) Reinforcements for Composites

by

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Kevlar and PBA(Poly 1,4-benzamide) reinforcements were prepared in 96% H_2SO_4. Water-methanol mixtures were used as the extracting solvent. Other solvent combinations were tried, but with less success. The structure obtained by SEM (scanning electron micrograph) showed small cells size but a non-uniform structure. Composites were made from this reinforcements using as matrices a variety of epoxy resins and acrylates. The curing times varied according to the matrix used. Structure and penetration of the matrix into the reinforcements was studied by optical microscopy.

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Isotropic Kevlar and PBA (poly 1, 4-benzamide)

Reinforcements for Composites

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Introduction:

Synthesis and production of liquid crystalline polymers have been subjects of interest in recent years due to the growing demand for high-modulus materials and for new, more efficient electrooptical devices. Polymers capable of forming lyotropic liquid crystals can exist as isotropic, anisotropic or biphasic solutions depending on the temperature, polymer concentration, molecular weight distribution, solvent-polymer interaction and aspect ratio of the rods (1).

Dilute polymer solutions can be cooled to form a co-continuous biphasic system under certain conditions. If the solution is subsequently frozen and the solid solvent removed by sublimation, a fibrous structure remains. This material has potential use as a three dimonsional reinforcement for composites.

Rigid rodlike polymers such as Kevlar and PBA (poly 1, 4-benzamide) are known to gel in sulfuric acid and dimethyl acetamide containing 3 to 5% LiCL. However, semirigid liquid crystalline polymer systems of interest for reinforcements often have low solubility in common sublimable organic solvents. Do to their low solubility in sublimable solvents, it is necessary to resort to an intermediate extraction to fabricate reinforcements from these polymers. This involves the gradual exchange at low temperatures of the original solvent for the polymer by a sublimable one.

During the last few years we have been able to prepare model three dimensional fibrous materials from poly-benzyl-L-glutamate (PBLG) using a variety of sublimable solvents (1). Here we focus on reinforcements based on aromatic polyamides such as Kevlar and PBA using the extraction method. Subsequently, composites have been made using these reinforcements with a variety of matrices such as epoxy resins and acrylates. These constitute unique materials with unusual properties.

Experimental

Starting materials:

Kevlar was obtained from E.I. DuPont. $\bar{M}w$=26,500 g/mol Poly (1, 4-benzamide) ($\bar{M}w$=12,000 g/mol) was prepared according to Yamazaki's procedure (2). All solvents were used as received.

Procedure:

The polymer solutions (0.5-5% polymer in 96% H_2SO_4 by weight) were prepared at room temperature and placed into a capped, cylindrical polyethylene mold (1.5cm x 2.5cm). The solutions were frozen (dry-ice-acetone bath), removed from the mold and placed into a 50/50 methanol-water mixture at -70°C. The reinforcements were extracted in this mixture for 3 days. Then, the concentration of water was increased to 75/25 (H_2O/methanol) and allowed to stand at 0°C for 2 days. Finally, the reinforcements were placed into water which was replaced daily for a period of 20 days. After this time, the reinforcements were freezedried at 50 millitorr.

The morphology of the reinforcements was studied using an scanning electron microscope (Model Amray 1000A) at 20 KV. Optical microscopy studies of the composites were done in a polarizing microscope (Nikon metaphot). The embedding media used were: a) MDA (4'-4' methylene dianiline) in Epon 828 (28%), b) butylacrylate containing from 0.5 to 2% benzoyl peroxide, and 0.1 to 0.5% divinyLbenzene.

Composites:

The composites were prepared by using the reinforcements with several matrices. In the case of the MDA/Epon 828 matrix, a 28% MDA/Epon 828 solution was prepared and heated to 60°C. At this temperature, a vacuum was pulled to remove any air trapped in the solution. The reinforcements were placed in a polyethylene mold and the warm matrix was added. The mixture was placed in a vacuum oven at 60°C for 20 min. and then the composite was cured at 80°C overnight. After this time, the composites were removed from the mold and postcured at 150°C for 2 hours and 180°C for 2 hours more.

The butyl acrylate-Kevlar composites were prepared by placing the Kevlar reinforcement into a 5-mm nmr tube; then a benzoyl peroxide/butyl acrylate solution (initiator concentration varied from 0.5-2.0% and the crosslinker concentrations varied from 0.1-0.5%) properly degassed was poured into the tube. The mixture was degassed by three freeze-thaw cycles and the tube was finally sealed under vacuum. The composites containing a 1 and 2% benzoyl peroxide were cured at 60°C for 32 hours. Composites containing a 0.5% and 1.0% initiator were cured at 100°C for 24 hours. Also, one composite was cured at 80°C containing a 1% initiator.

Mechanical measurements:

Modulus measurements in the composites were done using a penetrometer. (The L.S. Starrett Co. cat #4101). Tests were done on smooth surface of the composite and in the adjacent unreinforced matrix. The radius of the needle used for the test was 10^{-3}cm. The tensile compliance calculations were done accordinj to the method described by Clough, Gillen and Quintana[3].

Results:

Kevlar and PBA reinforcements have been prepared using sulfuric acid as solvent and a gradual extraction method involving mixtures of methanol /water at low temperatures. Elemental anaylsis of the reinforcements showed a 0.2% sulfuric acid left in the sample after extraction. Figure 1 shows the morphology of the reinforcements. As can be seen from this figure; the cell sizes of 1 μm are obtained. While these cells are not uniform over the entire area, the structure is locally highly regular and efficient; that is all the polymer appears to be confined to the struts and joints of the lattice. By further understanding of the phase decomposition mechanism, we anticipate improvements of the uniformity of cell sizes over the entire reinforcement.

Preliminary results suggest that epoxy resins such as MDA/Epon 828 penetrate poorly into the reinforcement. Less viscous matrix materials such as acrylics are currently being investigated.

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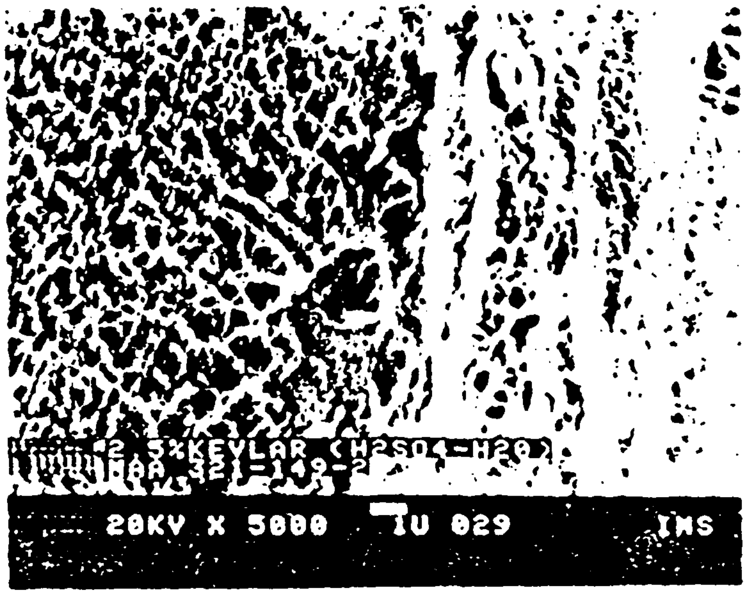

Figure 1. Kevlar Reinforcement from 2.5% by weight.
Kevlar ($\bar{M}_w$=26,500gr/mol)
Solution in 96% H_2SO_4: Extracted with Methanol-water at low temperatures.

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