

Polymer Composites Through *In Situ* Matrix Formation

P. BLESS, J. SEMEN,* and J. B. LANDO, *Department of
Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106*

Synopsis

Nylon 66 graphite composites have been prepared by the *in situ* polymerization of the monomer epitaxially crystallized onto the fiber surface. Nylon 66 monomer, whether oriented (crystallized from solution) or unoriented (deposited from an aqueous slurry) was found to polymerize to an oriented composite by a variety of techniques (spark discharge, resistance heating, and furnace heating). X-ray diffraction has demonstrated that the matrix orientation corresponds to the polymer chains aligning themselves with the graphite crystal edges along the fiber axis. Scanning electron microscopy of fracture surfaces has shown excellent adherence between the fiber and matrix with fracture occurring mostly in the matrix material.

INTRODUCTION

Hexamethylenediammonium adipate (HMDA), mp 197°C, has been shown to crystallize from methanol solution on a variety of graphite and carbon fiber substrates, such that a specific crystallographic direction is preferentially oriented along the fiber axis.^{1,2} Hexamethylenediammonium adipate, crystallized in this manner, undergoes an oriented (topotactic) reaction^{1,2} to the cyclic dimer of nylon 66 under conditions which would yield oriented nylon 66 in the absence of substrate.³ A strong and specific interaction of the monomer and the cyclic product with the graphite fiber is required to explain these results. It was proposed that the crystallizing polar monomer interacted with active sites on graphite crystallite edges such that this interaction is maximized. This is consistent with the observed monomer orientation. The specificity is further demonstrated by the fact that not only is the reaction product determined by these epitaxial interactions but also the conformation of the cyclic dimer product.^{1,2} These results strongly indicate that, if a monomer such as HMDA could be polymerized *in situ*, a strong interfacial bond between the fiber and the matrix would result.

* Present address: Midland Macromolecular Institute, 1910 West St. Andrews Drive, Midland, Michigan 48640.

RESULTS AND DISCUSSION

A preliminary investigation of the polymerization of hexamethylenediammonium adipate after epitaxial crystallization on unsized Thornel 40 graphite fibers was performed in 20,000-volt d.c. fields under discharge.⁴ Orientation of the fibers perpendicular or parallel to the electric field both resulted after times of the order of 10 sec in crystalline coatings of nylon 66 having a preferred orientation of the polymer chains along the graphite fiber axis. Similar experiments in the absence of the graphite fiber resulted in monomer degradation.

We have now repeated these experiments in an attempt to obtain aggregates of parallel graphite fibers (Thornel 50) in a nylon 66 matrix. Figure 1 is a scanning electron micrograph taken with a Materials Analysis Co. Model 700 high-resolution scanning electron microscope of the surface of a typical sample resulting from the spark discharge experiments. The relatively large amount of void space is apparent. There are a number of large cracks visible in micrographs of larger areas taken at lower magnification. The orientation of the polymer chains along the graphite fiber axis was confirmed by x-ray diffraction with CuK_α radiation using a cylindrical camera with a 57.3-mm diameter. This is the same orientation as that previously reported.⁴

It is obvious from Figure 1 that further investigation of the spark discharge method will be necessary to eliminate voids and cracks in the nylon 66 matrix. In addition, we have developed other methods of in situ polymerization of hexamethylenediammonium adipate. These methods developed from previously reported work on the polymerization of crystalline nylon 66 monomer.

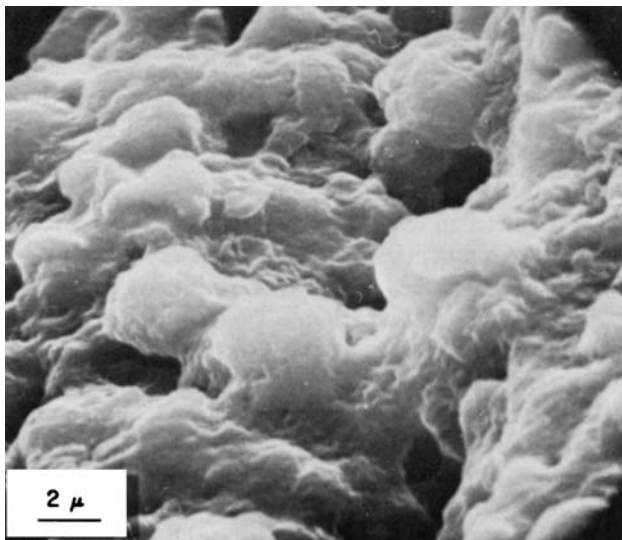


Fig. 1. Scanning electron micrograph of the surface of Thornel 50/nylon 66 sample prepared by spark discharge (5000 \times).

When a crystal of the monomer is heated at 120°C in the absence of graphite fiber substrate, no appreciable polymerization occurs.³ If a strong electric field is applied during annealing at 120°C, no polymerization occurs except when the *a*-axis of the monomer is aligned in the field direction.⁴ Virtually unoriented polymer is obtained. (The monomer crystallizes in a monoclinic unit cell with space group P_{21}/a , $a = 8.489 \text{ \AA}$, $b = 15.580 \text{ \AA}$, $c = 5.598 \text{ \AA}$, and $\beta = 102.9^\circ$.⁵ Under these conditions, complete conversion to polymer occurs within 24 hr at 120°C. The reactivity of the monomer under these conditions was thought to be attributable to resistance heating, since the *a*-axis is approximately the direction of most of the hydrogen bonds in crystals of the monomer. We have now confirmed these results.

When hexamethylenediammonium adipate is crystallized rapidly onto graphite fibers, the *a*-axis of the monomer is oriented along the graphite fibers. However, when crystallization occurs slowly, *c*-axis orientation results. Thornel 50 graphite fibers, having monomer crystallized in both orientations, were subjected to a strong "cylindrical electric field." This was achieved by placing the fibers along the longitudinal axis of a 3.5-in. length of 1.5-in. diameter copper tubing, the fiber being grounded and a 20,000-volt d.c. potential applied to the tubing. No spark discharge was observed under these conditions. It should be noted that heating at 140°C of the epitaxially crystallized monomers in both orientations in the absence of an electric field yields cyclic dimer, not polymer.² Heating for 24 hr at 140°C of fibers having *a*-axis-oriented crystals at 140°C in the "cylindrical electric field" yielded cyclic dimer, while *c*-axis-oriented crystals yielded virtually unoriented nylon 66. Since in the latter case the *a*-axes of the monomer crystals were approximately in the radial direction of the copper cylinder, the observations of Frayer and Lando⁴ are confirmed and the specific catalytic effect of the graphite fiber surfaces is again demonstrated.

Since resistance heating appeared to be a promising method of polymerization, we have used the Thornel 50 graphite fibers, in a standard a.c. circuit of from 2 to 10 volts, to obtain rapid resistance heating of monomer crystallized on the graphite fiber surface. Using this technique, it is not necessary to epitaxially crystallize the monomer on the graphite fiber surface to accomplish polymerization. By passing the fibers through a slurry of 2 g of monomer and 1 g of water, a reasonably uniform distribution of unoriented monomer is obtained after drying. Tapes of parallel bundles of coated fibers subjected for a few seconds to from 2 to 10 volts (depending upon the number of fibers) resulted in complete conversion of the matrix to nylon 66. As in the spark discharge experiments, the resulting polymer chains were oriented predominately along the graphite fiber axis. Figure 2 is a scanning electron micrograph at a magnification of 10,000 \times of the surface of a Thornel 50/nylon 66 tape (approximately 50% nylon 66). The finer structure of the polymer and the relative absence of voids and cracks when compared to samples prepared by the spark discharge method is apparent. The morphology of the nylon 66 is undoubtedly spherulitic

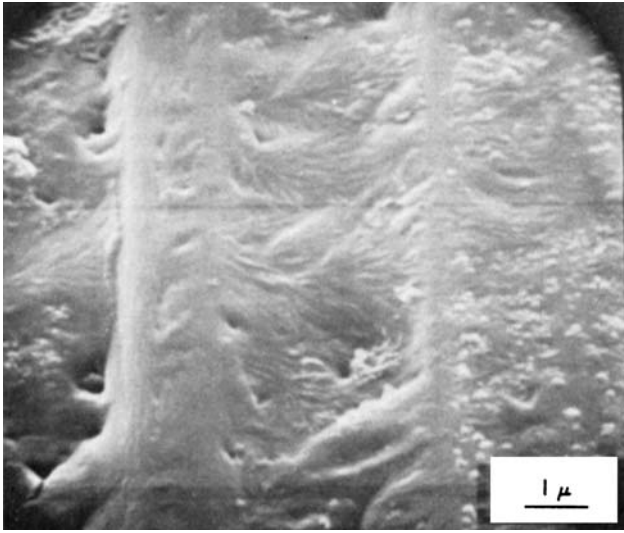


Fig. 2. Scanning electron micrograph of surface of Thornel 50/nylon 66 sample prepared by resistance heating (10,000 \times).

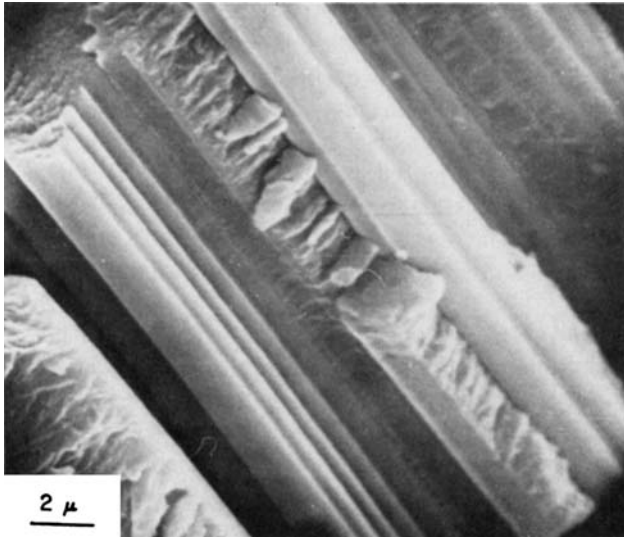


Fig. 3. Scanning electron micrograph of a fracture surface of Thornel 50/nylon 66 sample prepared by resistance heating (5000 \times).

in nature, with the fiber surface nucleating the crystallization. There is some evidence that stacks of lamellae are oriented with the chain direction parallel to the graphite fiber axis (in agreement with the orientation observed by x-ray diffraction).

Figure 3 is a scanning electron micrograph of a fracture surface of a similar sample at a magnification of 5000 \times . It should be noted that in the

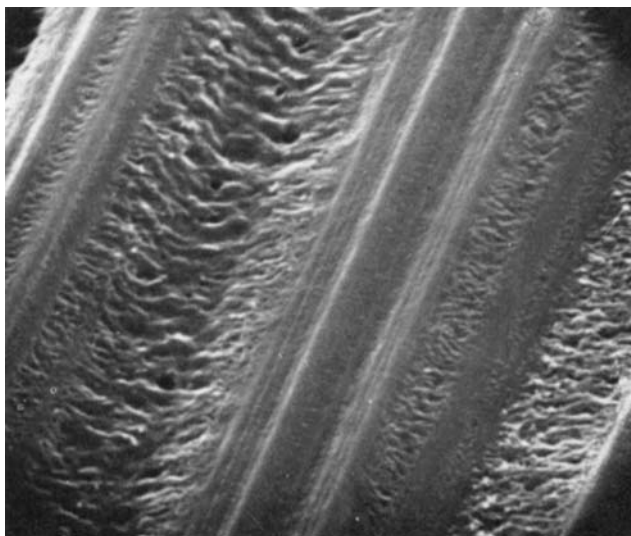


Fig. 4. Scanning electron micrograph of a Thornel 50/nylon 66 sample prepared by furnace heating in air at 180°C for 2 hr (5000 \times).

region of matrix fracture, the polymer has not pulled away from the fiber surface.

More recent work involving furnace heating of slurry-deposited hexamethylenediammonium adipate has shown that oriented nylon 66/Thornel 50 composites are obtained both above (230°C) and below (180°C) the melting point of HMDA (196°C). The heating in these experiments proceeded for 1 to 2 hr in an air atmosphere, and the catalytic influence of the graphite fiber surface is strongly demonstrated by the fact that degradation occurs in the absence of the fibers under these conditions. X-Ray diffraction has shown that the orientation of the nylon 66 matrix in composites prepared by this technique is identical to that of composites formed by either spark discharge or resistance heating. Scanning electron microscopy has revealed the morphology of the composites cured at 180°C (Fig. 4) to be almost as uniform as that of resistance-heated samples and definitely superior to that of samples prepared by spark discharge. Since any number of slurry-coated fibers can be arranged into any desired sample shape prior to polymerization, the furnace heating technique lends itself very well to the production of large, highly oriented, and uniform composite specimens.

In these preliminary experiments, resistance heating and furnace heating have been shown to be a possible useful method of composite formation through in situ polymerization of crystalline hexamethylenediammonium adipate. In addition, the catalytic effect of the fiber surfaces has been demonstrated in a variety of experiments.

It should be emphasized that the specific effect of the graphite fiber is demonstrated in the following different ways:

1. Cyclic dimer forms when epitaxially crystallized monomer is subjected to conditions which, in the absence of substrate, result in linear polymer.^{1,2}

2. Cyclic dimer forms when epitaxially crystallized monomer (*a*-axis oriented) is subjected to a strong d.c. field perpendicular to the fiber, whereas degradation occurs with this monomer orientation in the absence of fiber.

3. Epitaxially crystallized monomer having *c*-axis orientation yields virtually unoriented linear polymer when a strong d.c. field is applied perpendicular to the fiber, as occurs with this monomer orientation in the absence of fibers. However, when more severe heating conditions are applied (spark discharge, a.c. resistance heating, and oven heating near the melting point of the monomer), the existence of a partially molten mixture of monomer and oligomer results in nucleation of the polymer phase on the fiber surface and subsequent orientation of the polymer phase through interaction with the fiber. Under these conditions, polymer orientation results after unoriented or epitaxial deposition of the monomer on the fiber.

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