

GRAPHITE FILMS FROM POLYIMIDES I. STRUCTURAL DEVELOPMENT

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The development of graphitic structure in the carbon films prepared from different polyimide films was studied mainly by transmission electron and optical microscopies. The graphitization was found to occur through flattening the pores along the film surface.

The thermal transformation of various thin polyimide films (25–30 μm thick) was studied by optical microscopy (OM) and transmission electron microscopy (TEM). All the thin films observed (Kapton, Novax, Upilex A and PPT), except Upilex C, yield graphite by heat treatment up to 3000°C. However, depending on their oxygen lability and the chemical configuration of their initial polyimide molecule, they behave very differently. In addition, the graphitizability is favored by the easy release of volatiles through a thin film, associated to light stresses applied during the primary carbonization.

The film thicknesses decrease during heat treatment in a manner tightly connected to the graphitization mechanism. Fig. 1 shows the variation of the thickness plotted versus HTT. Except for Upilex C and PPT the films follow the same trend. Abrupt changes of slope occur, determining three regions. The first corresponds to primary carbonization during which a weak plasticity could occur. The decrease of the thickness is accompanied by the maximum release of oxygen and nitrogen whereas optical anisotropy develops in the film. The optical difference of path is low for the three films, but increases from Kapton to Novax, then Upilex A (from 35 to 52 nm). The second step more or less extended in temperature is a plateau ending with a second thickness drop. During this plateau the secondary carbonization occurs, producing a negligible amount of gases. A considerable improvement happens in optical anisotropy ($O_{dp} > 100\text{--}150\text{ nm}$), corresponding to a statistical long range orientation of the basic structural units (BSU). Inside the films, flattened pores develop with an increasing stacking order in their

walls as HTT increases. The flattened pores are sketched in Fig. 2 for the cross-sections of Kapton. 550°C and 2475°C are the temperatures to which occur the peaks of the derivative. All samples show the same sudden annealing of the aromatic layers distortions produced immediately after the ultimate drop of thickness. All films join on the last plateau of minimum thickness (about 8 μm). It corresponds to the maximum compactness (Fig. 2), i.e., to lamellae inside which graphitization could develop. From Kapton to Novax, then Upilex A, the last plateau is reached at a lower HTT with a decreasing drop of thickness due to the increasing flattening of pores. Kapton get the plateau at 2500°C with a thickness drop of 12 μm , Novax at 2400°C with a drop of 10 μm and Upilex A at 2100°C with a drop of 8 μm . The ultimate value of d_{002} and the final mosaic size of the crystallites are the same at 2800°C.

Upilex C (Fig. 1) is entirely different from the other films since it shows a small swelling with a persistent constant thickness up to 2800°C. It is entirely optically isotropic and nongraphitizing. It is also a porous carbon, but its pores are very small and isometrical as other nongraphitizing carbons (sketch of Fig. 1).

PPT represents the other extreme in behaviour (Fig. 1). Its thickness does not show any step but a smooth continuous decrease from 900–1000°C up to 1800°C. Its optical anisotropy is very strong and increases regularly. There is no pore development, but a local preferred orientation very largely extended (Fig. 3, stage 1). A continuous improvement of stacking order renders this sample absolutely similar to a graphitizing carbon, such as anthracene-based carbon. PPT shows the same stages as anthracene-based carbon, i.e., the BSU join into distorted layers, which themselves suddenly dewrinkle at about 2000°C, to yield flat and perfect layers. This ultimate stage corresponds to the last plateau of thickness observed in the other films. Here also graphitization begins to develop up to 3000°C.

The features common to all films are probably due to the fact that the volatile release is more quietly done in a thin film and to the fact that the stresses applied during carbonization (the films are heated sandwiched into two plates). Both of which are favorable for the preferred orientation and the graphitization. To these mechanical effects are added chemical ones which are responsible for the differences between the films. The chemical analysis data have shown that the oxygen release is more and more complete and precocious from Kapton to Novax, then Upilex A. It is stable even at 2800°C in Upilex C and totally labile at 1000°C for PPT. Correspondingly, the cross-linking decreases continuously from Upilex C, Kapton, Novax, Upilex A and PPT. The plasticity thus increases in the same order, improving the preferred orientation, then the graphitization. The stronger the cross-linking the more isometrical and the smaller the pore, explaining why Upilex C is nongraphitizing. It is necessary to

eliminate entirely oxygen before secondary carbonization to prevent pore formation and reach the graphitizing PPT film. For the intermediate products the plasticity is enough reduced to let pores develop but enough marked to allow their flattening by stresses. Graphitization thus occurs by a sudden breakage and collapsing of the more defective pore walls. These chemical effects are due to the stiffness and flatness of the starting polyimide molecules.

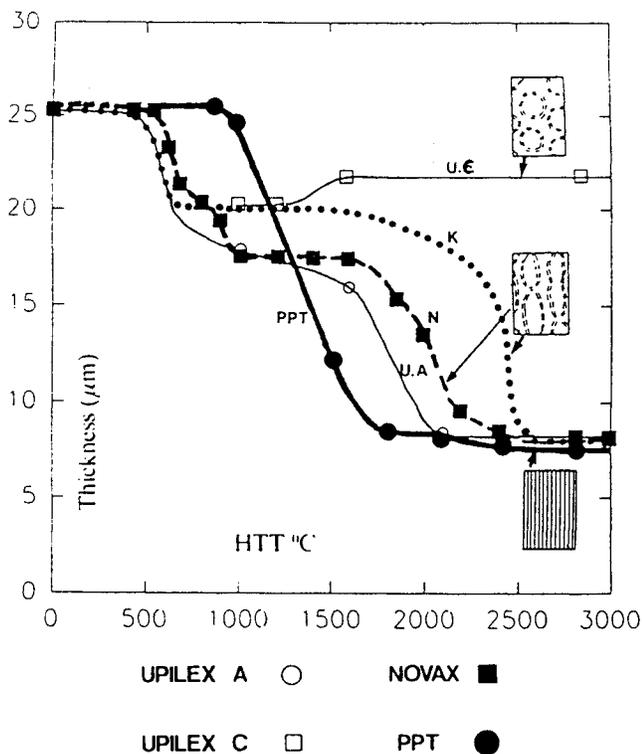


Figure 1 Changes of film thickness with HTT

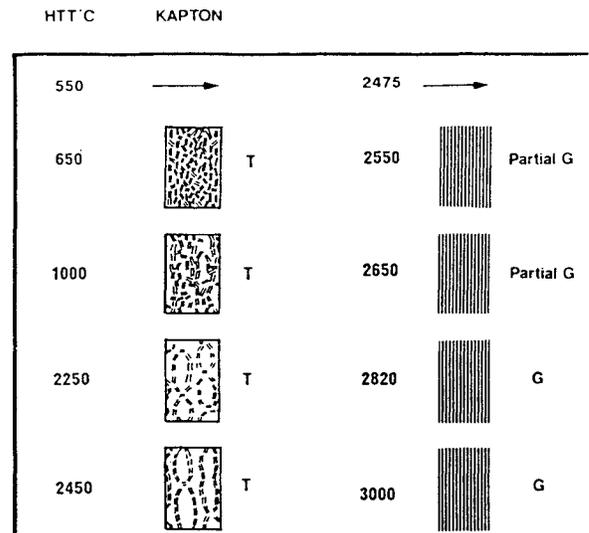


Figure 2 Texture change in Kapton-derived film with HTT

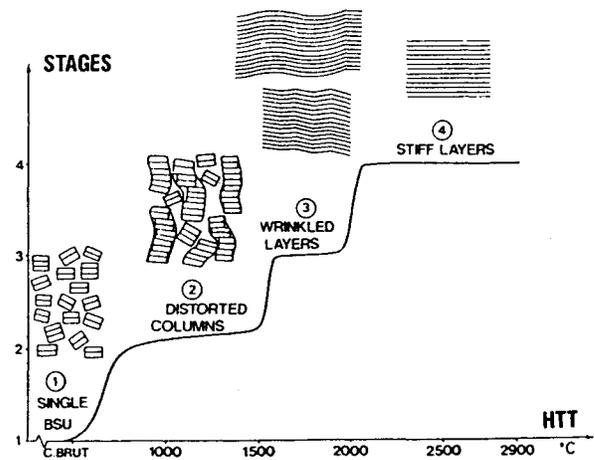


Figure 3 Scheme of texture change with HTT