

Formation of a Flexible Graphite Film from Poly(acrylonitrile) Using a Layered Clay Film as Template

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A graphite film was prepared from poly(acrylonitrile) by a template carbonization method using layered clay film. Poly(acrylonitrile) was first carbonized in the two-dimensional opening between the lamellae of the clay film and the resultant clay/carbon film was subjected to HF treatment in order to remove the clay framework. Then the film was further heat-treated up to 3000 °C. During the heating process, the fluoride residue produced in the HF treatment was vaporized and a graphite film was left. The original clay film and the resulting graphite film were characterized with a scanning electron microscope and an X-ray diffractometer. Furthermore, several physical properties such as the electrical resistivity and mechanical strength of the graphite film were investigated. It was found that the morphology and microstructure of the graphite film strongly depend on the microtexture of the original clay film used as a template. The most notable feature of this graphite film is its peculiar flexibility, which is not found in other graphite films. The origin of such flexibility was discussed in relation to the microstructure of the graphite film.

Introduction

Graphite film has been prepared from several kinds of precursors such as exfoliated graphite,¹ graphite oxide,^{2,3} mesophase pitch,⁴ and organic polymers.⁵⁻⁸ It is well-known that graphite sheet from exfoliated graphite is commercially available under the name of Grafoil. Highly crystallized and highly oriented graphite film can be prepared from the following thermoresistant polymer films; polyimide "Kapton",⁸ poly(*p*-phenylene-1,3,4-oxadiazole),⁶ and poly(*p*-phenylenevinylene).⁷ The degrees of graphitization and preferred orientation of these graphite films are excellent (almost the same as those of highly oriented pyrolytic graphite (HOPG)).

Recently, we have prepared a new type of carbon from the carbonization of an organic polymer in the two-dimensional opening between the lamellae of a layered clay such as montmorillonite (MONT) and taeniolite (TAEN).⁹⁻¹⁵ Brief description for this template carbonization method is as follows: A monomer such as

acrylonitrile or furfuryl alcohol is intercalated into the clay, followed by its polymerization and the subsequent carbonization at 700 °C in the two-dimensional opening of the clay. The resultant clay-carbon complex is washed with HF and HCl solutions to dissolve the clay framework of the complex, the carbon being thereby obtained as the insoluble fraction. The carbon was found to consist of planar macromolecules and was easily graphitized by further heat treatment, regardless of the type of precursor polymer. Macroscopically, this carbon was a powdery form, which would be inconvenient for practical usage.

In the present work, we have attempted to prepare graphite film from poly(acrylonitrile) (PAN) by using a similar template carbonization method. It is well-known that a cast film of layered clay can easily be prepared from clay-water sol. Thus, we employed several kinds of thin clay films as a template for the preparation of graphite film. The graphite films prepared thereby were characterized with scanning electron microscopy and X-ray diffraction. In addition, the physical properties of these graphite films, e.g., electrical resistivity and mechanical strength are measured. We have examined the effect of clay type on the structure and properties of the resultant graphite films and discussed their formation process.

Experimental Section

Preparation. The following three kinds of layered clays are used in this study: Na-MONT (Na-form montmorillonite, Kunimine Ind. Co.) and Na-,Li-TAEN (Na- and Li-form taeniolite, respectively, TOPY Ind.). Although MONT is a layered clay of the sumectite group and TAEN belongs to mica group, there is no essential difference in fundamental crystal structure between these two clays. A hydrosol of each clay mineral was cast on a glass slide. After drying at ambient temperature, the clay film was peeled off from the slide and a strip (30 mm × 10 mm) was cut from the film. The thickness of the resultant clay films is 60, 90, and 170 μm for Na-MONT,

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Na-TAEN, and Li-TAEN, respectively. The intercalation of acrylonitrile into the strip of each clay film was performed by using the same method as in the previous paper.¹⁰ Acrylonitrile vapor was allowed to stay in contact with clay film for 24 h at room temperature. From the weight increase due to the intercalation, the amounts of acrylonitrile in the clay films were estimated to be 0.14, 0.10, and 0.11 g/g of clay for Na-MONT, Na-TAEN, and Li-TAEN, respectively. The clay/acrylonitrile complex films were subjected to γ -ray radiation to polymerize the acrylonitrile between the clay lamellae. The resultant clay/PAN complex films were heat-treated at 700 °C for 3 h under a N₂ flow. As a result, the PAN between clay lamellae was carbonized to form a clay-carbon complex film.

The liberation of the carbon from the clay and the high-temperature treatment of the carbon were conducted by the following procedure: A clay-carbon complex film was put into 46% HF solution at 0 °C, to destroy the clay framework, and then it was heat-treated at 3000 °C. This heating process vaporized the fluoride residue and left only the carbon film.

Characterization. The crystallinity of the original clay films, the interplanar spacing, d_{002} , and the average crystallite size, L_c , of the heat-treated carbon film were determined with an X-ray diffractometer (XRD) (Shimadzu, XD-D1 with Cu K α radiation) by referring to a silicon standard. In every XRD measurement, special attention was paid for the sample film surface to be parallel to the surface of the sample holder.

The preferred orientation in the three clay films and the heat-treated carbon films was approximately estimated by XRD as follows. After the sample film was placed on the sample holder, the angle of the detector was fixed at the position for a maximum 00 l diffraction peak (004 diffraction ($2\theta =$ around 29°) for clay and 002 diffraction for carbon), and then only the specimen was rotated. The change in the intensity of the corresponding diffraction with the offset (ϕ) from the Bragg angle was measured. The resultant intensity vs ϕ curve was used to determine the degree of preferred orientation of the diffraction plane in the sample film.

The microscopic features of the clay and carbon films were observed with a scanning electron microscope (SEM, Hitachi, S900). The electrical resistivity along the surface of the carbon film was determined at room temperature with a conventional four-point probe method. The tensile strength and Young's modulus of the carbon films were measured at a stretching rate of 0.5 mm/min with a tensile testing machine (Shimadzu DCS-100).

Results

Clay and Complex Films. The crystallinity of the three clay films was evaluated from the peak width of the (004) diffraction line for each clay. The average crystallite size calculated from the width was 32, 132, and 57 nm for Na-MONT, Na-TAEN, and Li-TAEN, respectively. This result indicates a higher crystallinity for Na-TAEN as compared to the other clay films. The preferred orientation curves for the clay films are shown in Figure 1a, where the intensity of the (004) diffraction is plotted as a function of the offset (ϕ) from the Bragg angle. The Na-TAEN film exhibits the sharpest orientation curve, corresponding to the best preferred orientation. The Na-MONT film has a higher degree of preferred orientation than the Li-TAEN film.

Figure 2 shows the XRD patterns of the clay complex films at each treatment stage. The main peak at the lower diffraction angle for the clay complexes is the (001) reflection of the clay, and most of the others can be regarded as higher order (00 l) reflection. The values of the spacing determined from the (001) diffraction peaks are noted in this figure. For all cases, the spacing for the acrylonitrile and PAN complexes ranges between 1.2 and 1.3 nm. Since the spacing of completely dried

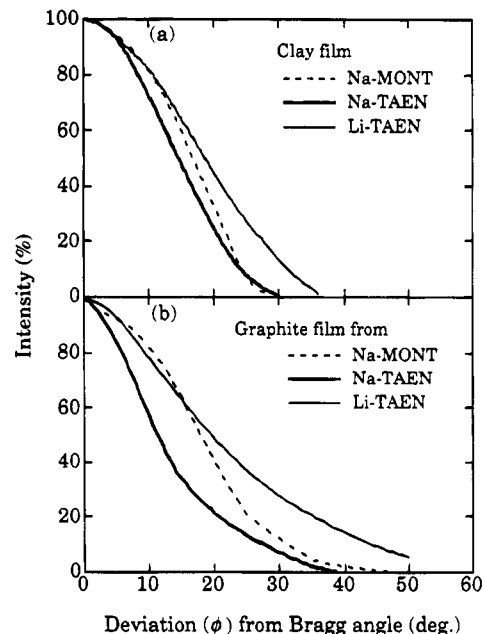


Figure 1. Orientation curves for the three clay films and the corresponding graphite films.

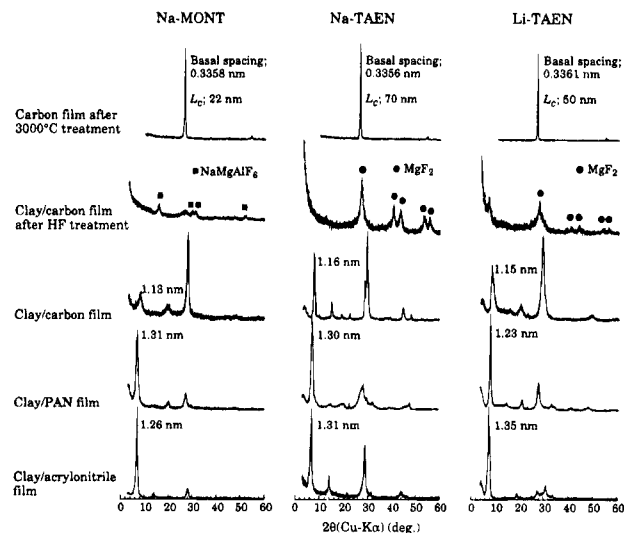


Figure 2. XRD patterns of the complex films and the graphite films.

MONT and TAEN is about 0.96 nm, there is, at least, one layer of acrylonitrile or PAN between the clay lamellae. The XRD profiles show no significant difference between the acrylonitrile and PAN complexes. This means that the structural change of the clay upon polymerization is not very great. Upon heat treatment, the spacing decreases to about 1.1 nm and the (001) bands become broad and weak. Despite these changes, the heat-treated films still exhibit the XRD bands which are attributable to the clay, suggesting that the framework of the clay was not destroyed. The HF treatment, however, completely changed the XRD pattern. Almost all of the peaks observed after HF treatment can be ascribed to fluoride compounds (NaMgAlF₆ or MgF₂), and this indicates the breakdown of the clay structure.

Morphology of the Clay and Carbon Films. The SEM photographs of the surface morphology of the original clay films are shown in the left side of Figure 3. In the Na-MONT film, many wrinkles are observed on the surface, while the surface of the Na-TAEN film

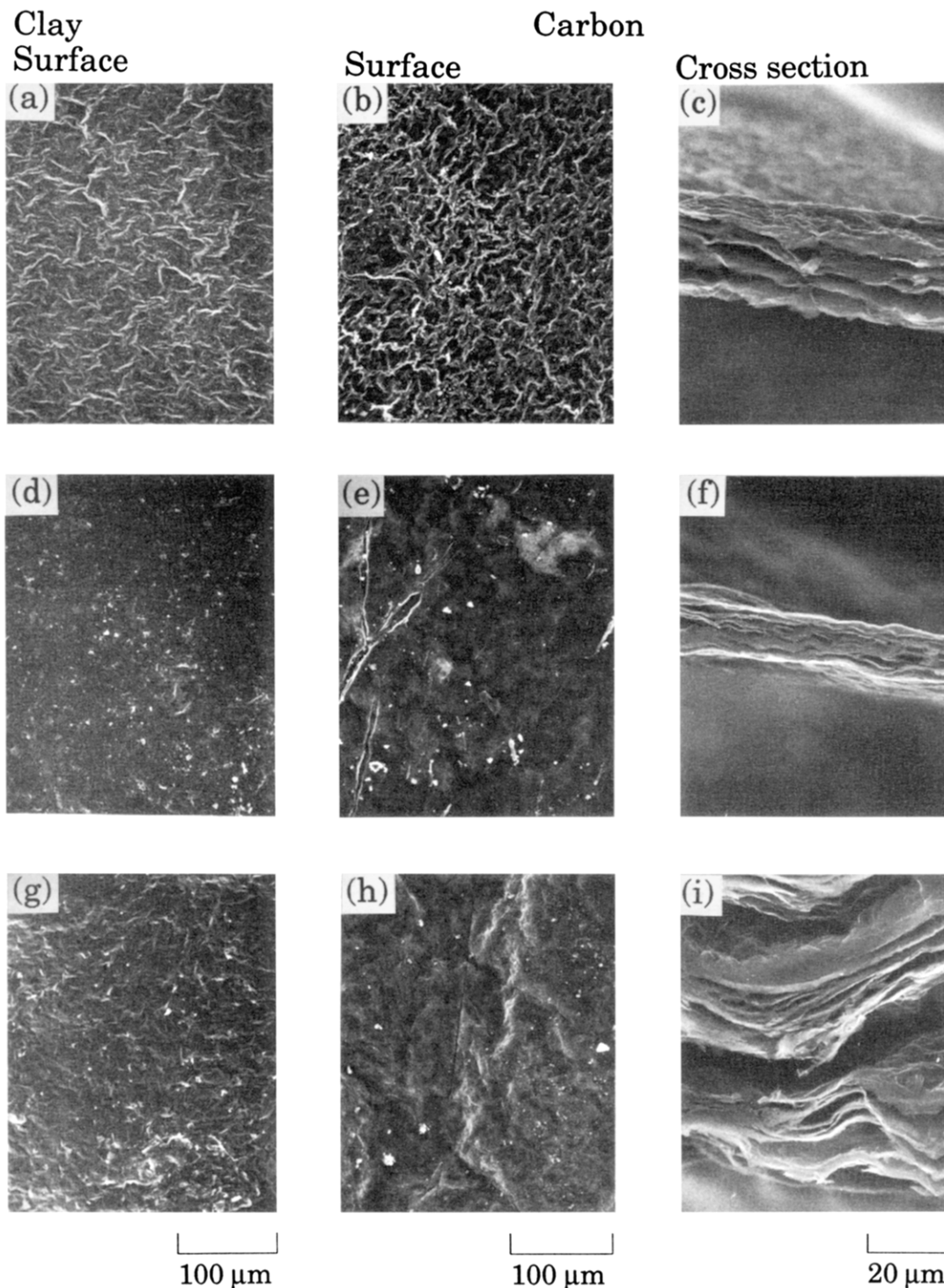


Figure 3. SEM photographs of the surface for the three clay films (Na-MONT (a), Na-TAEN (d), Li-TAEN (g)) and the surface and the cross section for the graphite films from Na-MONT (b, c), Na-TAEN (e, f), and Li-TAEN (h, i).

looks flat. In the case of Li-TAEN, such wrinkles are found to some extent on its surface, but the number of wrinkles is not so large as in Na-MONT.

Figure 3 (the middle and right sides) shows the SEM photographs of the surface and the cross section of the carbon films prepared in the three kinds of clay films. It is noteworthy that the surface morphology of each carbon film is very similar to that of the corresponding clay film. The film from Na-TAEN shows several cracks on its surface, but the other parts are rather flat and smooth, in comparison with the other two carbon films, where so many wrinkles are observed, especially in the film from Na-MONT. The stacking structure of many

wrinkled films is seen in the cross section of all the carbon films. The stacking becomes more oriented and less wrinkled in the following order; Li-TAEN, Na-MONT, and Na-TAEN.

XRD Analysis of the Carbon Films. The XRD patterns of the carbon films are shown in the upper part of Figure 2, where the values of the basal spacing calculated from the (004) diffraction line and L_c from the (002) line are given. The basal spacing in these films ranges from 0.3356 to 0.3361 nm. The value observed for the carbon film from Na-TAEN is particularly small and close to that of ideal graphite (0.3354 nm). A small (004) peak can be seen in all cases, but

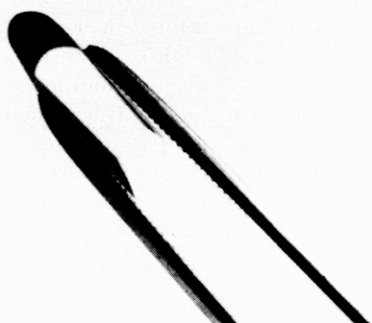


Figure 4. Photograph of the graphite film (Li-TAEN) held between tweezers.

Table 1. Electrical Resistivity and Mechanical Strength of the Three Graphite Films

physical properties	graphite film from		
	Na-MONT	Na-TAEN	Li-TAEN
electrical resistivity ($10^{-5} \Omega \text{ m}$)	2.8	1.5	2.0
tensile strength (MPa)	8.5	2.4	2.6
Young's modulus (MPa)	260	90	90

no (10) peak is found. There is some difference in the value of L_c among the three carbon films. The carbon film from Na-TAEN has the highest L_c and the film from Na-MONT gives the lowest value.

Figure 1b shows the preferred orientation curves for the three carbon films. Among them the film from Na-TAEN exhibits the best preferred orientation, followed by the film from Na-MONT, and then the film from Li-TAEN. These results are consistent with what is suggested by the SEM views of the cross section in Figure 3.

Physical Properties of the Carbon Films. Table 1 shows the values of electrical resistivity, tensile strength, and Young's modulus of the carbon films. The carbon film from Na-TAEN exhibits the lowest resistivity, but its value is much larger than that of a graphite crystal along basal plane ($4 \times 10^{-7} \Omega \text{ m}$),¹⁶ despite the high degree of graphitization for this carbon film. The film from Na-MONT shows a higher tensile strength and Young's modulus than the other two films from Na- and Li-TAEN.

Figure 4 shows a photograph of the carbon film from Li-TAEN, which was held between a pair of tweezers. The film was not broken and not cracked even when it was appreciably curved with the tweezers. This peculiar flexibility was also observed in the carbon films from the other clays.

Discussion

Judging from the values of basal spacing (d_{002}), we can conclude that the present carbon films can be classified as highly crystallized graphite films. The surface morphology of the graphite films obtained by this method strongly depends on that of the original clay film used as a template, as can be seen in Figure 3. There was no detectable (10) peak in all of the graphite

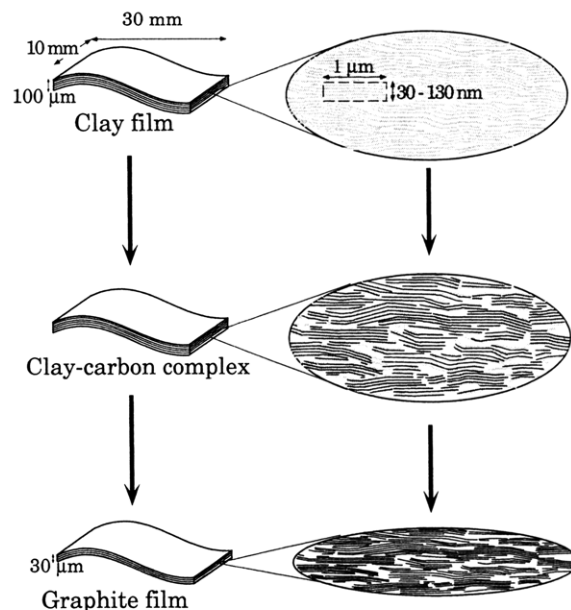


Figure 5. An illustration of the formation process of the graphite film in the opening between the lamellae of clay film.

films, indicating that the basal planes are highly oriented along the direction of the film plane, because the carbon film was set to be parallel to the surface of the sample holder for the diffractometer. Among these graphite films, that from Na-TAEN shows the highest degree of graphitization, preferred orientation, and lowest electrical resistivity. To understand the difference of this graphite film (Na-TAEN) from the other graphite films, it is necessary to know the structure of original clay film and the formation process of the graphite film from the clay film.

The structure of the clay film can be presumed from the results of the XRD analyses. The number of stacking lamella in the clay film can be calculated from the average crystal size of the (00 l) planes. There is no information about the size of the clay lamella. However, other researchers reported that the size of the clay lamella is about $1 \mu\text{m}$ in the case of MONT.¹⁷ It seems reasonable to suppose that the size of the TAEN lamella is also close to $1 \mu\text{m}$. As can be seen from Figure 1, the clay lamellae in the clay film are highly oriented along the direction of the film plane. The absence of ($hk0$) diffraction bands in the XRD patterns of the clay films is further evidence of such orientation. On the basis of the above mentioned information, an attempt was made to illustrate the microscopic texture of the cross section of the clay film. The drawing is shown in the upper part of Figure 5, where the gray lines correspond to the cross section of the clay lamellae. The actual number of layers in the film is much greater than in this drawing. In a unit crystallite, which is indicated by a dotted rectangle, there exist 30–140 lamellae. The middle part of Figure 5 shows the microscopic structure of the clay-carbon complex film. The black lines in the drawing represent carbon layers, which are located in the space between the clay lamellae. After the acid treatment and the subsequent high-temperature treatment, the clay lamellae (gray lines) are removed to leave the carbon layers (black lines) as in the bottom drawing in Figure 5. These drawings imply that the orientation

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structure of the graphite film would strongly depend on that of the original clay film. This is experimentally shown by a surprisingly good similarity in the pattern of orientation curves between the three graphite films and the corresponding clay films (Figure 1). Thus, the graphite film with the best preferred orientation was prepared from the clay film with the best preferred orientation, that is, the Na-TAEN film. Furthermore, both the good preferred orientation and high crystallinity of the Na-TAEN film are probably responsible for the formation of graphite with high crystallinity.

The most notable feature of the present graphite films is their flexibility, which is not found in the other graphite films. The preferred orientation of the graphite films prepared from some thermoresistant polymer films is better by far than ours. The graphite film from poly(*p*-phenylene-1,3,4-oxadiazole), for instance, gives a very sharp orientation curve (its full width at half-maximum is below 0.2°).⁶ For the graphite film from polyimide Kapton, the SEM photographs of its cross section show a regular and perfect stacking structure of graphite layers with no wrinkles.¹⁸ These highly oriented graphite films are, as far as we know, very rigid and brittle, and none of them shows such flexibility as was observed in our case. Since there is no essential difference in interplanar spacing, d_{002} , between our films and the films from thermoresistant polymers, the difference in flexibility should be ascribed to the microtexture of the two kinds of films. As can be speculated in the drawing of the clay-carbon complex film in Figure 5, a regular stacking of carbon and clay layers would be present in some parts of the complex film, but these stacking crystallites do not run perfectly parallel to each other. This unique structure remains almost unchanged after the removal of the clay framework. During the high-temperature treatment, the stacked carbon layers become a graphitic crystallite, but the further crystal growth along *a* axis is likely to be hampered due to this unique structure. Thereby, the graphite films in this work consist of highly crystallized but small graphite crystallites. These crystallites are oriented to some extent and probably linked with each other, just like the drawing in Figure 5. It can be easily imagined that this kind of structure allows the film to be curved without breaking. On the other hand, if the graphite film is comprised only of the perfect stacking of very wide graphite layers, the film would be rigid and easily cracked and broken when it is bent, as in the case of the graphite films from the thermoresistant polymer films.

The resistivity of the graphite films from thermoresistant polymers is found to be the order of $10^{-6} \Omega \text{ m}^8$, whereas our graphite films exhibit rather high resistivity (Table 1). In terms of their mechanical strength, our graphite films are weaker than the others reported so far. For example, a tensile strength of 500 MPa is found for the graphite film obtained from mesophase pitch,⁴ which, however, does not show such flexibility as was observed here. The unique microstructure of our graphite films could be responsible for their large electrical resistivity and weak mechanical strength. Since many small carbon crystallites compose a graphite film, the boundary between crystallites is the origin of high contact resistance for electric current, even if the resistivity of the carbon crystallite itself is low. Such crystallites are linked to form a film macroscopically. Thereby, its mechanical strength depends on the linkage parts, which would be mechanically weak.

Conclusions

A graphite film was prepared from PAN by the template carbonization method using a clay film. It was found that the graphite film resembles in morphology and microstructure very much the original clay film as a template. Among the three clay films employed in this study, the Na-taeniolite clay film, which has the most crystallized and oriented structure, produced the most crystallized and oriented graphite film.

The most remarkable feature of the present graphite film is its flexibility. The film did not break or crack even when it was appreciably curved. The graphite films prepared by this method exhibited relatively a large electrical resistivity and weak mechanical strength, in comparison with the other graphite films previously reported. Such properties of this graphite film can be explained on the basis of its unique microstructure, i.e., very small and highly crystallized carbon crystallites are oriented along the direction of film plane and these micro crystallites are linked together to form a film.

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