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Effects of a binder on properties of taeniolite–acriflavine complex films before and after carbonization

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Taeniolite–acriflavine complex films (about 10 μm in thickness) with less than 2 wt% of aluminium phosphate binder were prepared, followed by heat treatment (carbonization) below 1073 K under nitrogen in order to examine the effects of the binder on properties of the films. The results obtained are as follows.

(1) The binder made the film more dense without structural change on X-ray diffraction analysis. (2) The tensile strength of the film, especially after heating to high temperature, was improved by adding the binder. (3) The modulus of toughness was scarcely influenced by the binder. (4) No change was observed in the electric resistivity by adding the binder.

1. Introduction

A film derived from clay minerals has become of interest in recent years because of its high thermostability, durability and other properties [1, 2]. To the best of the author's knowledge it has not, however, been put to practical use. This is possibly a result of its poor mechanical properties. The present authors have examined some properties of the taeniolite–acriflavine complex film before and after heat treatment (carbonization) under nitrogen [3, 4], and revealed that compared with the usual taeniolite film, the complex film is (i) more flexible, (ii) not so brittle even after heating to a higher temperature and (iii) electric-conductive (1 Ω cm). Phenomenon (iii) is useful to give electric conductivity to an insulative clay film [5]. Phenomena (i) and (ii) are also favourable from the standpoint of practical use. The tensile strength of the film, however, was only several 10 MPa which is too small for practical use.

Such a small strength was thought to result from weak adhesion between the flaky taeniolite particles constituting the film and in this work, an attempt has been made to improve the strength by using a binder. A commercially available aluminium including an organic neutralizer was used because such a binder must also be effective to prevent the increase of electric resistivity caused by the resulting carbon after heat treatment.

2. Experimental procedure

2.1. Raw materials

Li-taeniolite with the chemical formula $Li^+(Mg_2Li)_{oct}(Si_4)_{tet}O_{10}F_2 \cdot nH_2O$ and the cation exchange capacity (CEC) of 101 meq/100 g was synthesized in Topy Industries Co., Ltd. and kindly supplied for this work. The acriflavine hydrochloride $[C_{13}NH_7(NH_2)_2 \cdot 2HCl]$ used had a dye content of 90% and m.p. of 533 K. A binder (trade name: Acolarm) supplied by Taki Chemical Co., Ltd., is primary aluminium phosphate $[Al(PO_3)_3 \cdot 3H_2O]$ neutralized with an organic amine of which there are further details available [6]. Some properties of the binder are shown in Table I. According to its specification the organic amine included starts to evaporate from the binder around 453 K.

2.2. Preparation of samples

Acriflavine hydrochloride was added into the 2% of Li-taeniolite aqueous sol (abbreviation: TNL) by the equivalent amount of CEC of TNL, followed by stirring at 353 K for 18 h to synthesize taeniolite–acriflavine complex (abbreviation: TAC). Water was added into TAC sol after centrifuging to prepare the 1.0–1.2% aqueous sol. Furthermore, the predetermined amounts of the binder were added into the sols to prepare some samples as shown in Table II.

The resulting sol was spread on a flat surface coated with silicon resin remover and dried at room temperature for 2 to 3 days. A small film (30 × 2 mm², about 10 μm in thickness) was put between carbon plates and then heated (carbonized) at 673 and 873 K for 1 h and 1073 K for 15 min under nitrogen. The heating rate was 0.5 K min⁻¹.

2.3. Measurements

The film was subjected to SEM observation, X-ray diffraction analysis using nickel-filtered CuKα radiation, the carbon content, mechanical properties and

TABLE I Properties of the binder (Acolarm)

P_2O_5	18 wt %
Al_2O_3	3.9 wt %
Specific gravity	1.33
Viscosity (298 K)	125 cps
pH	9.0–9.5

TABLE II Analyses of aluminium and phosphorus in the films

Sample	Content (wt %)	
	Al	P
TAC-A	0.060 (0.000)	0.004 (0.000)
TAC-B	0.079 (0.042)	0.105 (0.146)
TAC-C	0.110 (0.085)	0.207 (0.292)
TAC-D	0.244 (0.425)	0.535 (1.426)

( ) is the wt % calculated from an additional amount of Acolarm. The Acolarm was assumed to remain as $Al_2O_3 \cdot 3P_2O_5 \cdot 6H_2O$.

electric resistivity measurements; the methods are reported elsewhere [3, 4]. The aluminium and phosphorus in the film were analysed quantitatively as follows. 0.500 g of the film was dissolved in a mixture of HNO_3–$HClO_4$–HF, and evaporated to dryness. The resulting solid was dissolved again in 15 ml of HCl and diluted to 100 ml with water. The solution was subjected to analyses of aluminium and phosphorus by using IPC apparatus. The wavelengths used were 396.152 nm for aluminium and 213.618 nm for phosphorus.

3. Results

3.1. Addition or an amount of binder

Table II shows the contents of aluminium and phosphorus in the films. The catalogue of Acolarm says that the binder exists as aluminium primary phosphate below 453 K. The content of primary aluminium phosphate in the film was calculated on the base of the content of phosphorus in Table II. The contents were 0.38%, 0.71% and 1.88% for TAC-B, TAC-C and TAC-D, respectively.

3.2. X-ray analysis

Fig. 1 shows changes of the X-ray diffraction profiles of TAC-A and TAC-D with heat-treatment temperature. Both films, even after heating to 1073 K, clearly showed profiles resulting from the layer structure. The diffraction peaks of TAC-D before heating were somewhat weak possibly because of the presence of the binder. The interlayer distance (d_{001}) was calculated from the strong (001) diffraction peak. The d_{001} of TAC-A was 1.47 and 1.34 nm before and after heating to 1073 K, respectively. TAC-D exhibited peaks at 1.47 and 1.30 nm before and after heating to 1073 K, respectively. The d_{001} of TAC-B and TAC-C situated between those of both TAC-A and TAC-D.

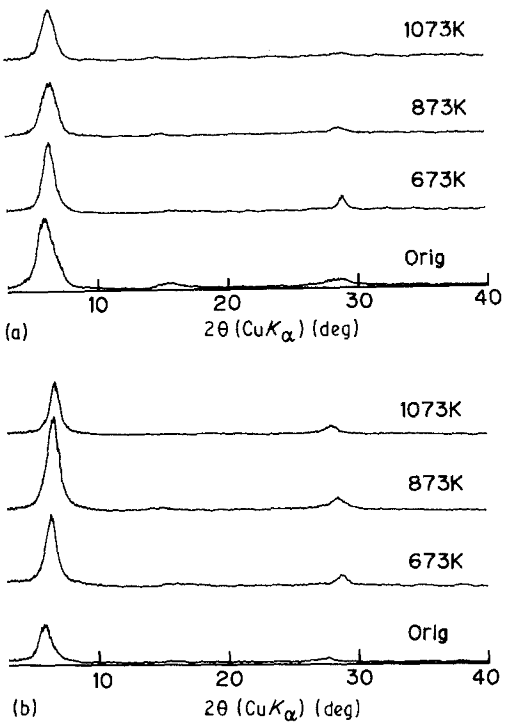

Figure 1 X-ray diffraction profiles of (a) TAC-A and (b) TAC-D films before and after heating.

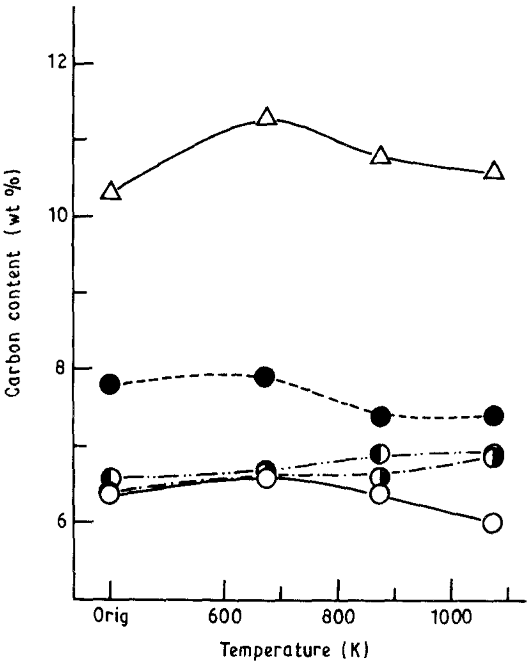

Figure 2 Carbon contents of TAC films and the binder (Acolarm) before and after heating. (○ TAC-A, ◑ TAC-B, ◐ TAC-C, ● TAC-D, △ acolarm).

3.3. Carbon content

Fig. 2 shows the carbon contents of the films. As stated previously, the binder contains about 10 wt % of carbon derived from the organic amine, which is higher than that (somewhat higher than 6%) of TAC. The carbon content of the film, therefore, increased with increasing additions of the binder. The increase of content at 673 K must attribute to the removal of water. At higher temperatures, the contents of TAC-A, TAC-D and TAC-B, TAC-C decreased and increased, respectively.

3.4. SEM observation

Fig. 3 shows the SEM photographs of the fracture surface of the films. The stacking structure of the flakes

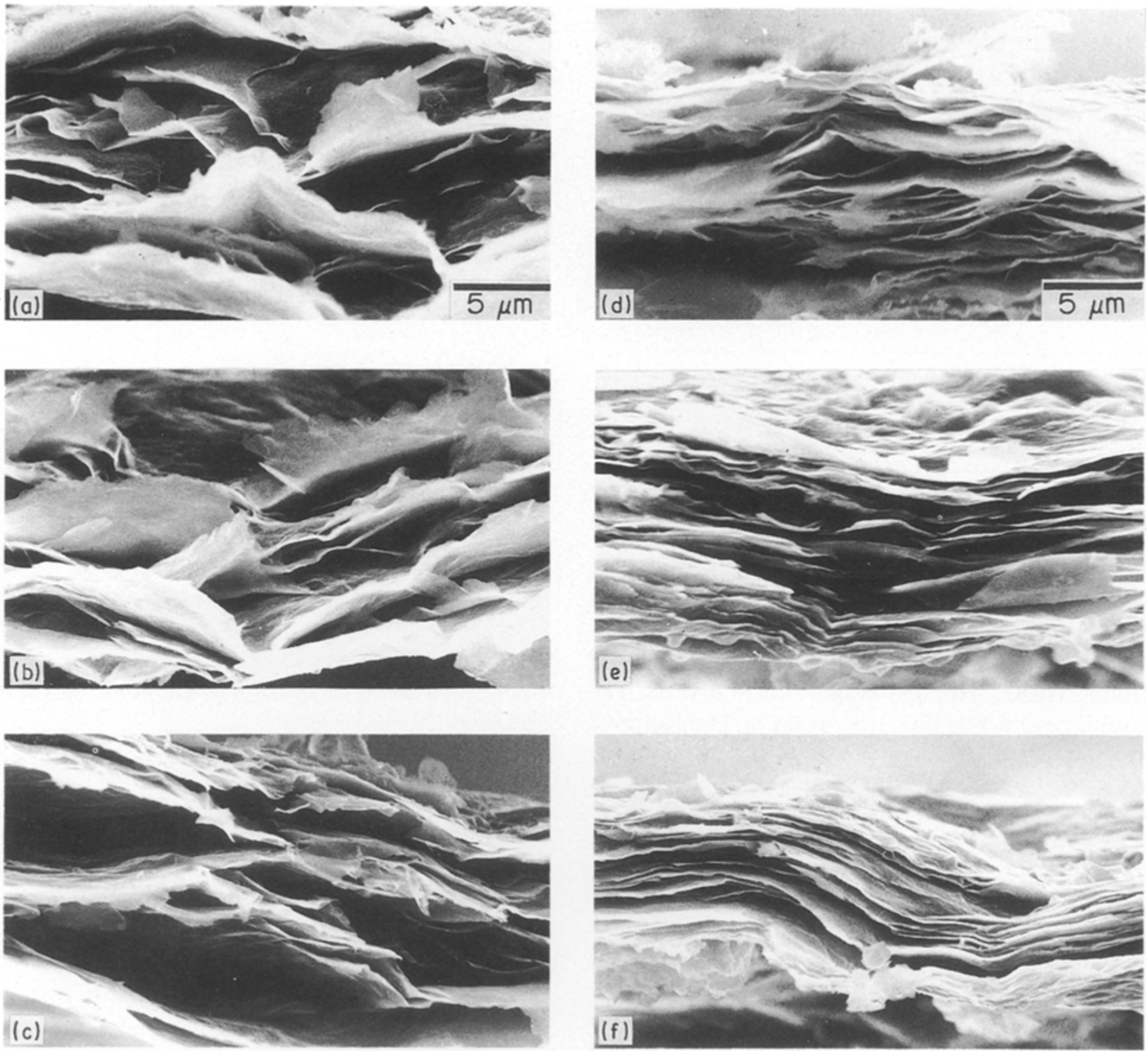

Figure 3 SEM photographs of the fracture surfaces of TAC-A and TAC-D films before and after heating. (a) TAC-A, original, (b) TAC-A, 873 K; (c) TAC-A, 1073 K; (d) TAC-D, original; (e) TAC-D, 873 K; (f) TAC-D, 1073 K.

was clearly observed in all films. The TAC-A film before heating (shown as Orig.) consists of rough stacking of the flakes and a flake pulled out from the film curls softly. Such structure was also seen after heating to 873 K but not after heating to 1073 K. The flakes in the TAC-D film stack more densely than in TAC-A. Such a structure was kept up to 1073 K. The fracture surface of TAC-D, on the whole, is more flat than that of TAC-A film, because it is difficult to pull out individual flakes from the TAC-D film. In addition, the film with a greater amount of the binder as TAC-D exhibited frequently splitting the films at the carbonization process (Fig. 4), possibly by the evolution of gas. Such a phenomenon was suppressed by using a smaller heating rate.

3.5. Mechanical properties

The mechanical properties shown here are the average of eight or more samples. Fig. 5 shows the typical load–elongation relationships for TAC-A and TAC-D films after heating to 673 K. By using such a diagram, the tensile strength and the modulus of toughness of the film were calculated. As can be seen from Fig. 5, the film became hard by adding the binder, leading to a small elongation. Fig. 6 shows the change of the tensile strength with heat-treatment temperature. The binder had no effect on the tensile strength of the film before heating, however, in the films with the binder, after heating to 673 to 873 K, the tensile strength increased in contrast to the decrease in the film without the binder. Heating to the higher temperature of 873 to 1073 K brought about a lowering of strength in all films, because the film became hard and brittle by sintering as seen in its SEM photograph. After heating to 1073 K, the tensile strength of TAC-D was about twice that of TAC-A.

Fig. 7 shows the modulus of toughness which is the energy to cut the film (corresponding to the area of triangle in Fig. 5). The modulus of fracture decreased somewhat in all films with increasing the temperature, except for the improvement and no change in TAC-D and TAC-C films at 873 to 1073 K, respectively. On the whole, the effect of the binder was small.

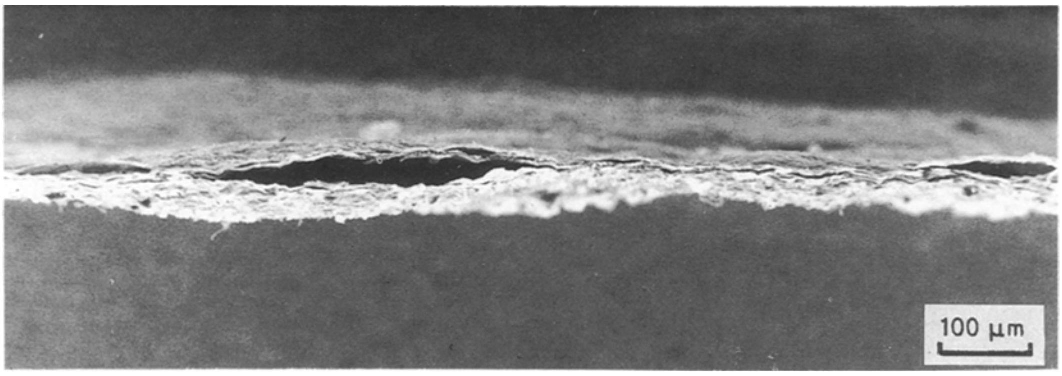

Figure 4 SEM photograph of the fracture surface of TAC-D film after heating to 1073 K.

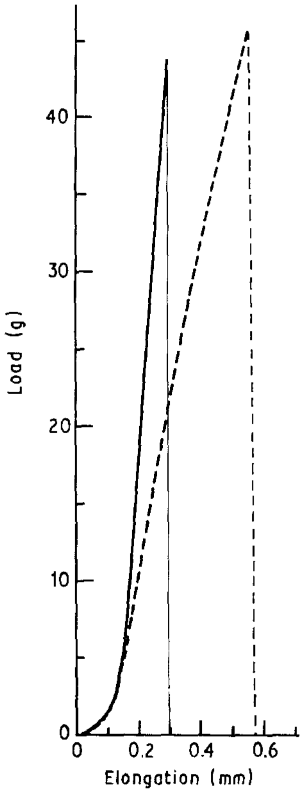

Figure 5 Typical examples of load-elongation curves of TAC-A (– – –) and TAC-D (——) films after heating to 873 K.

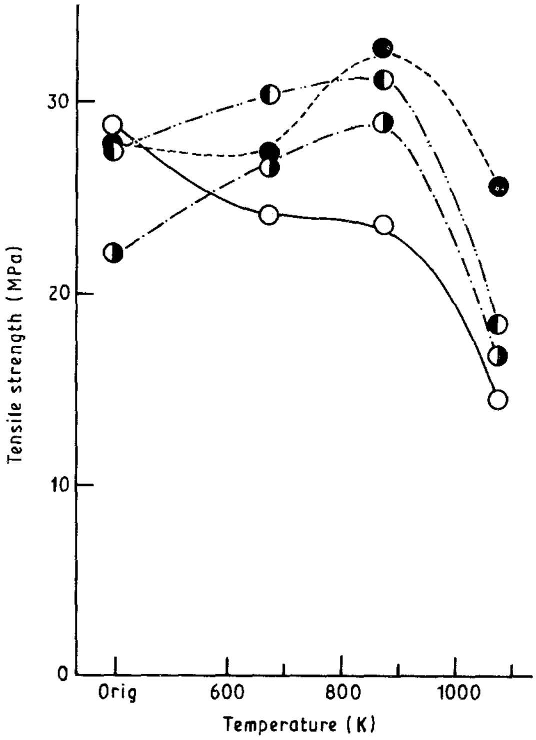

Figure 6 Changes of tensile strength of TAC films with heat-treatment temperature. (○ TAC-A, ◑ TAC-B, ◐ TAC-C, ● TAC-D).

3.6. Electric resistivity

Fig. 8 shows changes of the electric resistivity with heat treatment temperature. The resistivities of all films were lowered remarkably between 873 and 1073 K, but no clear relation was observed between an addition binder and the electric resistivity.

4. Discussion

The amount of binder added was quite small but clearly affected the structure and mechanical properties of the film. Its effect on the structure is discussed first. It is certain that the binder resulted in stronger adhesion between the flaky particles constituting the film in view of the following phenomena. (i) Addition of the binder made the stacking structure of the film denser. (ii) The flake pulled out was not observed at the fracture surface of the film with the binder. X-ray diffraction analysis gave no evidence that the binder reacted chemically with TAC at heating to 1073 K. Analogous (0 0 1) X-ray diffraction profiles of the films with and without the binder also suggest no chemical reaction between the two components. It will be concluded, therefore, that the binder acts only to adhere the flakes without chemical reaction as we expected.

The tensile strength of the film was improved by adding the binder. Such an effect became especially clear after heating to a high temperature. This phenomenon can reasonably be explained by the properties of this binder. i.e., the binder becomes hard and strong through dehydration polymerization and/or crystallization by heating [6]. In fact, TAC-A film after heating to 1073 K was too brittle to handle but this was not so for the TAC-D film heated to the same temperature. From the SEM photographs, it is also thought that the more densely stacked structure of TAC-D film improves the tensile strength of this film.

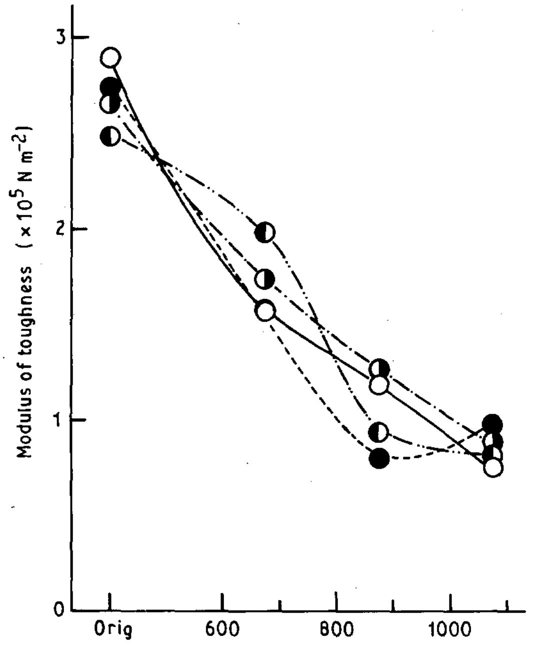

Figure 7 Changes of modulus of toughness of TAC films with heat-treatment temperature. (○ TAC-A, ◑ TAC-B, ◐ TAC-C, ● TAC-D).

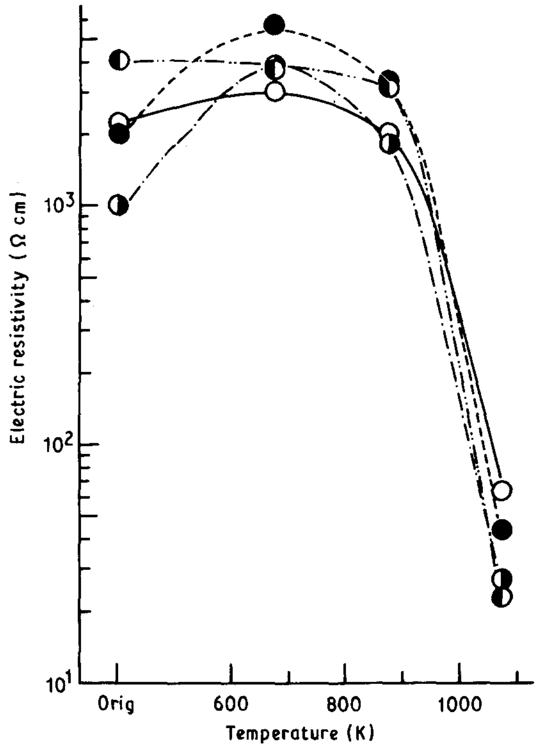

Figure 8 Changes of electric resistivity of TAC films with heat-treatment temperature. (○ TAC-A, ◑ TAC-B, ◐ TAC-C, ● TAC-D).

The relation between the tensile strength and heat-treatment temperature is substantially changed by adding the binder. It is, therefore, concluded that the tensile strength is influenced more remarkably by the adhesion strength between the flakes than the degree of stacking density of the flakes.

It is reasonable that as adhesion strength increases, the slipping between the flakes becomes more difficult at fracturing of the film, leading to a lowering of the flexibility. A small change of the toughness modulus in Fig. 7 may be caused by a synergistic effect between increasing tensile strength and decreasing elongation. Even the moduli of toughness were equal, therefore, the substantial mechanical properties are not necessarily the same, because they depend on an additional amount of the binder. For such considerations, it can be seen that a film with high tensile strength and high flexibility can be prepared by stacking the flakes in more densely, without a binder.

The electrical resistivity was scarcely changed by adding the binder. The binder contained higher carbon content rather than TAC film. This is the main reason for no change in the resistivity.

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