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Structure and mechanical properties of methyltrimethoxysilane-treated taeniolite films

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Lithium–taeniolite films (9–12 μm) were soaked in methyltrimethoxysilane (MTMS) for periods shorter than 48 h at room temperature. The MTMS was hydrolysed by water contained in the film, and the resulting polymer buried gaps in the film. The polymer existed also in the vicinity of the film surface. The taeniolite particles constructing the film seem to be bound by the polymers. Mechanical properties of the films after the MTMS treatment showed five times larger modulus of toughness than that of the untreated film. An impurity of fine LiF particles in the film lowered tensile strength and modulus of toughness.

1. Introduction

Taeniolite films have unique properties such as a high thermal stability, a high gas non-permeability, and so on. However, these films have not been used practically because of their low mechanical properties. Some techniques have been tried to improve the mechanical properties but have not given favourable results [1, 2]. We felt that the mechanical properties may be improved by making a cross-linkage between taeniolite particles in the film.

It is known that –OH groups exist on the external surface of oxides including taeniolite [3] and are used to modify chemical properties of the surface of oxides by reacting with alkoxysilane [3, 4]

$$\text{Oxide–OH} + \text{ROSiR}_3 \rightarrow \text{Oxide–O–SiR}_3 + \text{ROH} \quad (1)$$

When an alkoxysilane with two or three OR groups is used, –O–Si–O– bonds could be formed between the constituent taeniolite particles, leading to improvement of the mechanical properties of the film. The present work was carried out to certify this idea.

2. Experimental procedure

2.1. Materials

Lithium–taeniolite [$LiMg_2Li(Si_4O_{10})F_2 \cdot nH_2O$] was supplied by Topy Ind. Co.; details were reported elsewhere [1, 2]. Methyltrimethoxysilane ($CH_3Si(OCH_3)_3$ mol. wt 136.2, b.p. 102 °C) was supplied by Shin-etsu Chemical Co. and used without further purification.

2.2. Preparation procedures

A 2 wt % taeniolite aqueous sol was degassed under a reduced pressure of 160 mm Hg. The taeniolite content in the sol was substantially kept unchanged after the degassing. The sol was spread out on a plate coated with a remover, dried at room temperature and peeled off to prepare taeniolite (TNL) films of 9–12 μm thickness. The films of area $20 \times 20\ \text{mm}^2$ and $50 \times 50\ \text{mm}^2$ were removed for chemical analyses and measurement of mechanical properties, respectively. After drying at 120 °C for 24 h to remove the adsorbed water, the film was soaked in methyltrimethoxysilane (MTMS) for 3, 12, 24 and 48 h. Finally the films were dried at 120 °C for 24 h in air. The films are abbreviated as MTNL with a soaking time, e.g. MTNL-24. Readsorption of the water, however, may have occurred somewhat in the short time until the film was soaked.

2.3. Measurements

The presence of –OH groups and carbon in raw TNL was determined by the XPS analysis of Si'2p and C'1s core levels. The amount of MTMS (or its derivatives) in the MTNL film was estimated by carbon content, which was measured by a combustion method using tin particles as a combustion accelerator. X-ray diffraction using nickel-filtered CuK_α radiation was used to determine the basal spacing (d_{001}) of the TNL films before and after the MTMS treatment. The film, after coating with gold (25 nm), was observed by scanning electron microscopy (SEM). In order to examine the inside of the film, Scotch tape was adhered on both

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sides of the film and peeled off. A local area of the film was analysed by micro-focus X-ray diffraction and micro-Fourier transform–infrared spectroscopy (FT–IR). A Tensilon apparatus was used to obtain a stress–strain curve under a crosshead speed of 2 mm min^{-1}, from which fracture elongation, tensile strength, tensile modulus, and modulus of toughness were calculated. The width of the test piece and span distance were 2 and 30 mm, respectively. The data shown are the average of 12–16 samples.

3. Results

3.1. XPS

Fig. 1 shows Si′2p-XPS spectrum of the TNL film. The observed spectrum was mainly separated into two symmetrical profiles. Their bond energies are 103.30 and 102.50 eV and correspond to SiO_2 and SiOH, respectively [5, 6]. Because XPS is a surface analysis, one can conclude a large amount of surface –OH groups is present.

3.2. Carbon content and basal spacing

Table I summarizes the carbon content and the basal spacing ($d_{0\,0\,1}$) of the TNL and the MTNL films. The TNL film contained 0.2 wt % carbon, the presence of which was confirmed by the XPS analysis of the C′1s core level existing as C–C, C–H, –C–O and O=C–O groups as shown in Fig. 2. The carbon may have been introduced from the carbon electrode when the TNL was synthesized. The increase of the carbon content was just 0.4 wt % after soaking for 48 h. No change of $d_{0\,0\,1}$ of the TNL film was observed after soaking in the MTMS for 48 h, confirming that the percentage increase was carbon only due to surface reaction of TNL with MTMS.

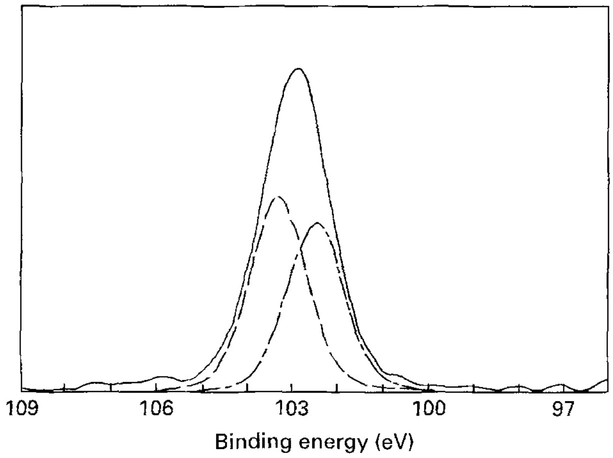


Figure 1 Si2p XPS spectrum of the TNL film. (– – –) SiO_2, (——–) SiOH.

TABLE I Carbon content and interlayer spacing ($d_{0\,0\,1}$) of the films

Specimen	Total C content (wt %)	C content due to MTMS (wt %)	$d_{0\,0\,1}$ (nm)
TNL	0.2	0.0	1.22
MTNL-3	0.5	0.3	1.22
MTNL-12	0.5	0.3	1.23
MTNL-24	0.5	0.3	1.22
MTNL-48	0.6	0.4	1.23

3.3. SEM observation

Scanning electron micrographs of the fracture surface of the TNL film are shown in Fig. 3. A characteristic

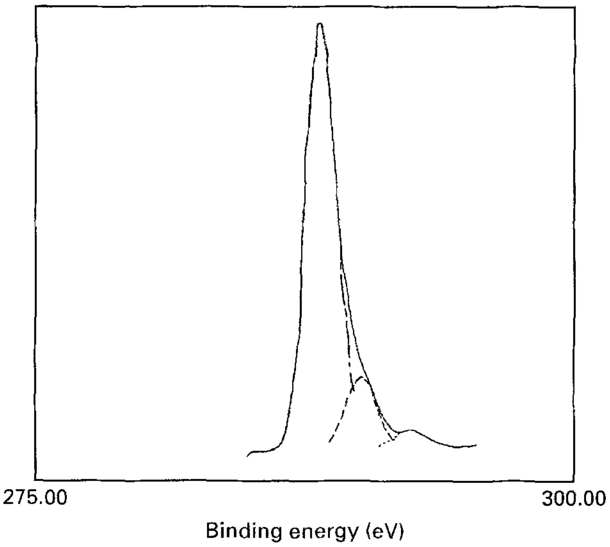
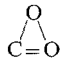


Figure 2 C1s XPS spectrum of the TNL film. (——) C′1s, (——–) C–C, C–H, (– – –) C=O, (- - -)  .

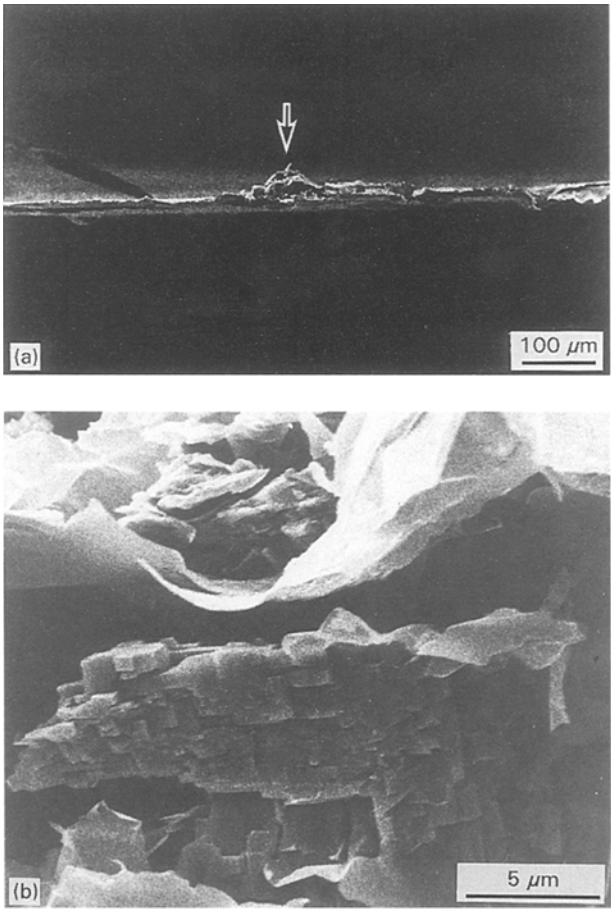


Figure 3 Scanning electron micrographs of the fracture surfaces of the TNL film.

area, arrowed, was always observed on the fracture surface. This is a coagulation of fine particles, as seen in an enlarged photograph (bottom).

Fig. 4 shows scanning electron micrographs of the inside of the TNL and the MTNL-48 films. A flat region (F) was observed in the TNL film. A characteristic area (G) was rarely observed. Area G consists of fine particles of several micrometres in size (TNL-(G)). This location corresponds to that arrowed in Fig. 3. A similar location was also observed in the MTNL film, but the edge of the fine particle was not as sharp as in the TNL film (MTNL-(G)).

3.4. Micro-focus X-ray diffraction and micro-FT–IR

Fig. 5 shows the micro-focus X-ray diffraction profiles for the locations of (G) and (F) in the TNL film in Fig. 4. The location (G) is clearly consisted of LiF crystal.

Fig. 6 shows the micro-FT–IR spectra of the MTNL-48. The reflection spectrum ((F)-R) of the location (F) in the MTNL film (Fig. 4) shows absorptions at 1270 cm^{-1} (δ Si–CH_3 (3)), 2970 cm^{-1} (ν C–H (1)) and 2850 cm^{-1} (ν C–H (2)), indicating the presence of –Si–CH_3. The strong absorption around 1640 cm^{-1} is attributable to δ H–O–H, which suggests the occurrence of the readsorption of water. The spectrum (B)-T is the transmission spectrum of a barrier region between the locations (G) and (F). The absorptions (1) (2) and (3) are clearly observed. These absorptions were observed weakly in a transmission spectrum of the location (G) ((G)-T), but were not observed in a transmission spectrum of the location (F) ((F)-T). In conclusion, MTMS is mainly located at the surface of the TNL film and in the matrix at the defects between TNL and LiF grains.

3.5. Mechanical properties

Fig. 7 shows the typical stress–strain curves of the TNL and the MTNL-48 films to demonstrate the improvement of mechanical properties due to the MTMS treatment. Some mechanical properties were obtained and plotted against carbon content, because the carbon content indicates the amount of –Si–CH_3 existing in the film. Three points were plotted against 0.3 wt % C content, because the MTLN-3, -12 and -24 showed equal carbon contents.

Fig. 8 shows the relation between fracture elongation and the carbon content. The fracture elongation, 0.52%, of the TNL film increased to 0.81% for the MTNL-48 film. The relation between tensile strength and carbon content is shown in Fig. 9. The tensile strength of the film is enhanced by the MTMS-treatment, although the data are slightly scattered. The

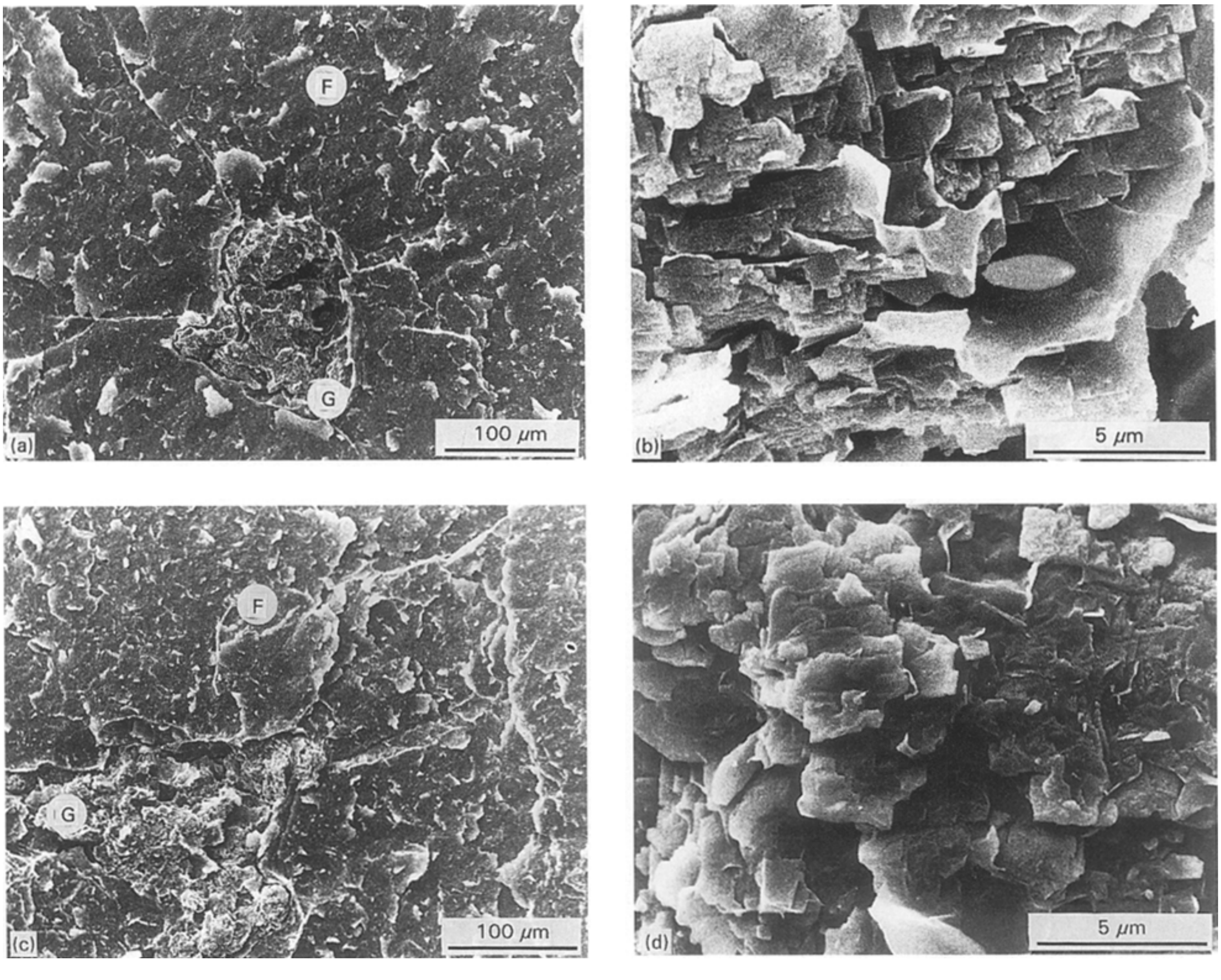


Figure 4 Scanning electron micrographs of the inside of the (a) TNL, (b) TNL-(G), (c) MTNL-48 and (d) MTNL-48-(G) films.

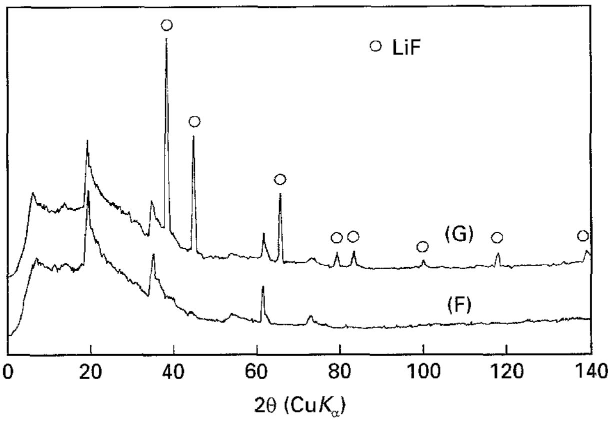


Figure 5 Micro-focus X-ray diffraction profiles of locations (G) and (F) in the TNL film (see Fig. 4).

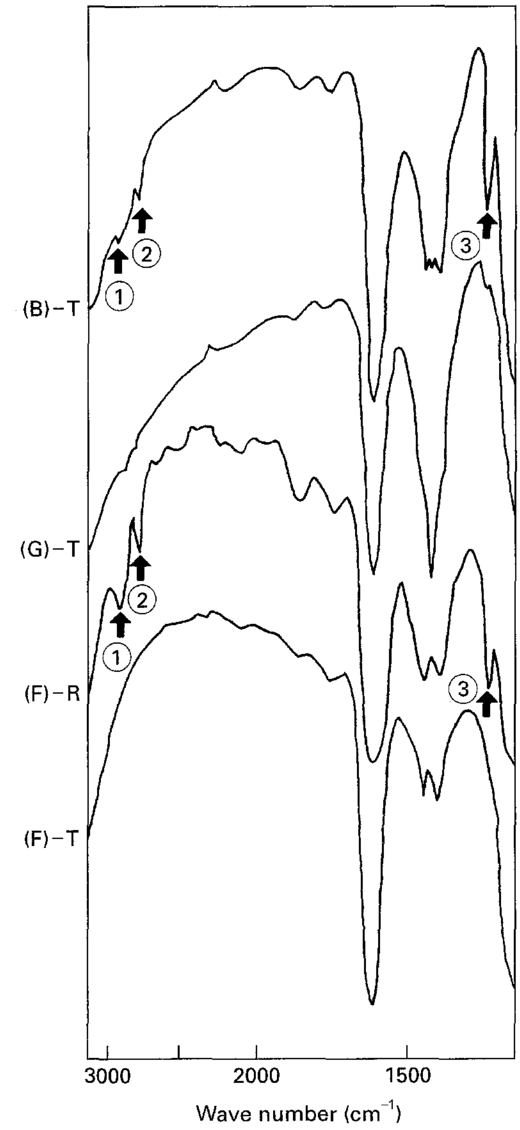


Figure 6 Micro FT–IR spectra of some locations in the MTNL-48 film (see Fig. 4).

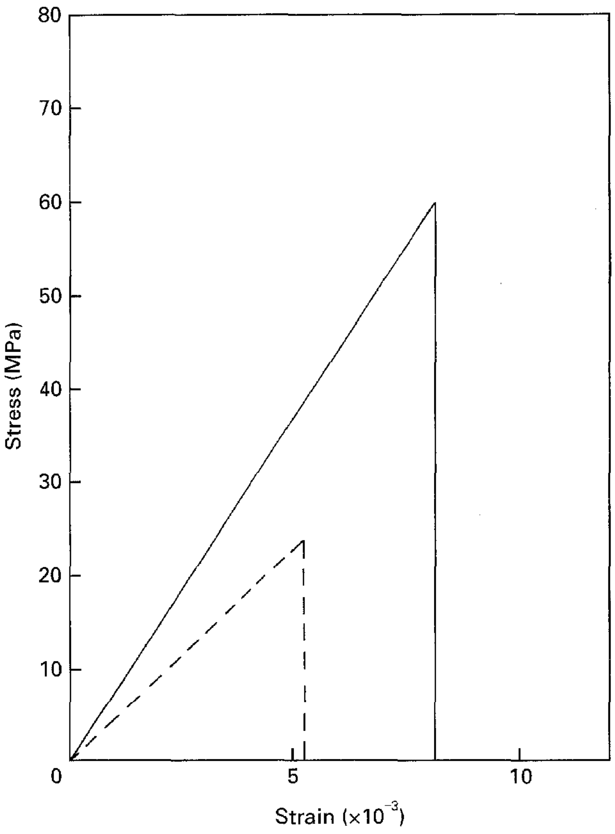


Figure 7 Typical stress–strain curves of the (---) TNL and (——) the MTNL-48 films.

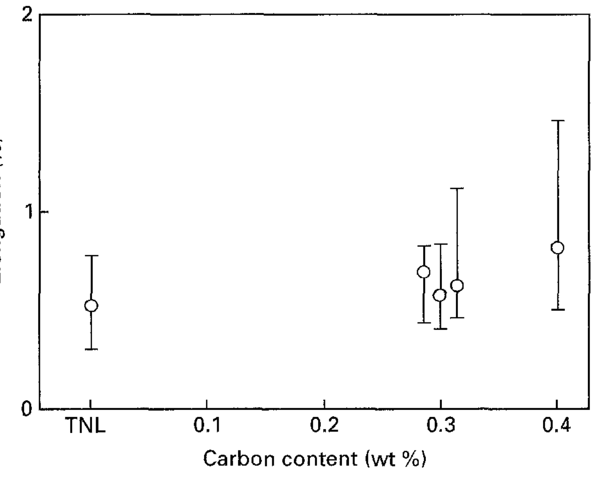


Figure 8 Relation between carbon content and percentage elongation of the films.

maximum strength for the MTNL-48 film was larger than 100 MPa.

Fig. 10 shows the relation between tensile modulus and carbon content. No clear effect was observed in this relation. Fig. 11 shows the relation between carbon content and modulus of toughness which corresponds to the areas of the triangles in Fig. 7. This value increased remarkably from 0.052 MPa for the TNL film to 0.22 MPa for the MTNL-48 film. The maximum values for the TNL and the MTNL-48 films were 0.01 and 0.59 MPa, respectively.

4. Discussion

4.1. Impregnation state of MTMS

The MTMS did not intercalate in the TNL, in view of the unchanged $d_{0\,0\,1}$ after the treatment. The unreacted MTMS was completely removed from the MNTL film by drying at 120 °C for 1 day. So, the carbon

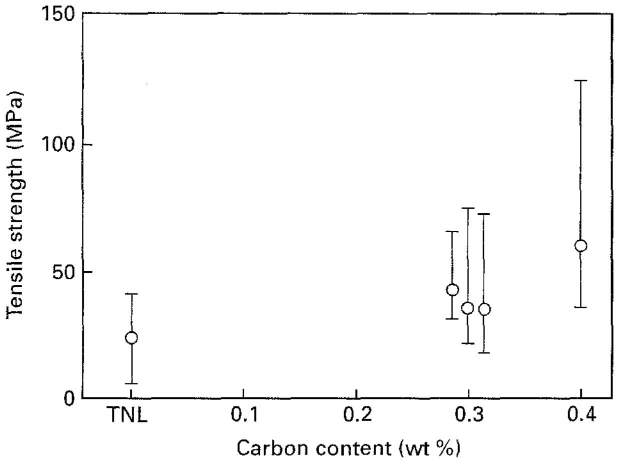


Figure 9 Relation between carbon content and tensile strength of the films.

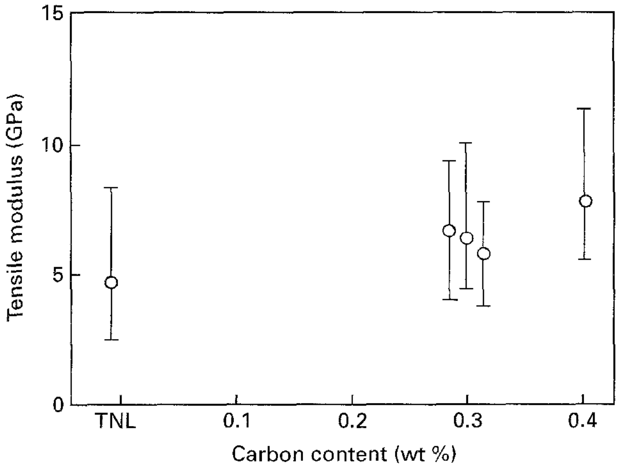


Figure 10 Relation between carbon content and tensile modulus of the films.

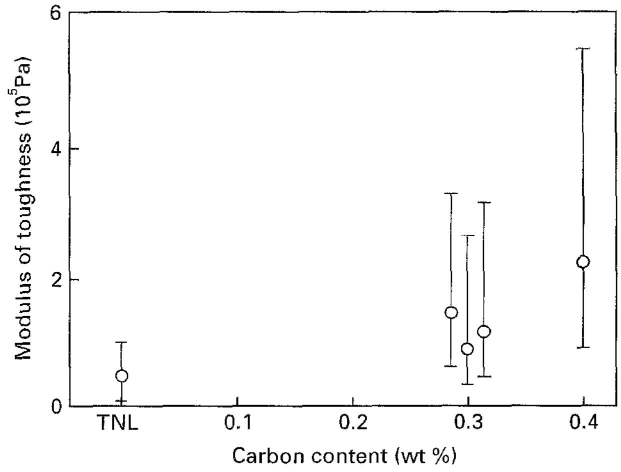


Figure 11 Relation between carbon content and modulus of toughness of the films.

content in the MTNL film (Table I) depends on $-Si-CH_3$ fixed on the TNL surface or remaining from a polymer derived from the MTMS stated below. On the basis of the results given elsewhere [3, 4], the $TNL-O-Si-CH_3$ bond will be formed because of the presence of $-OH$ on the TNL film (Fig. 1). On the basis of the 0.4 wt % C content (Table I), the grafted $-O-Si-CH_3$ is about 0.1 per unit molecular formula $[LiMg_2Li(Si_4O_{10})F_2]$ of TNL.

As stated in Fig. 6, the grafted $-O-Si-CH_3$ exists only in the vicinity of the film surface and around the LiF crystal, not throughout the film. The former was further certified by use of XPS as follows. Two

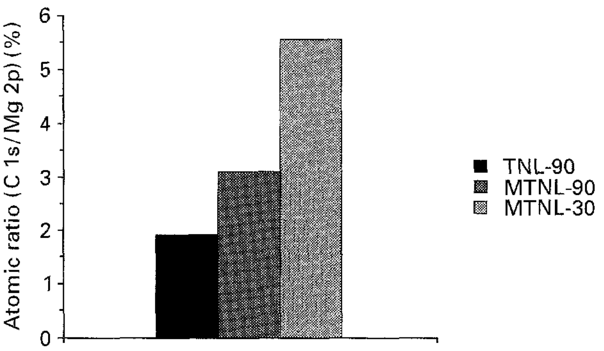


Figure 12 Atomic ratios (C′1s/Mg′2p) (%) given by XPS. TNL-90 and MTNL-90: analyser perpendicular to the film surface. MTNL-30: angle between analyser and film surface is 30°.

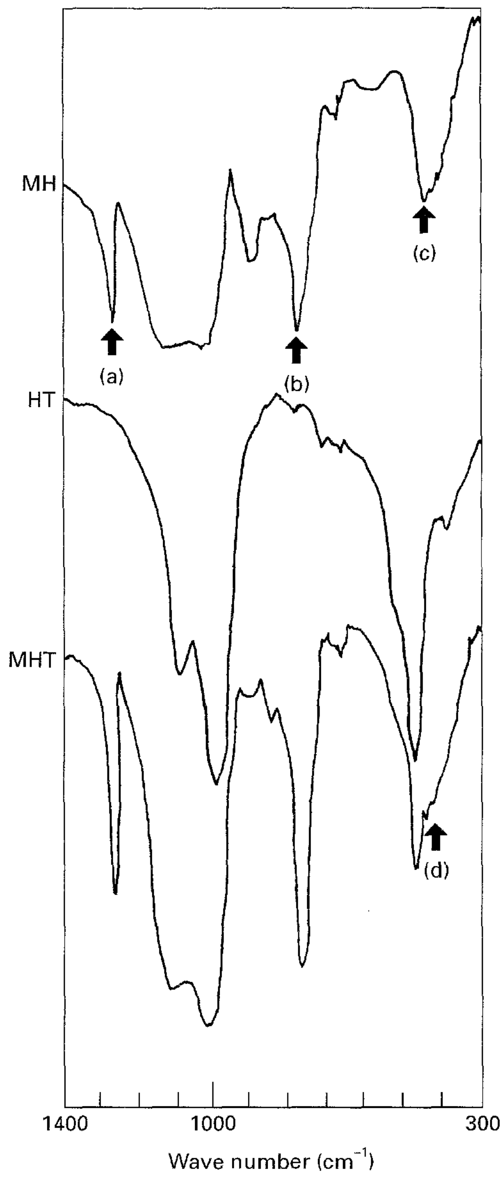


Figure 13 FT-IR spectra of the MH, MT and MHT (see text).

orientations of the analyser were used to examine the carbon concentration in the film surface. In the first experiment, the analyser was almost perpendicular to the film (90°), whereas a second experiment was realized with an angle of 30° between the direction of the analyser and the film surface, to decrease the depth analysed. Fig. 12 shows atomic ratios of C'1s/Mg'2p. It is clear that $-Si-CH_3$ is concentrated at the film surface. Fig. 4 showed that the edge of the LiF crystal became somewhat vague after the MTMS-treatment. The LiF crystal is suggested to be covered with a MTMS-derived polymer. The film surface is, of course, also covered with this polymer.

As described above, the formation of an MTMS-derived polymer is very important in discussing the effects of the MTMS-treatment. So an additional examination was carried out to certify the formation of the polymer. Three mixtures were allowed to stand for 2 days at room temperature, followed by drying for 1 day at 120 °C.

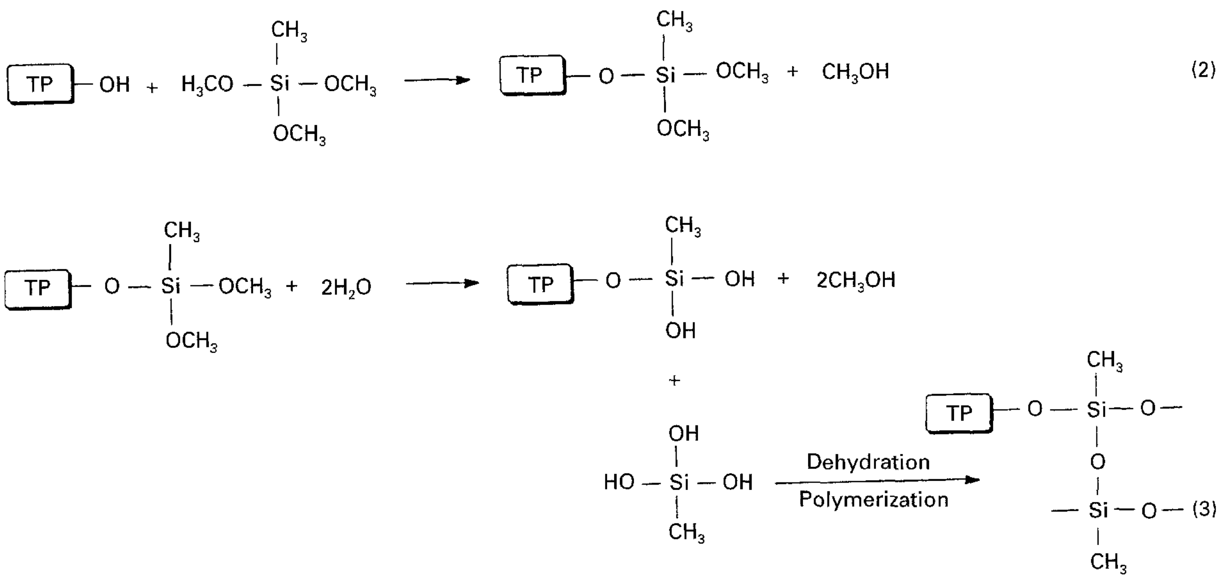
(i) Mixture-MH: 0.33 g MTMS and 24.5 g water; MTMS/water molecular ratio: $1.7 \times 10^{-3}:1$.

(ii) Mixture-HT: 0.5 g TNL and 24.5 g water; TNL/water molecular ratio: $0.9 \times 10^{-3}:1$.

(iii) Mixture-MHT: 0.33 g MTMS, 24.5 g water and 0.5 g TNL; MTMS/TNL/water molecular ratio: 1.7×10^{-3}: $0.9 \times 10^{-3}:1$.

Infrared spectra of the samples are shown in Fig. 13. The MH showed absorptions at (a) $1273\ cm^{-1}$ and (b) $781\ cm^{-1}$ (ν $Si-CH_3$) but not around $1190\ cm^{-1}$ (ν $Si-O-CH_3$) nor at $910-830\ cm^{-1}$ (ν Si–OH). These facts indicate that the MTMS hydrolysed and polymerised to form –Si–O–Si– bonds according to the following schemes.

TP–OH represents the taeniolite particle



$$\boxed{TP}-OH + H_3CO-\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{Si}}-OCH_3 \longrightarrow \boxed{TP}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{Si}}-OCH_3 + CH_3OH \tag{2}$$

$$\boxed{TP}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle OCH_3}{Si}}-OCH_3 + 2H_2O \longrightarrow \boxed{TP}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{Si}}-OH + 2CH_3OH$$

$$+\ HO-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{Si}}-OH \xrightarrow[\text{Polymerization}]{\text{Dehydration}} \begin{array}{l} \boxed{TP}-O-\overset{\displaystyle CH_3}{Si}-O- \\ \qquad\qquad\ \ |\\ \qquad\qquad\ \ O \\ \qquad\qquad\ \ | \\ \qquad\quad -\underset{\displaystyle CH_3}{Si}-O- \end{array} \tag{3}$$

This idea will be supported by the appearance of an absorption at $440\ cm^{-1}$ [δ Si–O–Si (c)], because by hydrolysis/polymerization, the product of $(CH_3)_2Si(OC_2H_5)_2$ is known to show an absorption around $460\ cm^{-1}$ (δ Si–O–Si). The MHT clearly showed absorptions (a) and (b). The shoulder (d) in the MHT must result from overlapping of the spectra of the MH and the HT. The MTMS in the gaps around the LiF particle and between the TNL particles polymerizes. As a result, the TNL particles in the vicinity of the film surface or around the LiF particle are bound by the MTMS-derived polymer.

4.2. Mechanical properties

The MTMS treatment improved mechanical properties, especially tensile strength and tensile modulus. The tensile strength is usually governed by the faults in the film, e.g. the LiF particle and a gap incorporated in the film. A gap in the vicinity of the film surface is buried by the MTMS-derived polymer. In addition, gaps around the LiF particles are somewhat buried, as suggested by covering of the particles by the polymer. These are the cause of the improvement of the tensile strength by the MTMS treatment. More fundamentally, of course, the LiF particles should be removed completely in order to improve the mechanical properties. The TNL is synthesized by fusing raw materials including LiF under a discharge using a graphite electrode. In this process, some amount of LiF remains unreacted, and carbon is introduced into the TNL as a contamination [8].

The tensile modulus reflects more intimately the whole structure of the film than the faults. The polymer in the vicinity of the surface must increase the tensile modulus for the MTNL film. The fracture elongation was influenced slightly by the MTMS treatment. In view of the increase of tensile modulus for the MTNL film, this increase results from the increased tensile strength of the film. The modulus of toughness is also improved with the increase in tensile strength. The present work suggests that a high-strength TNL film could be prepared by a thorough treatment of the whole of the TNL film, without the LiF particles, by MTMS. Such a work is now in progress and the results will be reported.

Acknowledgements

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