Effect of Thermally Treated Talc in Poly(amic acid) and Characterization of the Polyimide Composite Film

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An unusual increase in T_g of polyimide composite film consisting of semi-alicyclic polyimide (PI-1) and thermally treated talc (b') was observed by TMA measurement, where the T_g jumped as high as +50 K from the original one with 45 wt% of the baked talc. The degrees of (i) increasing viscosity of the solution with PI-1 precursor and the talc, (ii) increasing T_g of the composite film, and (iii) increasing tensile modulus of the composite film were all corresponded to the amount of thermal weight loss from the original talc. According to XRD and TEM observations, the morphological change of the stacking layer structure inherently talc owns was not occurred while the talc was subjected to bake at 700 °C in nitrogen. Since TG-MS elucidated that the emerged components during the thermal treatment was assignable to carbon dioxide, the original talc included some carbonate impurities. The volume of that contaminant involved in talc thus supposed to be correlation to the film thermal property.

Keywords : talc, poly(amic acid), polyimide, glass transition temperature, coefficient of thermal expansion

1. Introduction

Inorganic fillers such as mica, talc, SiO_2 , TiO_2 , CaCO_3 , BaSO_4 , etc are well-known materials to enhance the mechanical and thermal stabilities of industrial polymeric products (e.g. PE, PP, PET, PLA, PA, PI etc).[1-7] Especially, talc has been employed as a nucleating agent,[3-5] and a flame retardant for polymers.[6,7] Talc is one of the layered silicates classified as the softest natural mineral (Mohs hardness: 1.0) and its chemical formula is generally represented as $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. Impurities would sometimes make bulk talc slightly colored depending on the mined location. Their enormous usages broaden out in the field of cosmetic, paper, paint, plastic, and ceramic applications.

Because talc has lamella structure of nano-meter-thick layers and relatively high affinity to organic polymer materials,[2] one of the excellent effects is reducing the coefficient of thermal expansion (CTE) of polymer films.

Approximation of polymer's CTE to copper's one is important for electronic devices, for example, flexible printed circuit. Otherwise, mismatch of the thermal expansion may bring dimensional instability in the device. It is also notable for those devices to meet a thermal stability for reflow soldering at the temperature higher than 260 °C during the processing.

In the respect of the interesting structure of talc, we thus have focused on the way of how talc disperses and aligns in a polymer film, especially polyimide, as well as effective treatment of talc prior to use.

Common strategy to well-disperse inorganic fillers into polymeric materials has been developed in a way of organophilization of the filler surface by using alkylated surfactants (e.g. alkyl ammonium salt), which helps intercalation to widen the layer gap and increase affinity to organic compounds.[8] To downsize inorganic particles applying sol-gel methods is another option to avoid

Fig. 1. TGA trace of talc powder **a** and **b** as received in air.

Table 1. Characterization of talc **a** and **b**.

Talc	D_{50} ^{a)} [μm]	T_{d1} ^{b)} [°C]	$W.loss@700\text{ °C}$ ^{c)} [%]
a	≤ 4.4	859	0.5
b	≤ 3.9	628	2.9

^{a)} Median particle size in diameter (D_{50}) was determined by laser light scattering.[11]

^{b)} 1 % thermal thermal degradation temperature was determined by TGA (Fig.1).

^{c)} Weight loss at 700 °C in air determined by TGA (Fig.1).

getting obscure composite films.[9,10]

In this paper, we report our findings that certain talc functioned to significantly increase glass transition temperatures (T_g s) of polyimide films as well as decreasing their CTEs when the talc was baked at 700 °C before loading into poly(amic acid) varnish.

2. Experimental

2.1. Materials

Two types of talc (**a**, **b**) for this study was kindly donated from Asada Milling Co., Ltd. The product names were JM-156, and FFR, respectively.[11] These talc were baked in a muffle oven at 700 °C for 4 h in nitrogen (talc **a'**, **b'**). The other reagents and solvents were obtained commercially and used as received.

2.2. Synthesis of poly(amic acid) (PAA-1) and the corresponding polyimide (PI-1)[12]

To the slurry of pyromellitic dianhydride (PMDA; 0.700 mol, 153 g) in *N,N*-dimethylacetamide (DMAc; 446 mL), 2,5(6)-bis(aminomethyl) bicyclo[2.2.1]heptane (NBDA; 0.700 mol, 108 g) and DMAc (200 mL) were slowly added dropwise with stirring at 0 °C over 2 hr. PAA-1 varnish was obtained after the reaction for 20 hr at room temperature. The inherent viscosity using an Ubbelohde viscosimeter was determined to be 0.58 dL/g in DMAc (0.5 g/dL) at 35 °C. This varnish was stored in a refrigerator at 5 °C.

Scheme 1. Synthesis of PAA-1 and PI-1 with talc

Fig. 2. Dependencies of mechanical viscosities upon talc contents in PAA-1 varnish. Talc content was based on solid component in PAA-1 as 100 wt%.

2.3. Preparation of talc-dispersing PAA-1 solution

To PAA-1 varnish, a series of talc (**a**, **b**, **a'**, **b'**) whose weight was calculated against PAA-1 was added (15-45 wt% of solid component in PAA-1), followed by vigorously mixing by a hybrid deforming mixer (2000 rpm for 4 min). For a viscosity measurement, concentration of the original varnish PAA-1 was diluted down to 22 wt% due to increasing the viscosity with talc **b'**.

2.4. Film preparation

As for all the film preparation, respective talc-dispersing PAA-1 solution was directly cast on a glass plate using a bar-coater, followed by thermal curing at the elevated temperature up to 250 °C in an inert oven in nitrogen. The obtained film was then peeled out after soaking in hot water.

2.5. Measurements

Thermal gravimetric analysis (TGA) and thermal mechanical analysis (TMA) were performed on a Shimadzu TGA-50 at a heating rate of 10 °C/min and Shimadzu TMA-50 at a heating

Fig. 3. Thermal properties of the composite films: (a) TMA traces for PI-1 film (f1) and representative PI-1/talc composite films (f3, f6); (b) effect of increasing T_g increasing as function of talc content; (c) effect of decreasing CTE as a function of talc content. Talc content was based on solid component in PAA-1 as 100 wt%.

Table 2. Characterization of PI-1/talc composite films.

Film	Talc	Content ^{a)} [wt%]	T_g ^{b)} [°C]	CTE ^{c)} [ppm/K]	σ_t ^{d)} [MPa]	λ_t ^{d)} [GPa]	ϵ_t ^{d)} [%]	Transmittance ^{e)} [%T]
f1	N/A	0	290	47	85	2.41	4.9	90
f2	a	30	292	26	72	4.52	3.1	90
f3	b	30	292	27	68	4.52	2.3	90
f4	a'	30	300	25	70	4.54	3.1	89
f5	b'	15	323	31	79	3.95	4.1	89
f6	b'	30	333	21	73	5.30	2.2	90
f7	b'	45	341	17	29	3.03	1.4	89

^{a)} Talc content was based on PAA-1 as 100 wt% in the solution.

^{b)} Determined by TMA.

^{c)} CTE was calculated between the temperature 100–200 °C.

^{d)} Tensile strength (σ_t), tensile modulus (λ_t), and elongation at break (ϵ_t) were estimated as average out of 5 time measurement at an extension rate of 30 mm/min.

^{e)} Measured by hazemeter upon JIS-K7105.

rate of 5 °C/min, respectively. The load to a sample film for the TMA measurement was fixed as 3.0 g. Viscosity of the mixture of PAA-1/talc varnish was measured by Toki viscometer TVE-22H using a cone-plate rotor. Tensile test was conducted with a Shimadzu EZ-S. Sample pieces for the test were stamped out in 30 mm long and 5 mm wide. Light transmittance was measured by Tokyo Denshoku Hazemeter TC-HIIDPK upon JIS-K7105. X-ray diffraction (XRD) was carried out on a Rigaku RINT 2000. Transmission electron micrographs (TEMs) were obtained by Hitachi H-7000. The sample pieces were prepared by microtome to make both vertical- and horizontal section to the film surface. Thermogravimetry equipped with a mass spectroscopy (TG-MS) was performed on a Rigaku TG8120 in Helium at a heating rate of 20 °C/min (holding at 900 °C for 1 min), and HP6890, 5973 scanning from 10 to 300 m/z, respectively. Each sample load was ca. 10 mg. Infrared spectrum of the composite films (thickness: a few micron) was obtained by Shimadzu FTIR8100M in a resolution of 2 cm⁻¹.

3. Results and Discussion

3.1. Talc characterization

Because talc is natural mineral, impurities may be included in it relying on product locations. Therefore, we firstly evaluated the purities of a set of talc (a, b) by means of TGA. The TGA traces are shown in Figure 1 and the results are summarized in Table 1 as well as median particle size (D_{50}) characterized by laser light scattering.[11] Although the particle sizes of the two talc are similar ($D_{50} \leq 3.9 \mu\text{m}$ for a, $\leq 4.4 \mu\text{m}$ for b) in diameter, the weight losses up to 900 °C are different as shown in Figure 1. Talc b has larger weight loss in the range of 550 to 650 °C than that of talc a.

In this regard, thermal treatment of talc a and b was carried out in a muffle oven at 700 °C for 4 hr in nitrogen. The residual talc powder (a', b') showed much less thermal weight loss (<0.4 wt%) up to 700 °C (TGA is not shown here).

3.2. Preparation of poly(amic acid) varnish and its talc-dispersing solution

Representative poly(amic acid) (PAA-1) for this

study was synthesized by ring-opening polymerization of PMDA and NBDA in DMAc (Scheme 1). The inherent viscosity of PAA-1 was 0.58 dL/g in DMAc at 35 °C. This poly(amic acid) can be converted into a semi-alicyclic polyimide (PI-1) which has glass transition temperature (T_g) at 290 °C and high optical transparency in the visible range as listed in Table 2. Therefore, PI-1 is a good candidate for photosensitive application.[13]

Into the varnish of PAA-1, each of original talc (a, b) and the corresponding thermally treated talc (a', b') was added and mixed vigorously by using a hybrid deforming mixer. The mechanical viscosities of the mixed varnish of PAA-1/b and PAA-1/b' as a function of the talc content are plotted as Figure 2. The PAA-1 varnish was diluted to be 22 wt% as an original reference, showing the viscosity 1.62 Pa·s. An apparent increase of viscosity was observed especially when talc b' was added more than 30 wt% to the PAA-1 solution, while talc b did not change the viscosity dramatically. This implies that a strong interaction was taken place between PAA-1 and talc b'.

3.3. Characterization of the polyimide composite films

A series of polyimide composite films (f1-f7) was formed by thermal curing up to 250 °C in an inert oven with nitrogen and characterized as summarized in Table 2.

Firstly, T_g and CTE of the composite films were determined by TMA. Normal film of PI-1 (f1) and 30 wt% talc a or b containing film (f2, f3) showed very close T_g s as 290 and 292 °C, respectively. On the other hand, when 30 wt% of the baked talc a' or b' was incorporated into PI-1 film, the resulting films (f4, f6) showed T_g unprecedentedly increased up to 300 and 333 °C, respectively. The significant differences of TMA traces among f1, f3, and f6 are depicted in Figure 3(a). To the best of our knowledge, such an enormous increase in T_g reached over 300 °C was the first observation in the field of polyimide composite film. Figure 3(b) shows the dependencies of T_g on the content of each talc in the film, indicating the more the thermally treated talc was incorporated into the film the higher T_g was observed in TMA. Talc b' was much more effective for increasing T_g of the polyimide composite film. Figure 3(c) shows a similar tendency toward decreasing CTE of the composite film. With 30 wt% of talc b', slightly lower CTE compared to the same amount of the other talc was recognized. Moreover, with 45 wt% of talc b', f7 reaches CTE of 17 ppm/K which is

Fig. 4. IR spectra of polyimide composite films (f1, f3, and f6).

equal to that of copper. This trend is suitable for electronics application like flexible printed circuit. These improvements for rising T_g as well as lowering CTE may be explained by the stronger interaction between the polyimide and talc b' like increasing the viscosity of the solution of PAA-1/talc b' as described above.

Second, the mechanical film properties were evaluated by tensile test. Although the tensile strengths (σ_t s) of the composite films (f2-f7) were lower than that of the original PI-1 film (f1), those tensile moduli (λ_t s) were much greater than that of f1. It is noteworthy that 30 wt% talc b' (f6) reached the highest λ_t of 5.30 GPa, while f7 with 45 wt% talc b' went down to 3.03 GPa owing to film brittleness. A strong conjunction between PI-1 and talc b' is also suggested in tensile modulus.

Third, light transmittance of the films was measured as shown in Table 2. Although this measurement counts scattering light through the film, the all composite films (f1-f7) demonstrated a relatively good transmittance offering about 90 %.

IR spectra of the representative composite films were depicted in Figure 4. Characteristic absorption bands assignable to talc were recognized at 670, 1020, and 3677 cm⁻¹ from f3 and f6. The composite film involving 30 wt% non-baked talc b (f3) is almost identical to the original PI-1 film (f1) except additional signals originated from talc structure. However, the composite film including 30 wt% baked talc b' shows broad absorption around 3000-3600 cm⁻¹. This provably indicates incompleteness of imidization at the cure temperature. Hence talc b' acts unusual behaviors in terms of T_g of the composite film as well as viscosity of the dispersing solution, some strong interaction formed

between poly(amic acid) and thermally treated talc might prevent for complete imidization.

3.4. Morphology Observations by XRD and TEM

As expected that the size distribution of the talc might be changed during the process of baking talc and/or curing the composite film, XRD was conducted to investigate whether the morphological change could be happened. The results of XRD traces of talc **b** and **b'** are shown in Figure 5. However a small hump appearing at $2\theta=30.9^\circ$ was disappeared after the thermal treatment, three main signals assignable to talc layered structure was identical before and after the bake. No change of the talc lamella structure was also confirmed out of the composite film by comparing f3 and f6 (not shown).

TEM images depicted in Figure 6 suggest several points as follows: From Figure 6(a), 6(b), and 6(c), (i) similar morphologies were observed from f2 and f6, implying that the layered stacking structure could be mostly kept from both thermal treatment and film curing; (ii) deformation of talc lamella structure is seen owing to strong enough shear during the sample preparation; (iii) vertical-section of the composite films relatively shows an alignment of the talc parallel to the substrate; and (iv) in a comparison of Figure 6(b) and 6(d), anisotropic distribution of the talc in the PI film was observed due to the platelet like structure with a high aspect ratio.[14]

3.5. Characterization of the part of weight loss from talc

To clarify what components emerged out of the talc investigated for this study during the thermal treatment, TG-MS was carried out. As shown in Figure 7, both talc **a** and **b** indicated the same three distinctive peaks in the range of (I) 520-580 °C, (II) 620-730 °C, and (III) 850-900 °C. Each peak was then taken directly in mass spectroscopy and identified as both peaks (I) and (II) CO_2 ($m/z=44$),

Fig. 5. XRD traces for powder of talc **b** and talc **b'**.

and peak (III) H_2O ($m/z=18$). The volume of each emerged gas was correlated to the weight loss at the corresponding temperature range. Because talc has two equivalents of hydroxyl group in its general chemical formula, dehydration of talc is most likely to take place at the baking step. However, carbon dioxide was detected below the dehydration temperature originated from some impurities in talc.

Thus, the thermal treatment of talc is necessary

Fig. 6. TEM micrographs of the composite films: (a) vertical-section of f2 containing 30 wt % talc **a**; (b) vertical-section of f6 containing 30 wt % talc **b'**; (c) magnified image of Fig. 2(b); and (d) horizontal-section of f6.

Fig. 7. Dual TG-MS traces for talc (a) and (b) as a function of measuring time. The mass spectrum obtained from each peak I, II, and III in the mass chromatograms showed one m/z signal determined to be 44 for I, 44 for II, and 18 for III, respectively.

for decarboxylation from the original talc prior to addition in a solution of poly(amic acid), which leads the composite film to unusual thermal film properties. Identifying the impurities in the talc and resolving the mechanism of how that talc and its ingredient act to enhance the polyimide film properties are under investigation including exhaustive inspection with other type of polymers.

4. Conclusion

The polyimide composite film containing the thermally treated talc b' increased T_g significantly by +50 K at the high temperature above 300 °C relying on talc contents. This activation was only observed with certain thermally treated talc from which a few wt% of carbon dioxide was able to emerge. The baked talc was effective for the polyimide composite film in not only thermal stability but also tensile modulus up to 30 wt% loading while light transmittance was kept high as much as 90 %. No morphological change of the baked talc was observed according to XRD and TEM. From the results of TG-MS, it was found that decarboxylation was occurred from the talc around 500-700 °C lower than the temperature dehydration taken place (>850 °C). Decarboxylation before the addition of talc into poly(amic acid) varnish consequently played a roll of unprecedented highly jumping T_g of polyimide film.

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