

Preparation of Flexible Transparent Acryl/Alumina Nano-Hybrid Materials exhibiting Low Thermal Expansion Coefficient

Hideki Sugimoto, Chico Naruse, Yuta Takayanagi, Katsuhiro Inomata, Shogo Nobukawa, Eiji Nakanishi

Department of Life Science & Applied Chemistry, Graduate school of Engineering,

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555 Japan

TEL & FAX: +81-52-735-5270, E-mail: Sugimoto.hideki@nitech.ac.jp

Abstract: In this study, flexible transparent hybrid films with low thermal expansion coefficient were prepared by combination of alumina fillers and polymerizable/non-polymerizable surface modifiers carboxyl group. Four types of alumina fillers with different shape and size were used in this study, and could modify with surface modifiers containing carboxyl groups by electrostatic interaction and disperse homogeneously in resulting hybrid films regardless of the shape and size. So the hybrid films obtained showed highly transmittance around 90 %T, and it was considered, from atomic force microscopic analysis, alumina fillers were dispersed at near original filler size, without aggregation. Moreover, thermal mechanical analysis cleared that the use of pillar or fiber type filler is more effective to reduce CTE compared with plate type fillers, especially CTE of hybrid film prepared with fiber type filler was drastically decreased to 17 ppm/K, while the influence by the difference of filler shape/size was not observed on tensile properties, surface hardness. By use of fiber type alumina filler and combination of polymerizable surface modifier and non-polymerizable surface modifier which seems to interact with matrix, for optimizing of the crosslink density, it was possible to reduce CTE, while the good mechanical properties was kept. Finally, hybrid film indicating low CTE value as 19 ppm/K, high flexibility (windable against 0.4mm radius steel bar), and good tensile properties and surface hardness which were equal to or higher than those of matrix could prepared.

Keywords: Transparent, Flexible, Low coefficient of thermal expansion, Nano hybrid, Alumina,
Acrylic surface modifier

Introduction

Recently, polymer-inorganic hybrid materials which united features of the inorganics and features of the organic polymer are noticed in the possibility of achieving improved several properties and added functions. In particular, transparent polymer/nano-filler hybrid materials draw much attention in wide application range, and many reports regarding transparent nano-hybrid materials with significantly improved performance, such as high surface hardness, high tensile or bending properties, and controlled optical properties, have been published [1-8]. Recently, great attention has been paid on flexibility and thermal expansion coefficient (CTE) of polymer/nano-filler hybrid materials especially in optical applications [9-16]. The low-CTE feature is essential requirement property for flexible display material, to avoid generation of defects by gap of CTEs between flexible substrate and electrode because high temperature is applied (around 200°C) in the process of electrode deposition. In order to reduce CTE of hybrid materials, homogeneous dispersion of the low CTE nano-fillers to polymer is needed [12-17]. However, low compatibility between inorganic filler and polymer matrix may cause the phase separation, and it is difficult to satisfy both of high transparency and low CTE of resulting hybrid material in wide temperature range.

Bae et al. investigated about transparent flexible polyimide/silica hybrid materials, and finally obtained low CTE hybrid materials by control of molecular weight and conditions through sol-gel reaction of trimethoxysilane-terminated oligomeric polyamic acid [16].

Cheng et al. also reported that high performance hybrid materials with high glass transition temperature and low CTE can prepared by sol-gel reaction between polyhydroxyimide and metal alkoxide, and hydroxyl groups in polymer repeating units play important role for homogeneous dispersion of inorganic component [17].

As mentioned above, though the utilization of the polyimide with excellent thermal property is useful for the development of the low CTE material, high temperature is applied to form imide bond and optimization of the manufacturing process and molecular design are necessary in order to avoid the yellowing or deteriorate of property of films by water generated from the cyclization reaction at high temperature.

As is well known, polyacrylates indicate high transparency and good mechanical properties. Also, polyacrylates have some advantage such as low process temperature, heat- and photo-curable, and fast curing speed, and used extensively in the field of coating, painting and so on [18-23]. However, general polyacrylates exhibit poor thermal property (show large coefficient of thermal expansion), and therefore, the application range has been limited. If the transparent and flexible polyacrylate based hybrid materials with excellent thermal property can be prepared, it is expected to apply to flexible display substrate and so on.

In previous study, transparent hybrid materials with low CTE were prepared by combination of

alumina filler which can interact with the organic compounds with negative charge [24-26] and acrylate with carboxyl group as surface modifier [27]. The hybrid materials form dense cross-linked structure and show low CTE by curing of acrylate double bond introduced into the alumina surface, and so they have room of improvement on the flexibility.

The aim of this study is to prepare polyacrylate based transparent flexible hybrid materials with low CTE, therefore the influence of shape/size of alumina filler, combination of non-polymerizable surface modifiers on physical properties such as flexibility and CTE of resulting hybrid materials was examined. The four types of alumina nano-fillers were treated by polymerizable and non-polymerizable surface modifiers with negative charge at various ratio. Then casting with comonomer and UV irradiation were carried out to get hybrid films. Transparency, CTE and flexibility of the resulting films were evaluated by VIS measurement, thermal mechanical analysis (TMA). The flexibility of films was compared from the diameter of windable steel bar without fracture of the films.

Experimental

Materials

Four types of alumina nano-fillers were obtained from Kawaken Fine Chemical Co., Ltd., and were used as received. The size of each alumina nano-filler is 10 nm (diameter) ×50 nm (length) (pillar type, denote filler A), 20 nm (length) ×20 nm (width) ×5 nm (thickness) (plate type, denote filler B), 30 nm (length) ×10 nm (width) ×5 nm (thickness) (plate type, denote filler C), and 4 nm (diameter) ×1400 nm (length) (fiber type, denote filler D).

Succinic acid tri-(2-acryloyloxy-ethyl) ester (TOAGOSEI Co., Ltd., product name: M510, mixture with pentaerythritol tetra-acrylate (minor component) at molar ratio of 65:35 in ¹H-NMR, denoted as M3) was employed as polymerizable surface modifier because this surface modifier was superior in dispersion of alumina filler and could decrease CTE of resulting hybrid material effectively in previous study [27].

2, 2-bis[4-(acryloxy diethyl) phenyl] propane (Shin-Nakamura Chemical Co., Ltd, product name: A-BPE4) was used as comonomer (matrix). Molecular structures of polymerizable surface modifier and comonomer were shown in Figure 1.

Phthalic anhydride (Nacalai tesque, Inc.), succinic anhydride (Nacalai tesque, Inc.) and 1-heptanol were used to make surface modifier without acrylate group

1-hydroxy cyclohexyl phenyl ketone (product name: Irg.184) as photo initiator was obtained from BASF Japan Ltd.

All other solvents used in this study were purchased from Kanto Chemical Co., Ltd. without further purification.

Synthesis of non-polymerizable surface modifier

Two kinds of surface modifiers without acryl group were synthesized by additional reaction between alcohol and acid anhydride. A certain amount of 1-heptanol and 1.5 mole equivalent of phthalic anhydride or succinic anhydride against 1-heptanol were charged into three-neck flask equipped stirring motor and condenser tube and reacted at 140 °C. After 12 hours, the reaction system was cooled and left to stand at 0 °C for a day to precipitate unreacted acid hydride. Then unreacted acid anhydride was removed by centrifugation, and objective compound was obtained by evaporation of supernatant. From ¹H-NMR measurement, it was confirmed that objective compounds were obtained (see Figure 2). The non-polymerizable surface modifier synthesized from phthalic anhydride is denoted as C7p, and from succinic anhydride is denoted as C7s.

Preparation of surface modified alumina compounds

The surface modifiers were dissolved into acetone at 50 wt.%, and then this acetone solution was added to alumina slurry with stirring at room temperature. After 24 hrs, precipitate generated during the modification was recovered by centrifugation and washed twice with ion-exchange water. The precipitates were used as surface modified alumina after freeze and vacuum drying. The feed molar of COOH in surface modifiers for 1g of alumina filler was fixed at 3 mmol.

Preparation of alumina hybrid films

Each surface modified alumina filler modified at fixed amount or mix ratio was added into mixture of *N, N*-dimethyl formamide and A-BPE4 as comonomer (matrix) at 30 wt.% of alumina content, and dispersed homogeneously by stirring and ultra-sonication. Subsequently, 3 wt.% of Irg.184 as photo-initiator against total amount of acrylate component was added to the dispersion liquid. The dispersion liquid was applied on PET film by blade coater and drying on hot plate at 80 °C for 10 min. After drying, UV cure was carried out with 150W metal halide lamp to get acryl/alumina hybrid film. The thickness of hybrid films was adjusted around 50 μm.

Measurements

Zeta potential measurements (HORIBA model SZ-100) were estimated with acryl cell equipped carbon electrode (electro spacing: 6 mm) to confirm absorption of surface modifier to alumina. The alumina filler modified with each modifier was dispersed at 0.1 wt.% in aqueous medium adjusted same pH of initial slurry (pH 3.7) for the measurements.

¹H-NMR spectra were measured with BRUKER model ADVANCE200 FT-NMR spectrometer to confirm absorption and composition of surface modifiers on surface modified alumina filler and characterization of non-polymerizable surface modifier. Chemical shifts in ¹H-NMR spectra were reported as δ values (ppm) relative to tetramethylsilane (TMS) as an internal standard and deuterated dimethyl sulfoxide (DMSO-d₆) and chloroform (CF-d₃) were used for the measurement.

To evaluate inorganic content of surface modified alumina, thermogravimetric analysis (TGA) was carried out by Seiko Instrument model TG 30 in the region of 30-600 °C with platinum pan. Alumina powder was used as a reference material and the programming rate was 10 °C/min.

Transmittance of visible light for obtained hybrid materials was measured with UV/Vis spectrometer (Hitachi model U-3310 spectrometer, measurement region: 400-800 nm) to evaluate transparency of the hybrid materials.

Coefficients of linear thermal expansion (CTE) of the prepared hybrid films were determined by thermomechanical analyzer (Seiko Instruments Inc., model TMA/SS 6100). The dimension of the test specimen was 25 mm × 4 mm (length × width). Scanning range was set from 30 to 200 °C at a heating rate of 5 °C/min and at a fixed load of 10 mN under nitrogen atmosphere. The value in range from 50 °C to 200 °C in 2nd run was employed as CTE.

To evaluate the surface hardness of hybrid films, pencil hardness was measured with model KT-VF2391 pencil hardness tester (COTEC Corporation) in reference to JIS K5600-5-4 at room temperature.

Flexibility of hybrid films was estimated by wind roll test with steel bar have a diameter in the range from 0.4 mm to 7 mm, and the flexibility of the films was compared from the diameter of windable steel bar without fracture of the films.

The tensile test of the prepared hybrid films was carried out using a tensilon mechanical tester (ORIENTEC Co., Ltd., model RTC-1250A) at 25±1 °C. The specimen size and test speed were 60 mm × 5 mm (length × width) and 0.5 mm/min, respectively.

Transmission electron microscopic (TEM) measurement was carried out by JEOL model JEM-1200EX or JEM-2000FX at accelerating voltages of 200 kV to evaluate dispersion state of alumina in hybrid films. Measurement samples were cut down in thickness direction of films by an ultramicrotome in 80 nm thickness.

Dynamic mechanical analysis (DMA) measurements on the hybrid films were carried out using a Seiko model DMS-200 viscoelastometer from 25 to 200 °C at 1 Hz, at a heating rate of 2 °C/min.

Results and Discussion

Characterization of organically modified alumina fillers

Table 1 summarizes the feed compositions in preparation of surface modified alumina, inorganic content and zeta potential change after modification. Inorganic content after surface modification measured by TGA gave close agreement with theoretical value for each alumina filler, and it was confirmed that the zeta potential was decreased by treatment with surface modifier having COOH group.

Figure 3 illustrates ¹H-NMR spectra of M3 and alumina filler A modified with M3. From ¹H-NMR measurements, it was confirmed that each peak in surface modified alumina filler A agreed with

those of raw M3 except peak around 2.7ppm. The peak around 2.7 ppm attributed to ethylene group neighboring free carboxyl group in M3 varied to broad peak and shift to lower field [28]. Considering both the lowering of the zeta-potential after surface modification and peak shift of the carboxyl group in M3, the carboxyl group of M3 seems to become carboxylate ion and interact electrostatically with Al-OH group on alumina surface.

Transparency of alumina hybrid films

The transmittance at 600 nm and appearance of obtained hybrid films with each alumina filler modified by M3 were summarized in Table 2. The resulting hybrid films indicated high transparency around 90 %T regardless of type of alumina filler. The surface density of surface modifier on filler D decrease due to its large surface area in comparison with those of other fillers. It has been confirmed that tetra acrylate containing in M3 surface modifier was not removed during the operation of surface treatment, and coexisted with alumina after surface treatment [27]. So it was considered that the tetra acrylate which coexisting with filler promotes dispersion of filler D, and so resulting hybrid film could maintain high transparency in spite of lower surface density of surface modifier.

Figure 4 exhibits TEM images of each hybrid film. It was confirmed that each organically modified alumina filler was dispersing homogeneously in the resulting hybrid film. In addition, the differences in particle size and filler shape were recognized, and it seems to be dispersed at near original filler size, without aggregation.

Gårdebjer et al. studied about dispersibility of surface modified cellulose nano crystal (CNC) to several organic solvents by using Hansen solubility parameters and they reported that the results was useful to predict dispersion of modified CNC in polymer films [29]. Hansen solubility parameter consisting of three parts (dispersion, polar, hydrogen bonding interaction), they also mentioned that these interaction parameters between modified CNC and solvent/polymer is important, and it was desirable that these parameters should be as close as possible in order to obtain better dispersibility.

The Hansen solubility parameters of M3 used for surface modification of alumina filler and A-BPE4 used as comonomer were calculated as δ_{total} 22.0 (MPa)^{1/2}, δ_d 20.6 (MPa)^{1/2}, δ_p 3.5 (MPa)^{1/2}, δ_h 6.7 (MPa)^{1/2} for M3 and δ_{total} 21.3 (MPa)^{1/2}, δ_d 20.3 (MPa)^{1/2}, δ_p 2.5 (MPa)^{1/2}, δ_h 5.9 (MPa)^{1/2} for A-BPE4, M3 and ABPE-4 showed very close values (δ_{total} , δ_d , δ_p , δ_h correspond to Hansen solubility parameter and dispersion, polar, hydrogen bonding interaction parameters, respectively) [29-31]. Though the change of the entropy seems to also affect the transparency, several researchers reported that entropy change in mixing of nano-filler having high molecular weight and rigidity became extremely small [32, 33].

Moreover, Liu et al. described that, in their article about transparent superhigh ZnO content polymer nanohybrid film with butyl methacrylate and reactive ZnO nanoparticles, highly transparent nanohybrid film could be prepared by bulk polymerization because the aggregation of ZnO nanoparticles was avoided by formation of cross-linking structure between nanoparticle surface and polymer matrix,

increase of the interaction force between nanoparticles and matrix was significant way to prevent the aggregation of nanoparticles in nanohybrid preparation [34].

Similarly, in our system, it was considered that aggregation of alumina filler was suppressed because the cross-linking structure was formed by polymerizable groups introduced on alumina filler, so the change of the entropy during the polymerization seems to be small, not affected for the transparency.

These pretty close Hansen solubility parameter between surface modifier and comonomer resulted in high affinity of alumina filler modified with M3 and polymer matrix and high dispersibility of alumina filler observed in results of TEM measurements, so greatly contributed to maintain high transparency in conjunction with formation of cross-linking structure.

CTE of alumina hybrid films

Table 3 indicates the CTE value of each hybrid film obtained TMA analysis. The CTE value was decreased drastically by addition of surface modified alumina filler in comparison with poly(A-BPE4) as matrix.

Rashid and co-worker studied about thermal properties of epoxy composite with alumina treated 3-aminopropyl triethylsilane. They reported that the CTE value was significant decreased by improving adhesion of alumina/epoxy interaction with silane coupling agent and the change of CTE remained from 69 ppm/°C (neat epoxy) to 22 ppm/°C at 50 wt.% loading (68% decreased) [35].

Zhou et al. investigated about filler size effect on physical properties of alumina filled silicone composite, and remarked that composite using smaller fillers indicated lower CTE because smaller fillers have higher specific surface could form more physical cross-linking points and strong interaction between filler and matrix, and the CTE of prepared composite material was changed from 75 ppm/K to 53 ppm/K at 55 vol.% of alumina content [36].

In this study, the degree of the CTE reduction depended on the type of used filler, the hybrid film using filler D indicated lowest CTE in prepared hybrid films, 91% reduction from CTE of ABPE-4 as matrix. In the meanwhile, the smallest decreasing rate was 64% with filler C. This difference on CTE was caused from the difference of surface area of used alumina fillers. So, the hybrid film prepared with alumina filler D having huge interface between organic and inorganic components showed low CTE in order to limit thermal motion of polymer matrix strongly besides the effect of cross-linking formed polymerization group introduced on the alumina filler surface [27, 37]. And this method used in this study seems to have an advantage to reduce CTE effectively at comparatively low filler rate.

Figure 5 illustrates temperature dependence of $\tan\delta$ measured by DMA for each hybrid films. As for hybrid films using surface modified alumina fillers, in comparison with poly(A-BPE4), the peak temperature of $\tan\delta$ shifted to high temperature side, and the peak intensity of $\tan\delta$ also decreased.

Especially, the peak shift and lowering peak intensity of $\tan\delta$ were remarkable on the hybrid film using alumina filler D, the $\tan\delta$ was shifted over 140 °C and the peak intensity became below 0.1.

This change of $\tan\delta$ seems to derive from the filler shape, because the amount of surface modifier for each alumina filler is almost same, thermal motion of polymer matrix was prohibited strongly by interaction with filler D having wider interface. So these change of $\tan\delta$ seems to support the consideration in CTE decrease.

Mechanical properties of alumina hybrid films

Table 3 also summaries tensile properties, pencil hardness, and flexibility evaluated by wind roll test with steel bar. Regardless of type of alumina filler, Young's modulus, tensile strength at break, and pencil hardness of hybrid films were increased by addition of organically modified alumina. While elongation at break and flexibility estimated by wind roll test were decreased by addition of surface modified alumina fillers. Generally, it is known that addition of inorganic filler such as silica, alumina, and zirconia into polymer matrix lead to a better mechanical performance (increase of modulus, surface hardness and so on) [38-40]. As for the hybrid films prepared in this study, the elastic modulus and surface hardness were improved in the reflection of high stiffness and hardness of inorganic filler, but the difference by the shape of the inorganic filler did not observe.

Hikasa et al. investigated about influence of shape and size of powdered cellulose on mechanical properties of polypropylene based composite, and reported that the elastic modulus for PP/cellulose composite prepared with high aspect filler did not be high as expected [41]. They considered that, as the reason, slight improvement on elastic modulus originated from the dispersion state of the filler existing in resulting composite material, and the filler existing in bent state couldn't exhibit effective stiffening effect, since it can be transformed in small force in comparison with the filler existing extension state (the change of filler state from the bending to the extension will be prior generated).

As can be seen from TEM images shown in Fig. 4, the alumina fillers were dispersing isotropically in the hybrid film without orientation of fillers in a certain direction. Moreover, as filler D, fillers existing in bent state in the hybrid film were found. For these reason, it was considered that the effect of filler shape was decreased, and the difference in elastic modulus did not observed.

On elongation and flexibility, these properties were greatly lowered, in comparison with poly(A-PBE4) as the matrix, since dense cross-linkages were formed by the polymeric surface preparation agent.

The effect of the non-polymerizable surface modifiers on physical properties of the hybrid film.

As described above, 30_M3_D exhibited very lower CTE like 17 ppm/K as the result of homogeneous dispersion of alumina filler with high aspect ratio which was treated by polymerizable surface modifier, but it was difficult to keep low CTE while high flexibility because the cross-linking density was high.

Therefore, two kinds of non-polymerizable surface modifiers, C7p and C7s, were used together with

M3 to control cross-linking density of hybrid films and the effect on physical properties were investigated to combine low CTE and flexibility.

Table 4 lists feed ratios of surface modifiers and composition ratios of M3 to C7p and M3 to C7s after surface modification. The composition ratios were determined by integral ratio around 6.0-6.5 ppm attributed to protons at C=C double bond in M3, around 7.5-7.7 ppm attributed to protons at benzene ring in C7p, and around 4.1-4.3 ppm attributed to protons at methylene adjoining ester bond for C7s in ¹H-NMR spectra. Regardless of the mixture ratio of modifiers, it was confirmed that the ratios of the surface modifiers which adsorbed to the alumina surface were almost equal to the addition ratios.

Transmittance of hybrid films prepared by combination of M3 and non-polymerizable surface modifier was summarized in Table 4. As can be seen from the Table, the usage of non-polymerizable surface modifiers did not affect transparency of resulting hybrid films.

Figure 6 shows TEM image of 30_M3/C7p_9/1_D. As can confirm from TEM image, the fillers modified by combination of M3 and non-polymerizable surface modifier kept high dispersibility in hybrid film. The Hansen solubility parameters were slightly varied with composition ratio, δ_{total} 21.7-21.1 (MPa)^{1/2}, δ_{d} 20.3-19.7 (MPa)^{1/2}, δ_{p} 3.5-3.4 (MPa)^{1/2}, δ_{h} 6.6-6.5 (MPa)^{1/2} for M3/C7s and δ_{total} 21.7-21.3(MPa)^{1/2}, δ_{d} 20.4-19.9 (MPa)^{1/2}, δ_{p} 3.4-3.3 (MPa)^{1/2}, δ_{h} 6.6-6.4 (MPa)^{1/2} for M3/C7p, but these values were close to those of A-BPE4 as matrix nonetheless. The affinity change of modified alumina filler to matrix seems to be very small in preparation condition used in this study, therefore the resulting hybrid films maintained high transparency.

The CTE values estimated TMA measurements are also shown in Table 4. The CTE value was increased, since the cross-linking density was lowered by the introduction of non-polymerizable surface modifier, as the ratio increased. However, in comparison with hybrid films prepared with C7s as non-polymerizable surface modifier, the increase in CTE was able to be suppressed by using C7p surface modifier, and 30_M3/C7p_9/1_D hybrid film kept low CTE around 20ppm/K.

Figure 7 depicts temperature dependence of $\tan\delta$ for 30_M3/C7p_9/1_D and 30_M3/C7s_9/1_D hybrid films together with that of 30_M3_D hybrid film. Though the peak temperature of $\tan\delta$ shifted to cold side by the lowering of cross-linking density due to the use of non-polymerizable surface modifier, it was confirmed that the increase of the peak intensity was held in hybrid film prepared with C7p compared to the film with C7s. This result suggests that the thermal mobility of polymer was suppressed by the interaction due to benzene rings between the matrix and C7p, even if crosslink density lowered, and it seems to support that the increase in CTE was kept low.

Table 5 shows mechanical properties, flexibility evaluated by wind roll test, and pencil hardness of hybrid films prepared with M3 and C7p surface modifiers. The lowering of the crosslink density by use of non-polymerizable surface modifiers resulted in the increase of strain and flexibility and the lowering of elastic modulus and surface hardness. However, it was also confirmed that the mechanical properties of hybrid films prepared with C7p were the same or more than that of poly(A-BPE4) as the

matrix polymer.

Conclusions

As described above, the influence of shape/size of alumina filler, combination of non-polymerizable surface modifiers on physical properties such as flexibility and CTE of resulting hybrid films was examined.

All alumina fillers used in this study could modify with surface modifiers containing carboxyl group by electrostatic interaction at desired composition ratios, and this surface modification method was useful to achieve homogeneous dispersion of alumina filler. Consequently, high transparency of hybrid films could be maintained.

As for the influence of shape/size of alumina filler on CTE, it was confirmed that the use of pillar or fiber type filler is more effective to reduce CTE compared with plate type fillers, especially CTE of hybrid film prepared with filler D was drastically decreased to 17 ppm/K.

By use of filler D and combination of M3 and C7p, which seems to interact with matrix, for optimizing of the crosslink density, it was possible to reduce CTE, while the good mechanical properties is kept. Finally, hybrid film, 30_M3/C7p_9/1_D, indicate low CTE value as 19 ppm/K, high flexibility (windable against 0.4mm radius steel bar), and good tensile properties and surface hardness which are equal to or higher than those of matrix.

These transparency hybrid films with low CTEs are expected to contribute to the development of new display devices.

References

1. Kim WS, Jeong YC, Park JK (2005), *Appl Phys Lett* 87:012106
2. Kwon YK, Han JK, Lee JM, Ko YS, Oh JH, Lee HS, Lee EH (2008) *J Mater Chem* 18:579-585
3. De S, Lyons PE, Sorel S, Doherty EM, King PJ, Blau WJ, Nirmalraj PN, Boland JJ, Scardaci J, Joimel J, Coleman JN (2009), *ACS Nano* 3:714-720
4. Sangerman M, Messori M (2010) *Macromol Mater Eng* 295:603-612
5. Liu HT, Zeng XF, Zhao H, Chen JF (2012) *Ind Eng Chem Res* 51:6753-6759
6. Kim SM, Song EB, Lee S, Zhu J, Seo DH, Mecklenburg M, Seo S, Wang K (2012) *ACS Nano* 6:7879-7884
7. Huang J, Zhu H, Chen Y, Preston C, Rohrbach K, Cumings J, Hu L, *ACS Nano* (2013) 7:2106-2113
8. Mahmood WAK, Khan MMR, Azarian MH (2013) *J Non-Crystalline Solid* 378:152-157
9. Sullivan LM, Lukehart CM (2005) *Chem Mater* 17:2136-2141
10. Koerner H, Misra D, Tan A, Drummy L, Mirau P, Vaia R (2006) *Polymer* 47:3426-3435
11. Zhi C, Bando Y, Terao T, Tang C, Kuwahara H, Golberg D (2009) *Adv Funct Mater* 19:1857-1862

12. Sugimoto H, Nunome K, Daimatsu K, Nakanishi E, Inomata K (2010) *Colloid Polym Sci* 288:1131-1138
13. DeSarkar M, Senthilkumar P, Franklin S, Chatterjee G (2012) *J Appl Polym Sci* 124:215-226
14. Jung Y, Byun S, Park S, Lee H (2014) *ACS Appl Mater Interface* 6:6054-6061
15. Kim SK, Wang X, Ando S, Wang X (2015) *Eur Polym J* 64:206-214
16. Bae WJ, Kovalev MK, Kalinina F, Kim M, Cho C (2016) *Polymer* 105:124-132
17. Cheng SW, Huang TT, Tsai CL, Liou GS (2017) *J Mater Chem C* 5:8444-8453
18. Yilmaz O (2014) *Prog Org Coat* 77:110-117
19. Wu J, Li P, Ma X, Liang Q, Yuan T, Ma G (2015) *J Appl Polym Sci* 132:42756
20. Bentio JG, Castillo E, Caldito JFC (2015) *Phys Chem Chem Phys* 17:18495-18500
21. Thomas P, Dakshayini BS, Kushwaha HS, Vaish R (2015) *J Adv Dielect* 5:1550018
22. Soumya S, Sheemol VN, Amba P, Mohamed AP, Ananthakumar S (2018) *Solar Energy Materials and Solar Cells* 174:554-565
23. Shen J, Hu Y, Li LX, Sun LW, Kan CY (2018) *J Coat Technol Res* 15:165-173
24. C. P. Lin CP, S. B. Wen SB (2002) *J Am Ceram Soc* 85:1467-1472
25. Tanada S, Kabayama M, Kawasaki N, Sakiyama T, Nakamura T, Araki M, Tamura T (2003) *J Colloid and Interface Science* 257:135-140
26. Ong BC, Leong YK (2012) *THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING* 90, 1484-1493
27. Sugimoto H, Imamura K, Sakami K, Inomata K, Nakanishi E (2015) *SEN'I GAKKAISHI* 71:333-338
28. Claudio ES, Horst MA, Forde CE, Stern CL, Zart MK, Godwin HA (2000) *Inorg Chem* 39:1391-1397
29. Gårdebjer S, Andersson M, Engström J, Restorp P, Larsson A (2016) *Polym. Chem.* 7:1756-1764
30. van Krevelen DW, Hoftyzer PJ (1976) *Properties of Polymers, their estimation and correlation with chemical structure*, 2nd edn, Elsevier, Amsterdam
31. van Krevelen DW (1990) *Properties of Polymers, their correlation with chemical structure; their numerical estimation and prediction from additive group contributions*, 3rd edn, Elsevier, Amsterdam
32. Vaia RA, Giannelis EP (1997) *Macromolecules* 30:7990-7999
33. Bergin SD, Nicolosi V, Streich PV, Giordani S, Sun Z, Windle AH, Ryan P, Niraj NP, Wang ZTT, Carpenter L, Blau WJ, Boland JJ, Hamilton JP, Coleman JN (2008) *Adv. Mater.* 20:1876-1881
34. Liu HT, Zeng XF, Zhao H, Chen JF (2012) *Ind. Eng. Chem. Res.* 51:6753-6759
35. Rashid ESA, Rasyid MFA, Akil HM, Ariffin K, Kool CC (2011) *Proc. IMechE. Part L: J. Materials: Design and Applications* 225:160-169
36. Zhou W, Yu D, Wang C, An Q, Qi S (2008) *Polymer Engineering and Science* 48:1381-1388
37. Guo H, Minus ML, Jagannathan S, Kumar S (2010) *ACS Appl Mater Interfaces* 2:1331-1342
38. Qu X, Guan T, Liu G, She Q, Zhang L (2005) *J Appl Polym Sci* 97:348-357

39. Sugimoto H, Daimatsu K, Nakanishi E, Ogasawara Y, Yasumura T, Inomata K (2006) *Polymer* 47:3754-3759
40. Wu SY, Huang YL, Ma CCM, Yuuen SM, Teng CC, Yang SY, Twu CH (2012) *Polym Int* 61:1084-1093
41. Hikasa S, Fujiwara K (2013) *Seikei-Kakou* 25:103-107

Table 1 Surface modification condition of alumina fillers, inorganic content and zeta potential change after modification

Filler type	Feed molar of COOH in surface modifier	Inorganic content		Zata potential change (mV)
		Theoretical (wt %)	Measured* (wt %)	
A			35.4	71.0→39.9
B	3 mmol/1g of	36.2	36.8	69.0→43.6
C	alumina filler		36.4	69.0→43.6
D			35.5	69.5→38.2

* Determined by TGA

Table 2 Transmittance at 600 nm and appearance of prepared hybrid films

Sample name	Transmittance at 600 nm (%T)
30_M3_A	90
30_M3_B	90
30_M3_C	90
30_M3_D	90
Poly(A-BPE4)	90

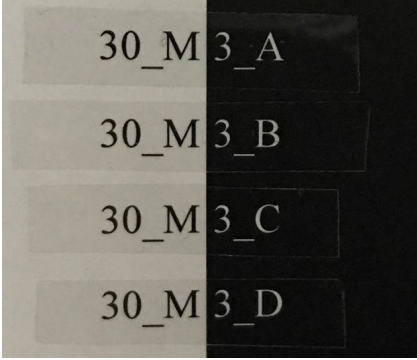


Table 3 Physical properties of prepared hybrid films and matrix polymer

Sample Name	30_M3_A	30_M3_B	30_M3_C	30_M3_D	Poly(A-BPE4)
CTE (ppm/K)	42	54	69	17	193
Tensile modulus (GPa)	4.0	4.0	4.1	4.2	1.5
Tensile strength (MPa)	35	37	30	38	32
Strain (%)	1.2	1.2	1.0	1.3	4.0
Pensile hardness	4H	4H	4H	4H	B
Windable radius (mm)	1.5	1.5	1.5	1.3	0.3

Table 4 Compositions of M3 and non-polymerizable surface modifiers for alumina filler D, transmittance and CTE of resulting hybrid films

Sample code	M3/C7s (mol/mol)		Transmittance at 600 nm (%T)	CTE (ppm/K)
	Feed ratio	Composition ratio*		
30_M3_D	100/0	100/0	90	17
30_M3/C7s_9/1_D	90/10	91/9	89	23
30_M3/C7s_7/3_D	70/30	65/35	89	35
30_M3/C7p_9/1_D	90/10	87/13	89	19
30_M3/C7p_7/3_D	70/30	74/26	89	30

* Determined by ¹H-NMR

Table 5 Physical properties of hybrid films prepared with M3 and C7p surface modifiers

Sample Name	30_M3/C7p_9/1_D	30_M3/C7p_7/3_D	30_M3_D	Poly(A-BPE4)
Tensile modulus (GPa)	2.8	2.0	4.2	1.5
Tensile strength (MPa)	39	39	38	32
Strain (%)	2.8	3.1	1.3	4.0
Pencil hardness	2H	H	4H	B
Windable radius (mm)	0.3	0.3	1.3	0.3

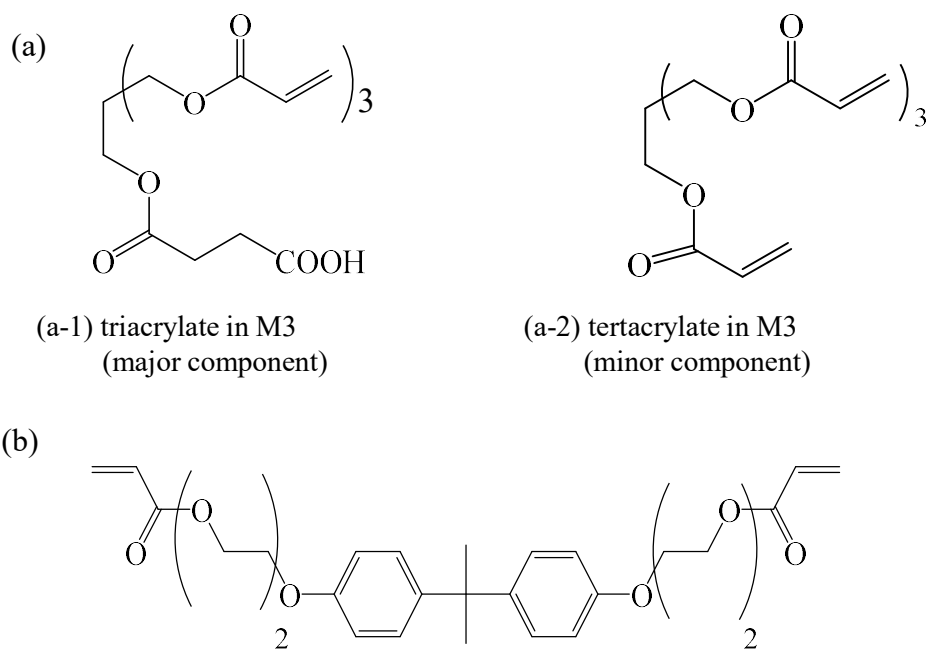


Figure 1. Molecular structures of polymerizable surface modifier and comonomer A-BPE4

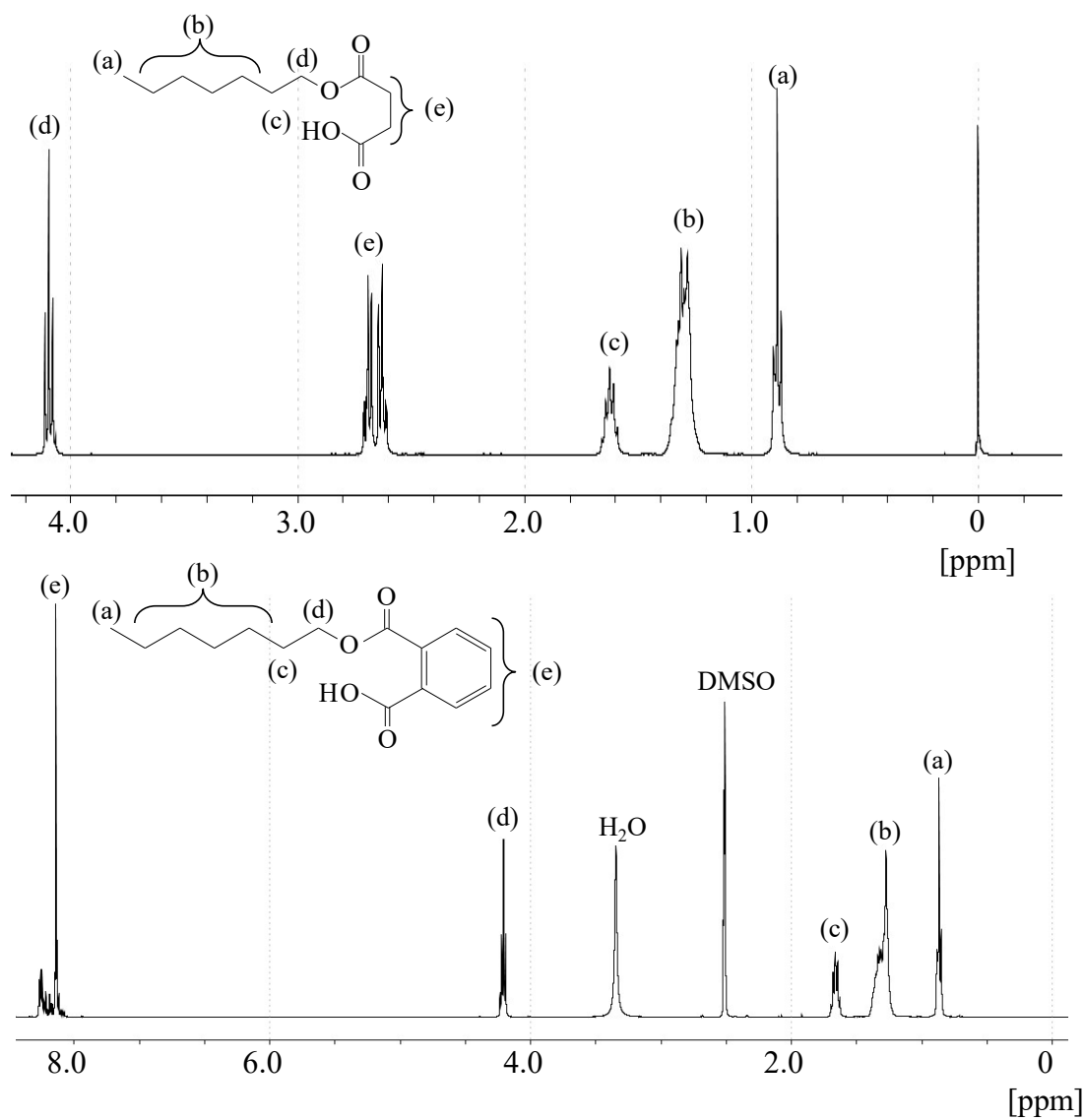


Figure 2. $^1\text{H-NMR}$ spectra of non-polymerizable surface modifiers, top: synthesized from succinic anhydride (C7s), bottom: from phthalic anhydride (C7p)

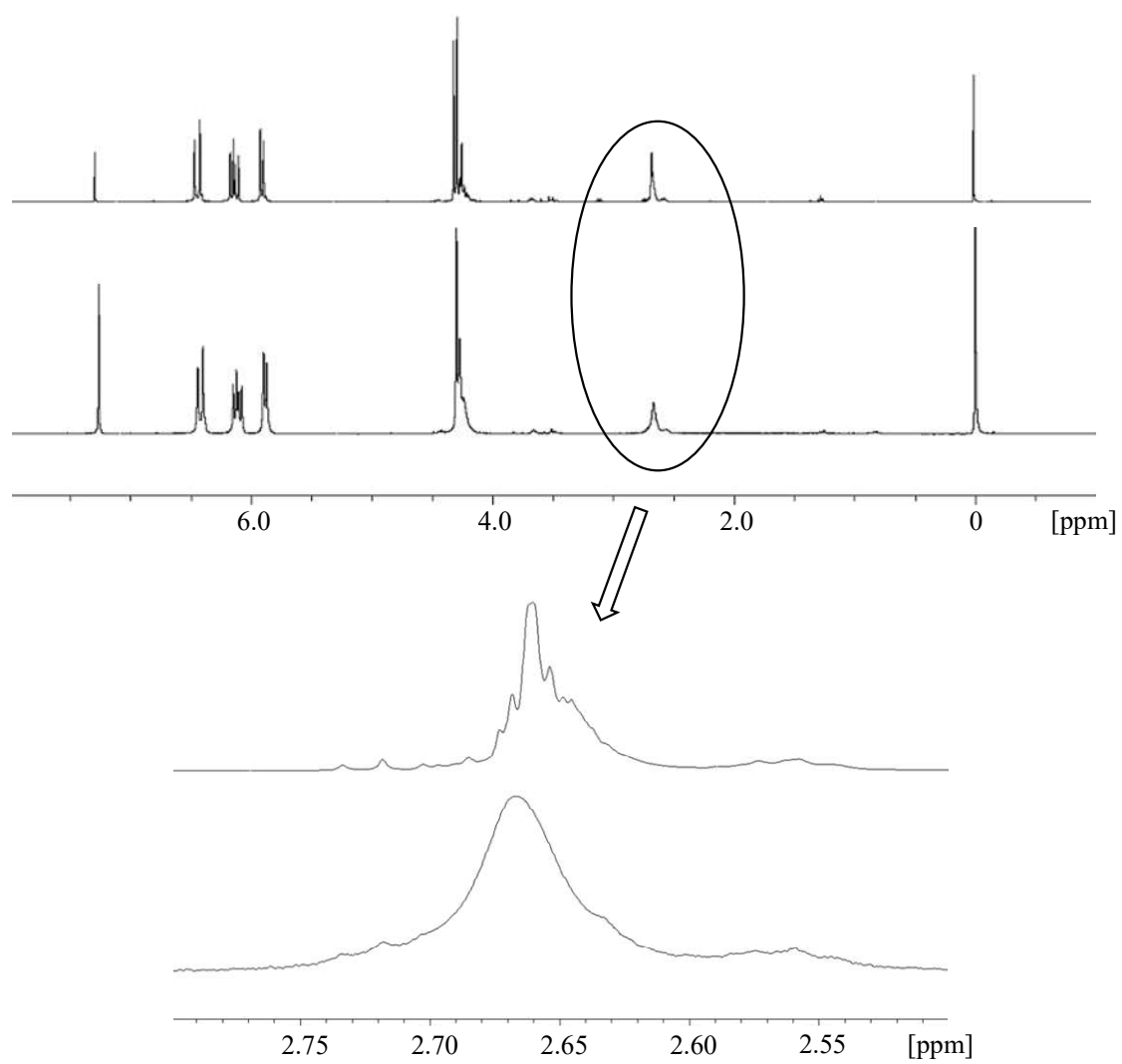


Figure 3. $^1\text{H-NMR}$ spectra of M3 and alumina filler A modified with M3

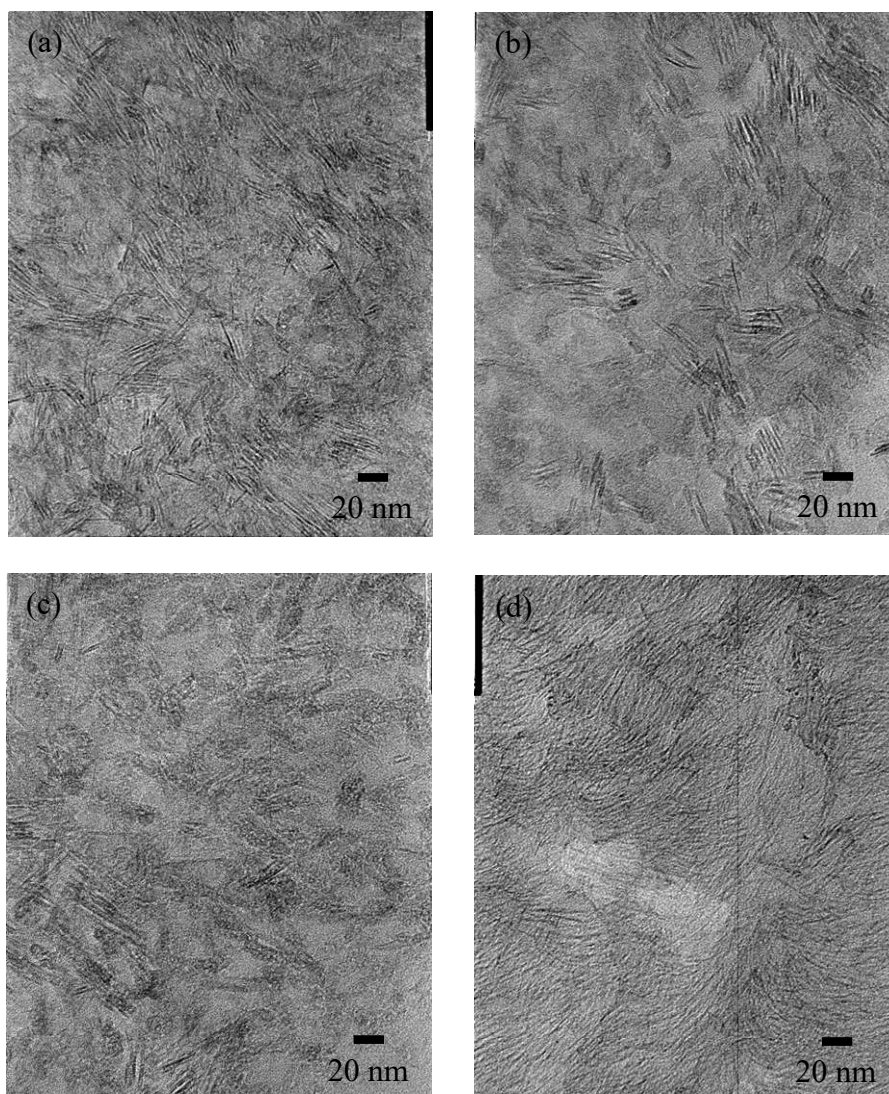


Figure 4. TEM images of prepared hybrid films, (a) 30_M3_A, (b) 30_M3_B, (c) 30_M3_C, and (d) 30_M3_D (scale bar = 20 nm)

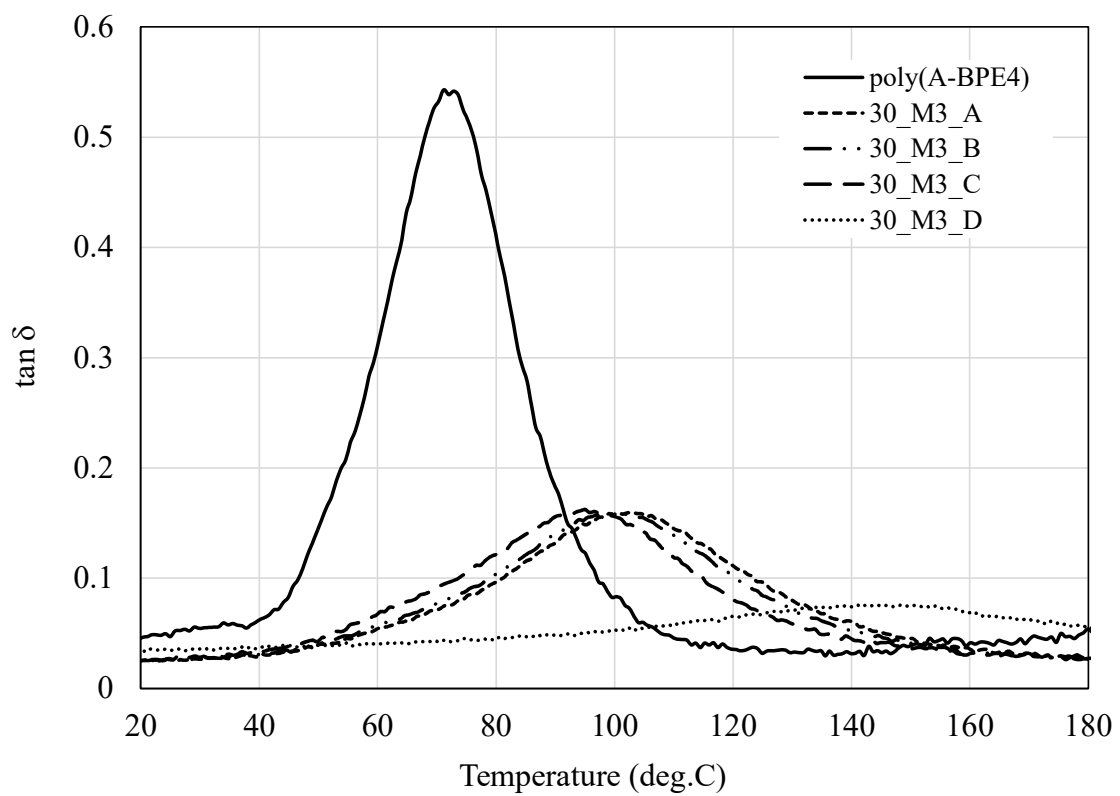


Figure 5. Temperature dependence of $\tan \delta$ for prepared hybrid films

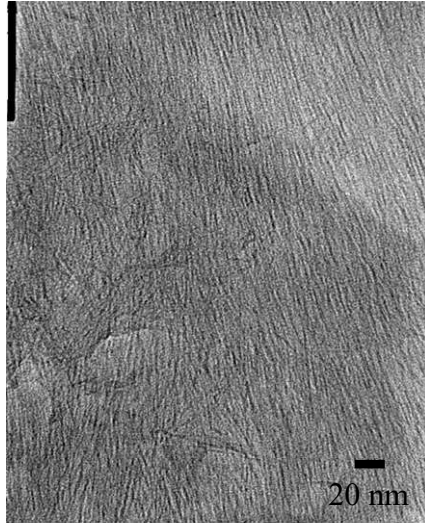


Figure 6. TEM image of 30_M3/C7p_9/1_D hybrid film (scale bar = 20 nm)

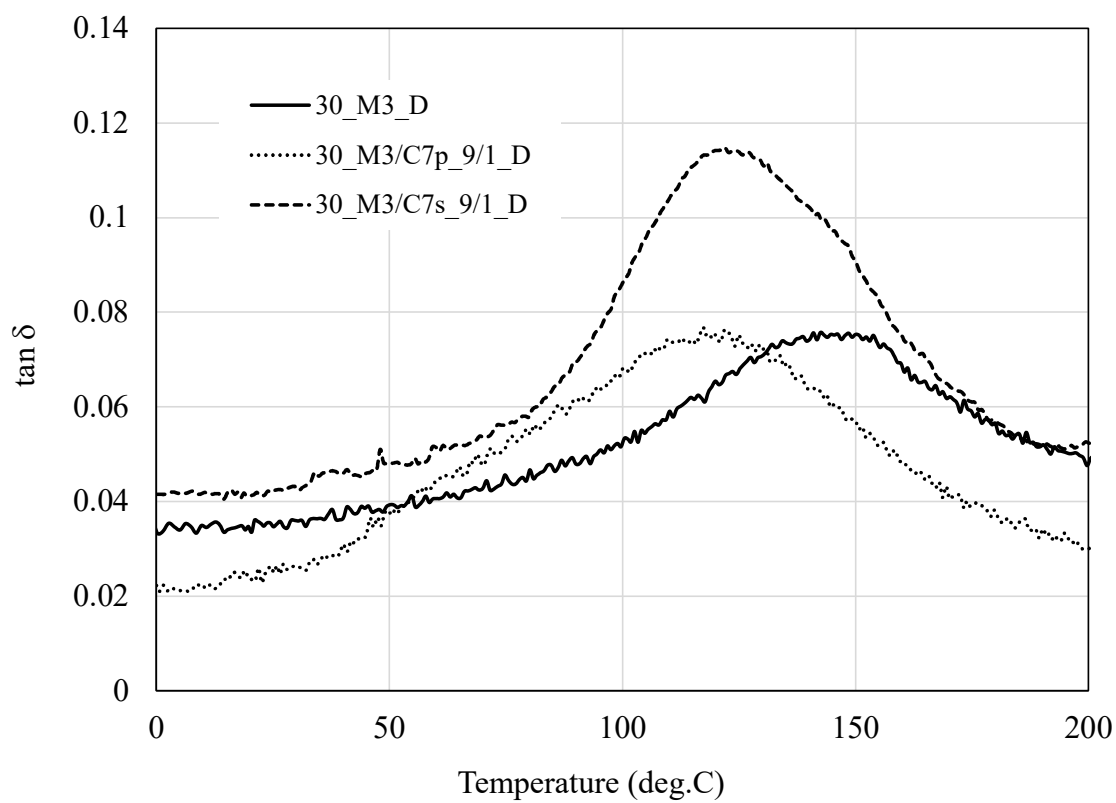


Figure 7. Temperature dependence of $\tan \delta$ for 30_M3/C7p_9/1_D and 30_M3/C7s_9/1_D hybrid films