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Study on acrylic resin/titania organic–inorganic hybrid materials prepared by the sol–gel process

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Abstract

Acrylic resin/titania organic–inorganic hybrid materials were prepared by the two approaches. One approach (BL method) was blending titania produced by the sol–gel process with synthesized acrylic resins containing various content of acrylic acid (AA). Another approach (IS method) was the in situ polymerization of acrylic monomers in synthesized titania sols. The structure and mechanical, thermal and optical properties of the hybrid films were investigated by small angle X-ray scattering (SAXS), atomic force microscopy (AFM), dynamic mechanical analysis (DMA), Instron testing machine, thermogravimetric analysis (TGA) and ultraviolet–visible spectroscopy (UV–VIS), respectively. Titania phase in the hybrids showed an open structure and nano-scale size. However, aggregation of titania occurred in the systems prepared by IS method or without AA contained. The mechanical properties, thermal stability and UV shielding properties of organic polymer were obviously improved with titania networks embedded. It was found that BL method could prepare homogeneous hybrids with better integrative mechanical properties in comparison with IS method.

Keywords: Sol–gel; Titania network; Hybrid

1. Introduction

Organic–inorganic hybrid materials have been extensively studied recently [1–4] since they could exhibit better mechanical, thermal, biological, magnetic, optical, electronic and optoelectronic properties [5–8] compared with the corresponding pure organic or inorganic materials. A lot of organic–inorganic hybrids could be prepared by sol–gel process, which has proved to be a very good opportunity for the synthesis of variety of organic–inorganic hybrid materials at macro or micro-scale even at molecular level [9,10].

Various organic–inorganic hybrids based on titania prepared by the sol–gel process have attracted increasing attention in recent years, due to unique mechanical, thermal, optical and electronic properties. For example, Matsuura et al. [11] had successfully prepared polysilane–titania hybrid thin film with higher photo-durability than polysilane or polysilane–silica hybrid thin film. A new ceramic coatings based on blown soybean oil with titania network had been successfully prepared by Teng and co-worker [12]. Lee and Chen [13] had synthesized the high-refractive-index PMMA–titania hybrid thin films, which could potentially be used as optical thin films.

In the present study, the thermoplastic acrylic resin/titania organic–inorganic hybrid materials were synthesized by two methods. One approach was in situ polymerization of acrylic resins in the presence of titania sols obtained from the hydrolysis of titanium *n*-butoxide. Another approach was carried out by directly blending the synthesized acrylic resins with titania sols via mechanical stirring at ambient temperature. The crosslink between two phases was formed through the reaction of –OH or/and –OR groups on titania networks with –COOH from acrylic acid, which has been reported in previous literatures [12,14,15]. The structure and mechanical, thermal and optical properties of the hybrid films were investigated by small angle X-ray scattering (SAXS), atomic force microscopy (AFM), dynamic mechanical analysis (DMA), Instron testing

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machine, thermogravimetric analysis (TGA) and ultraviolet–visible spectroscopy (UV–VIS), respectively.

2. Experimental

2.1. Materials

Butyl acrylate (BA, >96%), methyl methacrylate (MMA, >97%), acrylic acid (AA, >98%) and butyl acetate (>98%) were purchased from Shanghai Gaoqiao Petrochemical Company (China). Titanium *n*-butoxide ($Ti(OBu^n)_4$, >98%), acetylacetone (acac, >98.5%) and absolute ethonal (EtOH, >99.7%) were purchased from Shanghai Chemical Reagent Company. All these chemicals are used without further purification. 2,2′-azobisisobutyronitrile (AIBN) was obtained from Shanghai Chemical Reagent Company and recrystallized before use.

2.2. Synthesis of thermoplastic acrylic resins

A 500 ml round-bottom flask equipped with mechanical stirrer, thermometer with a temperature controller, an N_2 inlet, a Graham condenser and a heating mantle was used. A part of butyl acetate was first charged into the flask. When the flask was heated to 75 ± 2 °C under a slow stream of N_2, the mixture of AA, BA and MMA (weight ratio BA/MMA = 2/3), 0.6 wt% initiator (AIBN) based on the total monomer weight and residual butyl acetate were added into the flask using an addition funnel over a period of 1 h. After addition of all ingredients, the reaction was maintained at 70 ± 2 °C for additional 6 h to complete the reaction. In order to investigate the effect of crosslinking density on the properties of the hybrid materials, the AA content was ranged from 0, 2 to 5 wt% based on the total monomer weight and the corresponding acrylic resin were labeled as AA0, AA2, AA5, respectively.

2.3. Preparation of titania sols

$Ti(OBu^n)_4$ (0.2 mol) and 0.2 mol of acac were dissolved in 40 ml of EtOH by stirring for 10 h at room temperature, then the HCl solution in water (the molar ratio $Ti(OBu^n)_4/H_2O/HCl = 1:4:0.05$) and 40 ml of EtOH were slowly dropped, followed by hydrolysis of $Ti(OBu^n)_4$ for 24 h under vigorous stirring to form yellow transparent sols.

2.4. Preparation of acrylic resin/titania organic–inorganic hybrid materials

Acrylic resin/titania organic–inorganic hybrid materials were prepared via two different methods described as follows:

BL method: acrylic resin/titania organic–inorganic hybrid materials were prepared by directly blending the synthesized acrylic resins with titania sols via mechanical stirring at ambient temperature. Assuming the sol–gel reaction was complete, the theoretical titania content was 2, 4, 6, 10 and 15 wt%, respectively, based on the solid content weight of the pure acrylic resin.

IS method: the in situ polymerization of acrylic monomers was carried out in the synthesized titania sols. Butyl acetate and titania sols were first charged into the flask under stirring, followed by a similar procedure described in Section 2.2. The variation of titania content was from 2 to 10 wt%.

All hybrid samples were labeled as 'M-AAm-Tn', where 'M' represented the preparation method, 'AA' acrylic acid, 'T' titania, 'm' and 'n' indicated the content of AA and titania in the hybrids, respectively. For example, the sample BL-AA2-T4 was prepared by BL method and the contents of AA and titania were 2 and 4 wt%, respectively.

All of polymer films were prepared by casting acrylic resin/titania solutions onto clear glass substrates and dried at room temperature for 30 days before measurement.

2.5. Characterization

SAXS: SAXS measurements were performed at a PW 1700 X-ray scattering instrument (Philips company, Holland), using copper radiation with $\lambda = 0.154$ nm and pinhole collimation of the incident beam. Background collection was performed under the same conditions as the sample data collection prior the data collection. The background counts were scaled and removed from the scattering beam.

AFM: AFM images of the hybrid films were recorded by a Multimode Nanoscope III instrument (Digital Instrument Inc., USA) in tapping mode with a silica probe (NSC 11) and a frequency of 2 Hz. The scan size varied between 2 and 5 μm and the roughness analysis was performed on 5 × 5 μm images. The average surface roughness (Ra) is the mean vertical deviation of the surface relative to the center plane. The root mean square roughness (Rms) is the standard deviation of the *Z* values (the height) calculated within the given area as: $\mathrm{Rms} = \sqrt{(\sum(Z_i - Z_{\mathrm{ave}})^2)N}$, where Z_i is the current Z value, Z_{ave} is the average of the Z values, and N is the number of data points with the given area [16].

DMA: Dynamic mechanical measurements were carried out on DMA242 (Netzsch Inc., German). The samples were quickly cooled to −30 °C and equilibrated for 3 min at that temperature and then heated to 130 °C at a frequency of 1 Hz with a constant heating rate of 5 °C/min under nitrogen atmosphere.

Static mechanical property: Tensile properties were determined by an Instron model DXLL 1000-20000 testing machine (Shanghai, China). The specimens for tensile tests were dumbbell cut from the molded polymer films according to Die C of ASTM-D412 and carried out at a crosshead speed of 200 mm/min and 23 ± 2 °C. A 20 mm benchmark and the original cross-sectional area were utilized to calculate their tensile properties. The ultimate tensile strength and elongation were automatically calculated by the computer connected to the Instron. The average of at least five measurements for each sample was reported, the experimental error was ±5%.

Thermogravimetri analysis (TGA): The thermal curves of TGA were obtained using a PEPKIN ELMER thermal gravimetric and differential thermal analysis instrument (America). The temperature ranged from the room temperature to 600 °C with heating rates of 10 °C/min in the N_2 flow.

Ultraviolet–visible spectra (UV–VIS): The absorbance and transmittance spectra of the hybrid films in the range of 200–700 nm wavelength light were determined on an UV–VIS spectrophotometer (Hitachi UV-3000, Japan) with the scan speed of 300 nm/min.

3. Results and discussion

3.1. Structure of acrylic resin/titania organic–inorganic hybrid films

3.1.1. Small angle X-ray scattering (SAXS)

The structure of inorganic titania phase in the hybrids could be determined by SAXS. The intensity distribution as a function of angle was dependent on the shape, size, concentration and interfacial roughness of the heterogeneities [17,18]. In this work, the goal was to study the radius of gyration (R_g), which gave a measure of the mean square distance of the scattering centers within inorganic networks from the center of gravity and therefore was related to sizes of networks. R_g could be evaluated from the slope in the linear region of a plot of $\ln(I(q))$ versus q^2, according to Guinier's relation [19]:

$$I(q) \propto \exp(-q^2R_g^2/3) \quad (1)$$

where $I(q)$ is scattering intensity, scattering vector $q = (4\pi/\lambda)\sin(2\theta/2)$, 2θ is the scattering angle and λ is the wavelength of the beam. Another useful Porod formula [19] was shown in Eq. (2):

$$I(q) \propto q^{-D} \quad (2)$$

where D is the power law exponent obtained from the slope in the linear region of a double logarithmic plot of $I(q)$ versus q. The power exponent reflects fractal dimension, thus it is a measure of the compactness or shape of materials such as a sharp and smooth surface between the two regions of different electron density ($D = 4.0$), surface fractal ($3 < D < 4$) and mass fractal ($1 < D < 3$) [20].

Fig. 1 described the SAXS profiles of AA2 and the corresponding hybrids with different content of titania networks. In contrast to the corresponding acrylic resin, the hybrids exhibited an interference peak around $q = 0.07\ \mathrm{nm}^{-1}$ caused by the short-range periodicity of titania-rich domains. In addition, an increase in the scattering intensity with higher titania content indicating a decrease in miscibility although the scattering intensities for all samples were quite low [21]. The Guinier plots and Porod plots of SAXS data for the hybrids prepared by BL method showed a linear region, as illustrated in Fig. 2. The R_g and D obtained from the slopes of the curves were listed in Table 1. The power law exponent for all hybrids was much lower than 3, suggesting that titania networks had mass fractal and open structure. With increasing titania content, R_g and D increased from 10.3 to 12.6 nm and 1.3 to 1.5, respectively, which could be due to the aggregation of titania to form larger inorganic networks.

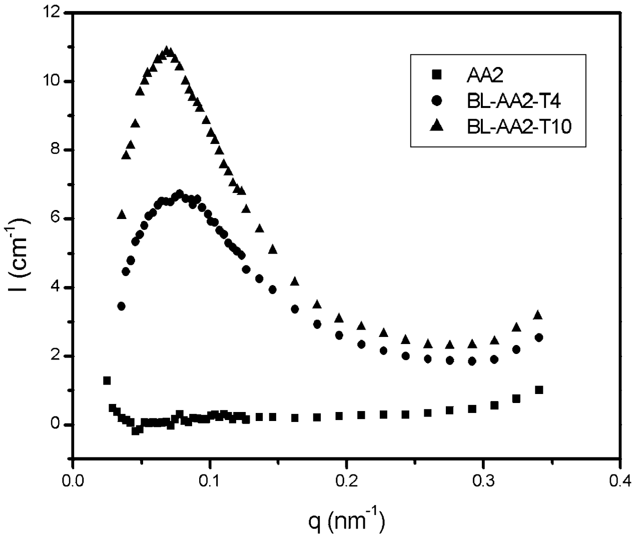

Fig. 1. SAXS profiles of AA2, BL-AA2-T4 and BL-AA2-T10.

Fig. 3 showed the Guinier plot and Porod plot of SAXS data for the hybrid with 10 wt% titania prepared by IS method. In comparison with Fig. 2a, the Guinier plot of IS-AA2-T10 exhibited two linear regions. The R_g of mono-dispersed titania were 12.9 nm calculated from the slope in the high q region. However, in the low q region, SAXS curve showed a much higher slope corresponding to a higher R_g value of 63.9 nm, which was mainly resulted from further polycondensation of titania networks at high polymerization temperature (70–75 °C). In Fig. 3b, IS-AA2-T10 exhibited a higher D than the corresponding hybrids prepared by BL method, indicating that titania networks in hybrids from IS method have more compact

Table 1
R_g and D of the hybrids

Label	R_g (nm)	D
BL-AA2-T4	10.3	1.3
BL-AA2-T10	12.6	1.5
IS-AA2-T10	12.9[a] 63.9[b]	1.9
BL-AA0-T10	13.4[a] 51.5[b]	2.1
BL-AA5-T10	–	0

[a] R_g for mono-dispersed inorganic networks.
[b] R_g for aggregated inorganic networks.

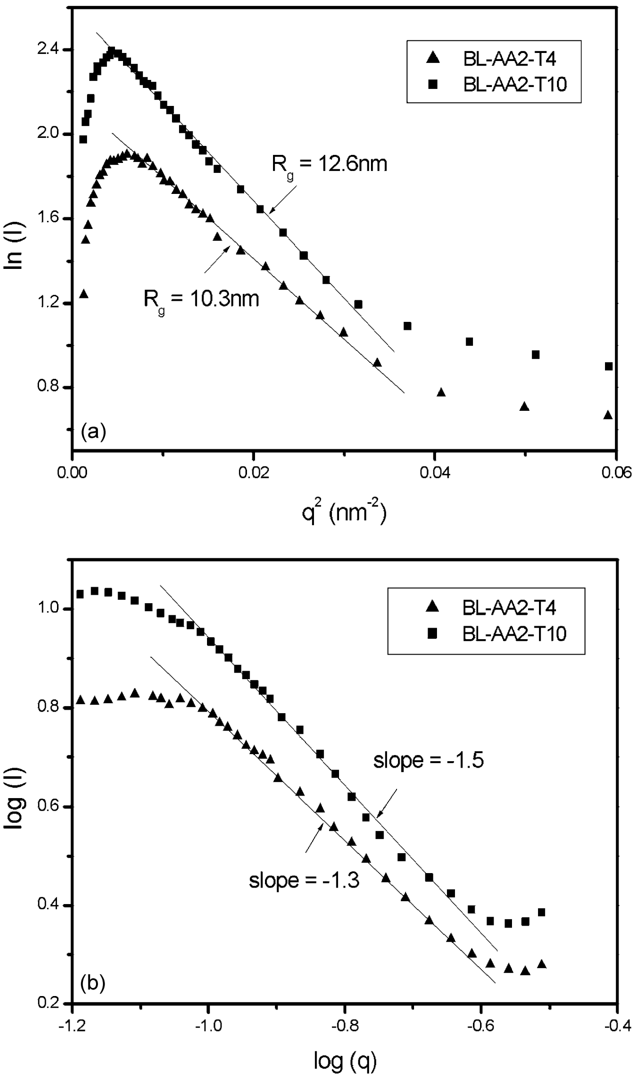

Fig. 2. (a) Guinier plots of SAXS data for BL-AA2-T4 and BL-AA2-T10. (b) Porod plots of SAXS data for BL-AA2-T4 and BL-AA2-T10.

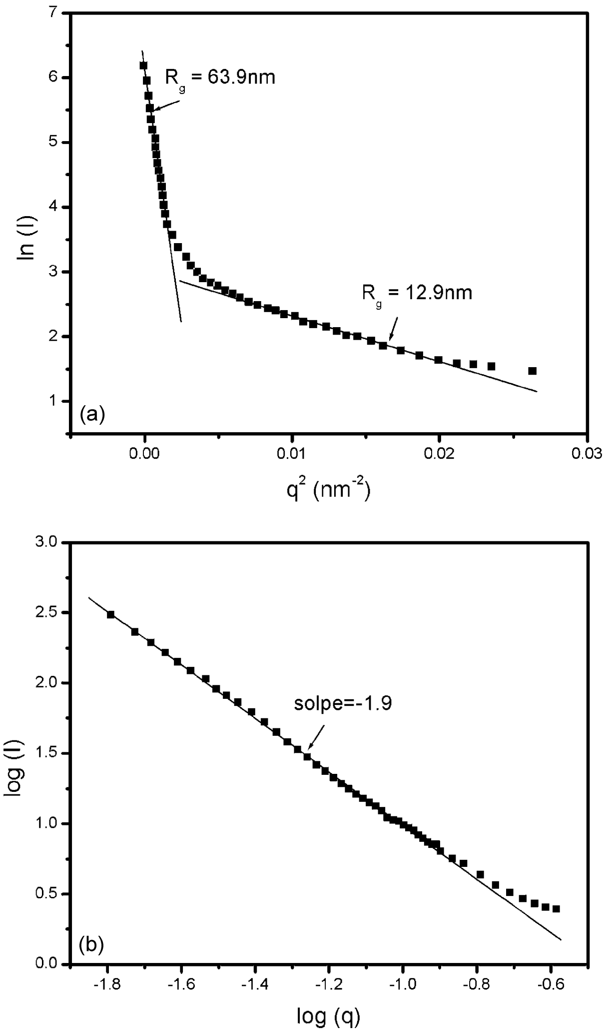

Fig. 3. (a) Guinier plot of SAXS data for IS-AA2-T10. (b) Porod plot of SAXS data for IS-AA2-T10.

structure than from BL method. In addition, higher SAXS scattering intensity for IS-AA2-T10 was due to the increase in phase separation between organic matrix and inorganic domains. Therefore, it was interesting to find that more homogeneous acrylic resin/titania hybrids were formed via BL method compared with IS method. The possible reason could be explained as follows: In theory, the in situ polymerization should cause more interlocked structure between the organic and inorganic phase. However, titania sols with nano-size were very reactive and prone to condensation or aggregation themselves especially at relatively high temperature for the in situ polymerization, resulting in relatively small numbers of functional groups (–OH or/and –OR) bonded to Ti reacting with –COOH groups from AA, and increase in phase separation as well. The sample IS-AA2-T10 with larger size and higher scattering intensity than BL-AA2-T10 could demonstrate this conclusion. On the contrary, the BL method was carried out at ambient temperature, the –OH and –OR groups on titania networks preferred to react with –COOH from acrylic resin rather than themselves, resulting in evenly dispersed titania networks in organic matrix. The fact that the crosslinking density between two phases dramatically increased but network size varied slightly with increasing titania content, which would be discussed in detail later, could further confirm this analysis.

The effect of various content of AA in the hybrids on the structure of inorganic titania phase was investigated in our work. The sample BL-AA0-T10 presented a similar SAXS profile with IS-AA2-T10, and the R_g and D were also listed in Table 1. Titania networks showed a low stabilization in a system without –COOH groups and tended to aggregate themselves. As the content of AA increased, miscibility of the two phases was expected to be improved due to more –COOH groups reacting with Ti–OH or/and Ti–OR, which was approved by the SAXS measurement as shown in Fig. 4. The SAXS profile for BL-AA5-T10 exhibited a very low scattering intensity with a slope of near zero in the linear region, indicating no definite phase separation,

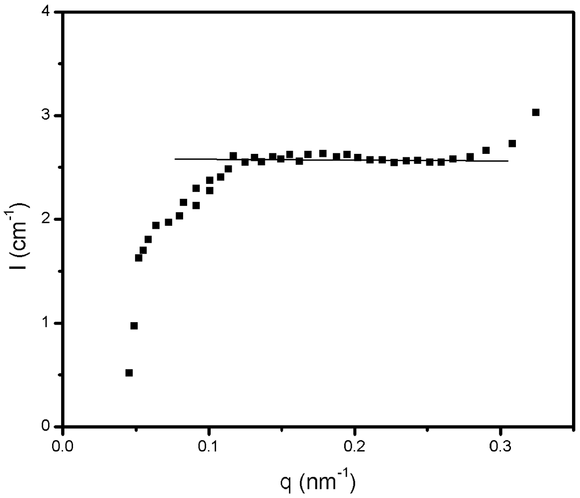

Fig. 4. SAXS profile of BL-AA5-T10.

namely, homogenous dispersion of the inorganic phase in organic polymer could be obtained.

3.1.2. Surface morphology by AFM measurements

The three-dimension AFM images of the pure acrylic resin film and the corresponding hybrid films with different content of titania prepared by BL method were shown in Fig. 5 and the surface roughness values were summarized in Table 2. It was observed that the surface roughness values increased gradually with increasing titania content, suggesting that more titania were resided at the surfaces of the hybrid films as more titania were embedded. Table 2 also illustrated the influence of the different preparation methods on the surface roughness of the hybrid materials. The hybrid film from IS method had slightly rougher surface than the corresponding hybrid film from BL method due to aggregation of titania networks during the in situ polymerization of organic monomers at relatively high temperature, as discussed above (see samples IS-AA2-T10 and BL-AA2-T10). The AA content had an obvious impact on the surface morphology of the hybrid films. The sample BL-AA0-T4 exhibited much rougher surface than other films, which might be due to the instability of titania networks in the system without –COOH groups, leading to aggregation of titania networks. However, just introducing 2 wt% AA in the system could significantly reduce the surface roughness (see sample BL-AA2-T4), but further increasing AA content caused no obvious change in the surface roughness.

Table 2
The surface roughness of the pure acrylic resin and the hybrid films

Label	Rms (nm)		Ra (nm)	
	$2\times 2\ \mu m^2$	$5\times 5\ \mu m^2$	$2\times 2\ \mu m^2$	$5\times 5\ \mu m^2$
AA2	0.28	0.33	0.22	0.26
BL-AA2-T4	0.38	0.45	0.30	0.35
BL-AA2-T10	0.61	0.70	0.44	0.56
BL-AA2-T15	0.66	0.80	0.52	0.63
IS-AA2-T10	0.66	0.78	0.48	0.62
BL-AA0-T4	1.86	7.94	1.54	5.07
BL-AA5-T4	0.38	0.44	0.30	0.34

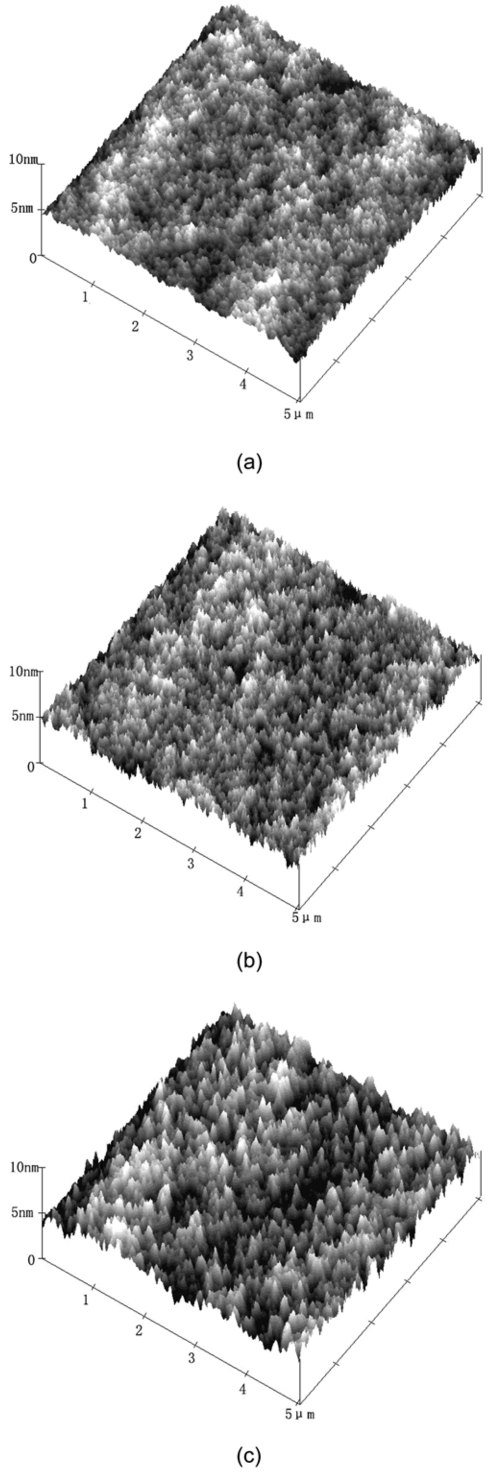

Fig. 5. The AFM images ($5\times 5\ \mu m^2$) of the films: (a) AA2; (b) BL-AA2-T4; (c) BL-AA2-T10.

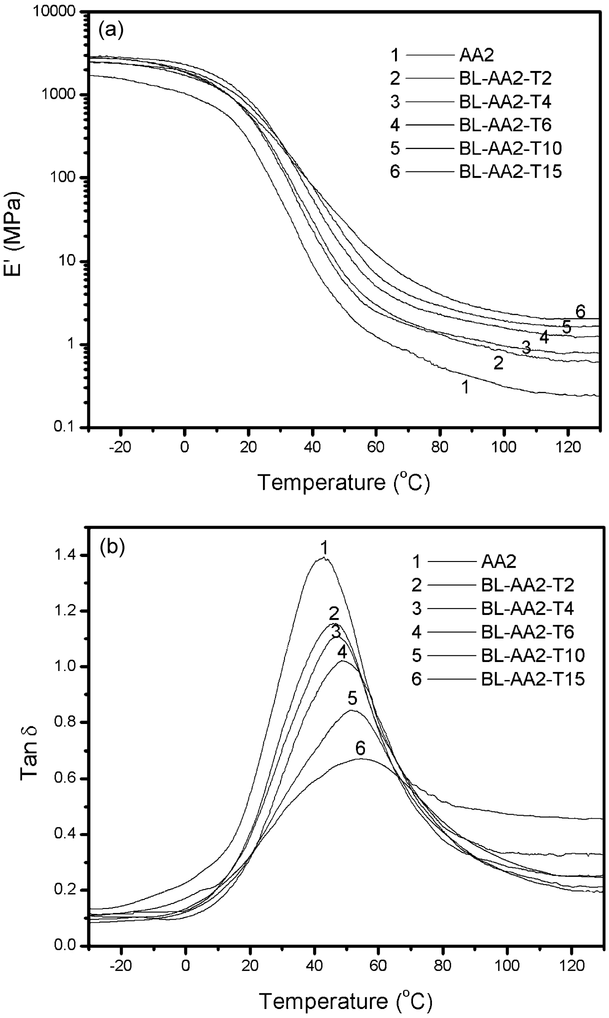

Fig. 6. DMA curves for AA2 and the corresponding hybrid films with increasing titania content prepared by BL method: (a) the storage modulus; (b) loss tangent.

3.2. Mechanical properties

3.2.1. Dynamic mechanical analysis (DMA)

The storage modulus (E') and tan δ as a function of temperature for the pure acrylic resin film and the corresponding hybrid films prepared by BL method were shown in Fig. 6. The E' gradually increased as titania content in the hybrid films increased. The crosslinking density of the hybrid films could be calculated from the storage modulus according to the following equation [22]:

$$\nu_e = E'/(3RT) \quad (T \gg T_g) \tag{3}$$

where ν_e is the crosslinking density (the number of moles) of elastically effective network chains, E' is the storage modulus, R the gas constant and T the absolute temperature. The relationship is effective when T is more than 50 °C above T_g. Table 3 calculated the crosslinking density of the hybrids based on the storage modulus at 130 °C. The crosslinking density increased with increasing titania content because more –OH or/and –OR groups on titania networks could react with –COOH groups from AA to form the stable covalent bands. Fig. 6b presented the loss tangent curves of the hybrids with various amounts of titania prepared by BL method. The tan δ peak which reflected the micro-Brownian segmental motion of amorphous acrylic resin were defined as the glass transition temperature (T_g) and summarized in Table 3. As the titania content increased, the T_g shifted to higher temperature, suggesting that segmental chain mobility was restricted due to increasing crosslinking density between the organic polymer and inorganic networks. The tan δ peaks were broadened as higher titania content, indicating an increase in phase separation [10,23], which was agreed with SAXS analysis. At the same time, the relaxation strength (the height of the tan δ peak) significantly decreased with increasing titania content. Such a reduction of the tan δ peak for organic–inorganic hybrid materials was attributed to the increase in crosslink of polymer with inorganic network or the entrapment of the polymer chains within inorganic networks, resulting in the reduction of the polymer chain mobility [24].

Table 3
DMA data for the pure acrylic resin film and the hybrid films

Sample	E'[a] (Mpa)	$\nu_e \times 10^2$ (mol/m^3)	T_g (°C)	Relaxation strength
AA2	0.24	[b]	42.8	1.39
BL-AA2-T2	0.61	6.1	46.1	1.16
BL-AA2-T4	0.79	7.9	46.9	1.11
BL-AA2-T6	1.25	12.4	49.2	1.02
BL-AA2-T10	1.65	16.4	52.3	0.84
BL-AA2-T15	2.05	20.4	55.5	0.67
IS-AA2-T2	0.51	5.1	46.5	1.21
IS-AA2-T6	0.78	7.8	48.6	1.10
IS-AA2-T10	1.14	11.4	52.2	0.94
AA0	0.21	[b]	41.6	1.38
BL-AA0-T4	0.39	[b]	44.5	1.16
AA5	0.25	[b]	43.5	1.40
BL-AA5-T4	1.50	14.9	52.4	0.97

[a] Storage moduli at 130 °C.

[b] Actual values of crosslinking density were close to zero determined by swelling coefficient via Soxhlet extraction at 80 °C for 24 h.

Fig. 7 illustrated E' and tan δ curves as a function of temperature for the pure acrylic resin film and the corresponding hybrid films with various titania content prepared by IS method. A similar result to the above was obtained that the storage modulus increased with increasing titania content. The crosslinking densities of hybrid materials calculated according to the Eq. (3) were also listed in Table 3. As more titania embedded, the crosslinking density increased from 5.1×10^{-2} to 11.4×10^{-2} mol/m^3. The shift of tan δ peaks towards higher temperature and the reduction of the relaxation strength also indicated restriction of segmental chain mobility due to increasing crosslinking density between the organic polymer and inorganic networks. As the content of titania increased, the glass transition regions were

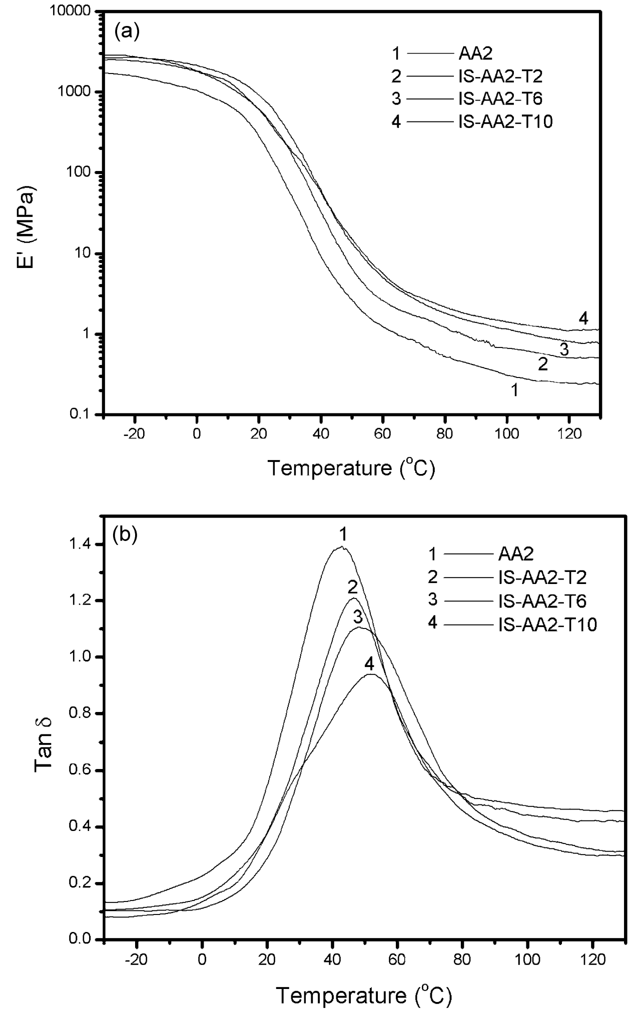

Fig. 7. DMA curves for AA2 and the corresponding hybrid films with increasing titania content prepared by IS method: (a) the storage modulus; (b) loss tangent.

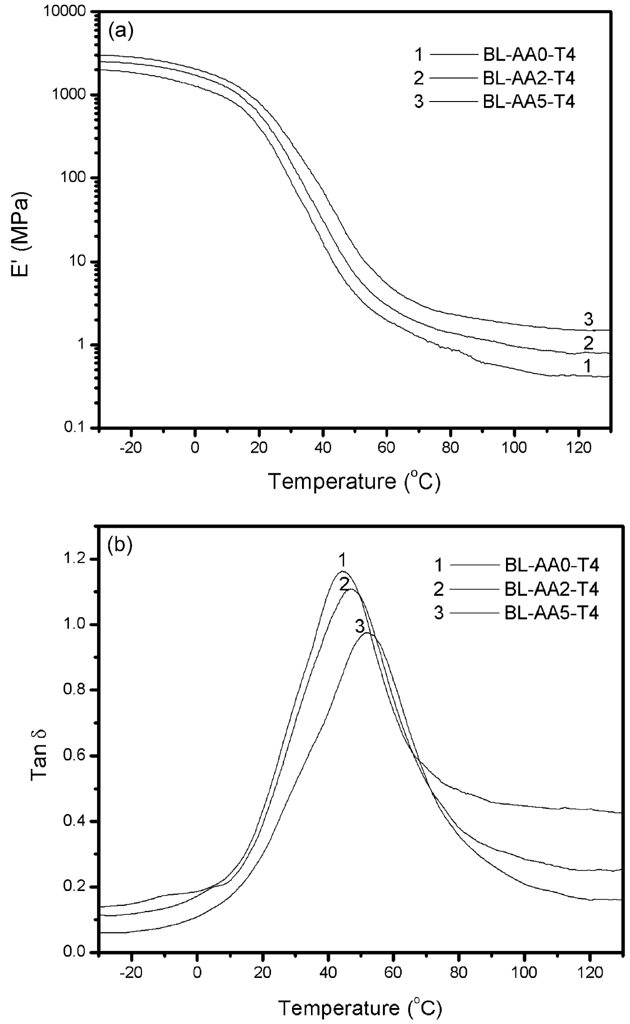

Fig. 8. DMA curves for the hybrid films with increasing AA content: (a) the storage modulus; (b) loss tangent.

broadened, suggesting an increase in phase separation between organic polymer and inorganic networks.

The data in Table 3 showed that the hybrid films prepared by IS method had lower storage modulus and crosslinking density than the corresponding samples prepared by BL method, which further confirmed the results and analyses in SAXS. Again, this was probably because high polymerization temperature of organic monomers caused the aggregation of titania networks themselves, decreasing the numbers of reactive groups (–OH or/and –OR) on titania networks to react with organic polymer. To our surprise, the T_g did not vary too much but kept the close values for the hybrids through different preparation methods probably because the decrease in T_g by lower crosslinking density was counterbalanced by the increase in T_g by an denser structure of inorganic networks (higher power law exponent value) for the hybrids from IS method.

Fig. 8 showed the storage modulus and tan δ curves as a function of temperature for the hybrid films with various AA content. The storage modulus and the crosslinking density obviously increased with increasing AA content (see the data for samples BL-AA0-T4, BL-AA2-T4 and BL-AA5-T4 in Table 3), which was mainly due to more –COOH groups reacting with –OH or/and –OR groups on titania networks, accompanied by increasing T_g and decreasing relaxation strength since the variation of AA content slightly affected the dynamic mechanical properties of the pure acrylic resin as shown in Table 3 (see samples AA0, AA2 and AA5).

3.2.2. Tensile properties

Table 4 summarized the tensile strength, elongation-at-break and tensile modulus of the hybrids. A considerable increase in the tensile strength and tensile modulus for the hybrid films prepared by both BL and IS methods was observed as the titania content increased, which was attributed to the increase in the crosslinking density between the polymer and inorganic networks. The IS method caused lower tensile strength than BL method because the former caused lower crosslinking density than the latter. Table 4 indicated that the AA content in the polymer also had an

Table 4
Tensile properties for the pure acrylic resin films and the hybrid films

Sample	Tensile strength (Mpa)	Elongation-at-break (%)	Tensile modulus (Mpa)
AA2	5.51	188	111
BL-AA2-T2	7.31 (32.7%[a])	198	128 (15.3%)
BL-AA2-T4	8.40 (52.5%)	214	146 (31.5%)
BL-AA2-T6	9.16 (66.2%)	171	158 (42.3%)
BL-AA2-T10	9.75 (78.0%)	145	172 (55.0%)
IS-AA2-T2	6.63 (20.3%)	184	129 (16.2%)
IS-AA2-T6	8.43 (53.0%)	164	159 (43.2%)
IS-AA2-T10	9.06 (64.4%)	129	170 (53.3%)
AA0	5.97	163	115
BL-AA0-T4	6.28 (5.2%)	158	134 (16.5%)
AA5	5.58	172	122
BL-AA5-T4	11.27 (102.0%)	120	253 (107.4%)

[a] The increasing percentage of tensile strength or modulus for the hybrid films in comparison with the corresponding acrylic resin films (noted in brackets).

obvious impact on the tensile properties of the hybrid films. For the sample BL-AA0-T4, there was no crosslinking points formed between the two phases, and the tensile strength and tensile modulus just increased by 5.2 and 16.5%, respectively, compared with the pure acrylic resin films. As AA was introduced into the polymer, the tensile properties were obviously improved, and the tensile strength and tensile modulus for BL-AA5-T4 increased by 102.0 and 107.4%, respectively. In general, the elongations at break decreased for the hybrid films with rigid inorganic materials filled, compared with the corresponding acrylic resins.

3.3. Thermal stability

Fig. 9 presented TGA curves of pure acrylic resin and the corresponding hybrids prepared by BL method. For the pure acrylic resin, the weight loss took place at two steps. The first step with gradual weight loss was due to the evaporation of physically absorbed water and residual solvent from room temperature to -270 °C. The major weight loss in the range of 270–400 °C was ascribed to the decomposition of polymer. The TGA curves for the hybrid materials, especially with high content of titania, displayed three steps (below 300, 300–400 and 400–450 °C, respectively). The first two steps corresponded to the TGA curve for the pure acrylic resin. The third minor weight loss at 400–450 °C might be caused by the decomposition of titania bonded groups such as –OH and unhydrolyzed –OR. The thermal stability of the hybrids was investigated by the decomposition temperatures (T_d) at the major weigh loss, which was determined from the first derivative of the TGA curve. The T_d notably increased from 316 to 372 °C as 2 wt% titania embedded, suggesting that the thermal stability of the hybrid materials was improved compared with the pure polymer. However, the T_d kept invariable with further titania added. The TGA curves for the hybrids prepared by IS method had a similar result as the above and the T_d values were about 375 °C. Table 5 listed the theoretical and experimental residual mass of the hybrid materials. It was obvious that the actual residual mass was higher than the theoretical value due to the trapping of the polymer moieties in titania networks [1,24]. The black color of the polymer residues after the TGA runs also provided the evidence for this conclusion.

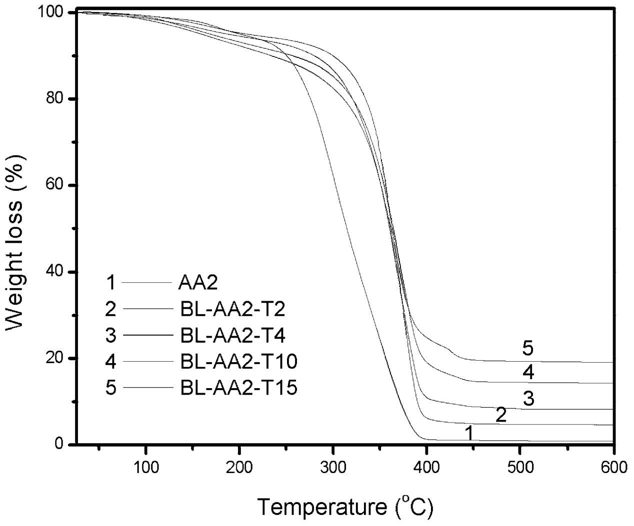

Fig. 9. TGA curves for AA2 and the corresponding hybrid films with increasing titania content prepared by BL method.

Table 5
The theoretical and experimental residual mass of the hybrid materials prepared by BL method after heated at least to 600 °C

Theoretical value (wt%)	2	4	10	15
Experimental value (wt%)	4.8	8.7	14.6	19.5

3.4. Optical properties

Figs. 10 and 11 showed the UV–VIS absorbance and transmittance spectra of pure acrylic resin and the corresponding hybrid films prepared by BL and IS methods, respectively. For the pure acrylic resin, there was almost no absorption in the range of 290–400 nm wavelength. When titania were introduced into the polymers, an obvious absorbance in the UV region was observed, and increased significantly with higher titania content. TiO_2 bulk materials had a band-gap of 3.2 eV (absorption edge at 387.5 nm) [25] and the blue-shift occurred for the hybrid materials. Titania with nano-size scale exhibited a quantum size effect and the band gap shift ΔE_g dependence of the radius R was [26]:

$$\Delta E_g = \frac{h^2}{8MR^2} - \frac{1.8e^2}{\varepsilon R} \qquad (4)$$

Where h is Planck's constant, μ is the reduced effective mass of the electron, e is the electron charge, ε is the dielectric constant of the solid. The first term, proportional

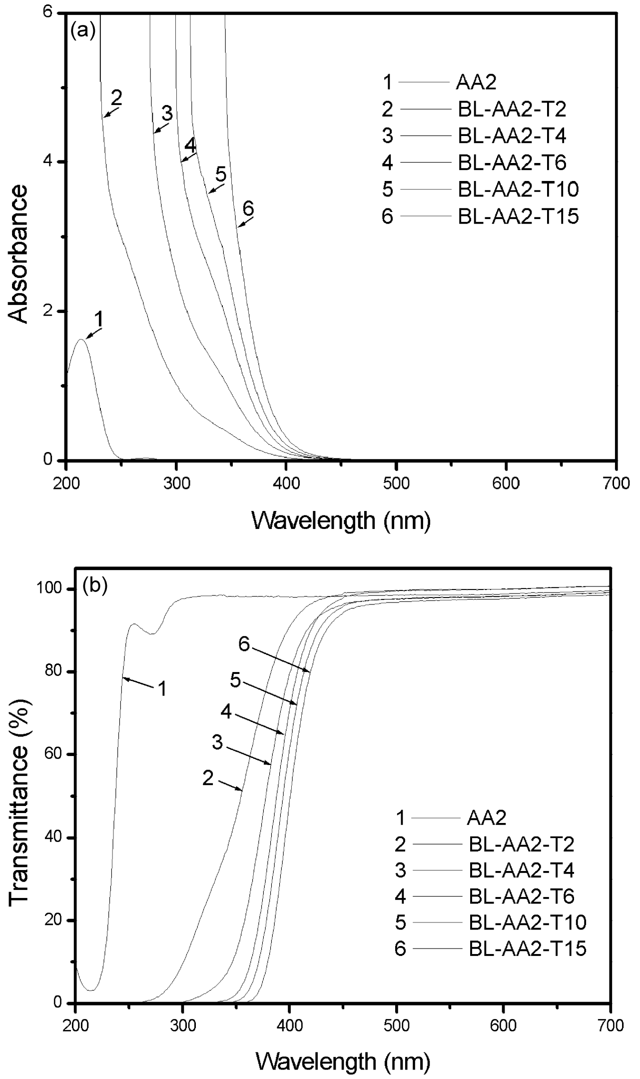

Fig. 10. UV–VIS spectra of AA2 and the corresponding hybrid films prepared by BL method: (a) absorbance spectra; (b) transmittance spectra.

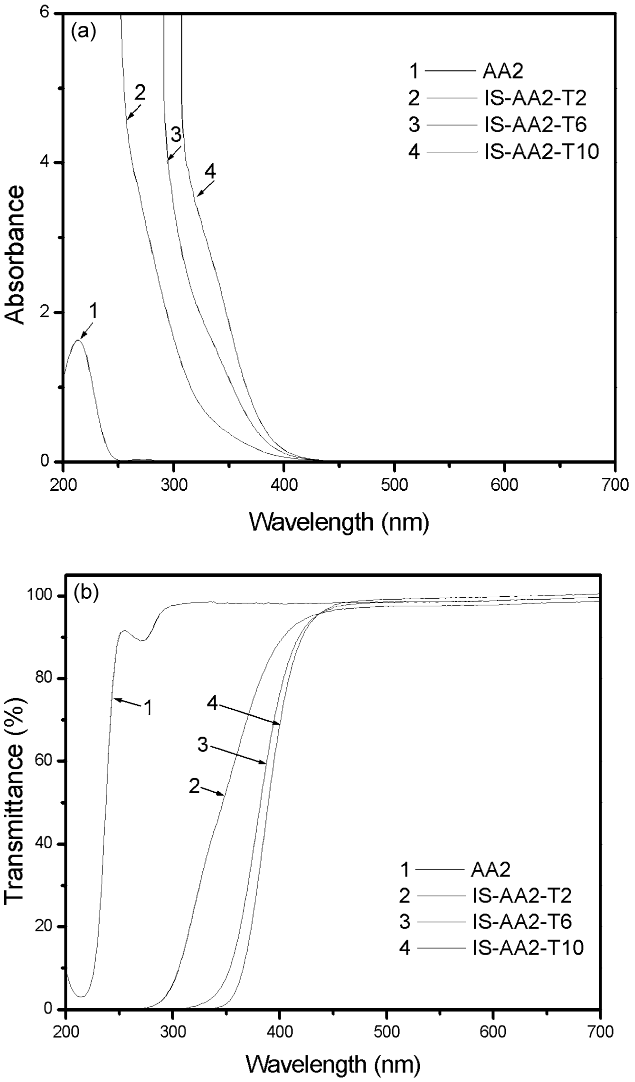

Fig. 11. UV–VIS spectra of AA2 and the corresponding hybrid films prepared by IS method: (a) absorbance spectra; (b) transmittance spectra.

to R^{-2}, is the shift to higher energy gap due to quantum localization, while the second term, proportional to R^{-1}, is the shift to lower energy gap due to the electrostatic interaction between the electron and the hole. When the size of titania was small enough, the band gap value increased, leading to the blue-shift of absorption edge. However, the absorption edge shifted to low-energy side with increasing titania content as shown in Figs. 10a and 11a. This might be attributed to the increase in the size of titania network, which was investigated by SAXS measurement.

The transmittance spectra of the hybrid films even with 15 wt% titania content exhibited excellent optical transparence in the visible range (400–700 nm). But the transmittance in the UV region decreased with increasing titania content in the hybrid films, suggesting that acrylic resin/titania organic–inorganic hybrid materials could improve the UV shielding property of the polymer without decreasing the transparence.

4. Conclusion

Acrylic resin/titania organic–inorganic hybrid materials were prepared by blending acrylic resin with titania networks or via in situ polymerization of acrylic monomers in the presence of titania networks which were firstly prehydrolyzed from the precursor of $Ti(OBu^n)_4$ with hydrochloric acid as the catalyst and acac as the stabilizer.

The hybrid materials with open structures and nano-scale sizes could be obtained by blending or in situ methods. The surface roughness, storage modulus, T_g, tensile strength, tensile modulus, thermal stability and UV absorption of the hybrid films notably increased with titania networks embedded. As the AA content increased, the phase separation reduced and crosslinking density increased, accompanied by an improvement in mechanical properties. Different preparation methods had an obvious influence on the structure and properties, especially mechanical properties of the hybrids. Blending method caused monodispersed sizes of titania networks in the hybrids, while in situ polymerization resulted in some aggregation of titania in the hybrids and increase in phase separation. The hybrid films prepared by blending method had smoother surface and better mechanical properties than in situ polymerization since the former caused better miscibility between two phases and greater crosslinking density than the latter.

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