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Silane functional effects on the rheology and abrasion resistance of transparent SiO_2/UV-curable resin nano-composites

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ABSTRACT

Transparent UV-curable nano-composite coatings consisting of nano-sized SiO_2 and acrylate resin have been developed to improve the abrasion resistance of organic polymers. The nano-sized SiO_2 particles were surface-modified using various amounts of 3-methacryloxypropyltrimethoxysilane (MEMO). The MEMO concentration effects on the rheological behaviors, optical and abrasion resistance properties were investigated using a viscometer, FTIR, UV–visible spectrophotometer. The results showed that the steric-hinderance established on the nano-sized SiO_2 surface due to the grafted MEMO can effectively improve the dispersibility of nano-sized SiO_2 in acrylate suspensions. The MEMO-modified nano-sized SiO_2 in acrylate solutions at low and high solid concentrations exhibited Newtonian and shear thinning flow behaviors, respectively. Moreover, the maximum solid concentration was estimated to be 0.23. As the MEMO/SiO_2 weight ratio increases from 0.2 to above 0.6, the abrasion resistance was significantly improved and the pencil hardness increased from 4H to 6H, which may be attributed to the complete MEMO coverage on the SiO_2 surface, thereby enhancing the dispersion, compatibility, and cross-linking density between the MEMO-modified SiO_2 particles and acrylate resin.

1. Introduction

It is well known that the addition of inorganic nano-particles, typically SiO_2 or Al_2O_3, to radiation-curable acrylate can result in a strong increase in scratch and abrasion resistance in these coatings [1–3]. The scratch and abrasion resistance of the coatings depend on the content and dispersion of the inorganic nano-particles [4]. However, the inorganic nano-particles are very hydrophilic and cannot be dispersed directly in low-polar acrylate resins. The surface modification of nano-sized SiO_2 particles with a coupling agent, 3-methacryloxypropyltrimethoxysilane (MEMO) in radiation-curable acrylate formulations can offer superior performance, such as improved dispersibility, increased compatibility between SiO_2 and acrylate monomers and adhesion strength between the SiO_2 particles and polymer matrix due to silane molecule vinly groups grafted onto the SiO_2 surface, participating in acrylate monomer free radical polymerization [5,6]. To our knowledge, the MEMO concentration effects on the rheological behaviors, optical and abrasion resistance properties of MEMO-modified SiO_2/acrylate systems have not been well understood. In this study, UV-curable nano-composite coatings consisting of MEMO-modified SiO_2 and acrylate resin were prepared and MEMO concentration effects on the rheological behaviors, optical and abrasion resistance properties were investigated using a viscometer, FTIR, UV–visible spectrophotometer.

2. Experimental procedures

MEMO prehydrolysis (Degussa, AG) was conducted by gently mixing MEMO, deionized water and ethyl alcohol with MEMO: deionized water: ethyl alcohol = molar ratio of 1:2:1 for about 3 h. The nano-sized SiO_2 (QS-102, Tokuyama; mean particle size: 15 nm; specific surface area: 200 $m^2\ g^{-1}$) was first intensively stirred in n-isopropanol (Mallinckrodt Chem., 99.5%) using a magnetic stirrer at around 600–700 rpm for about 1–2 min, followed by ultra-sonication in an ice bath for 30 min, then mixed with the desired prehydrolyzed MEMO (weight ratio of MEMO to SiO_2 = 0.1, 0.2, 0.4, 0.6, 1.0, and 1.5) and refluxed at 70 °C for 3 h.

One part of the reaction mixture was washed 3 times with n-iospropanol (IPA) and centrifuged at 20,000 rpm. The clear supernatant was decanted from the solid deposit. The solid deposits, comprising the SiO_2 nano-particles grafted with MEMO, were dried at 80 °C for 6 h. Subsequently, the MEMO-modified SiO_2 was mixed with 1,6-hexanedioldiacrylate (HDDA) and concentrated using a rotary evaporator under reduced pressure to remove the IPA, alcohol, and water to obtain a suspension with different solid contents.

A 1:1 by weight mixture of MEMO-modified SiO_2/HDDA suspension and a commercial acrylate resin (4390A, Fonton, Taiwan) added with 3 wt% 2-Hydroxy-2-methyl-1-phenyl propanone phtoinitiator (HDMAP, Additol, Cytec, Taiwan) was used as the coating solution.

The wet coatings (about 12 μm) were prepared from the coating solution on transparent PET films. Coated samples were kept at 150 °C and cured in an UV curing machine chamber consisting of two consecutive medium-pressure Hg lamps (maximum power of 120 $W\ cm^{-1}$) for 10 min.

The grafted MEMO and UV cured coatings were characterized using Fourier transform infrared spectroscopy (EQUINO 55, Brucker, Germany). The rheological behaviors of the examined suspensions were characterized using a viscometer (VT-

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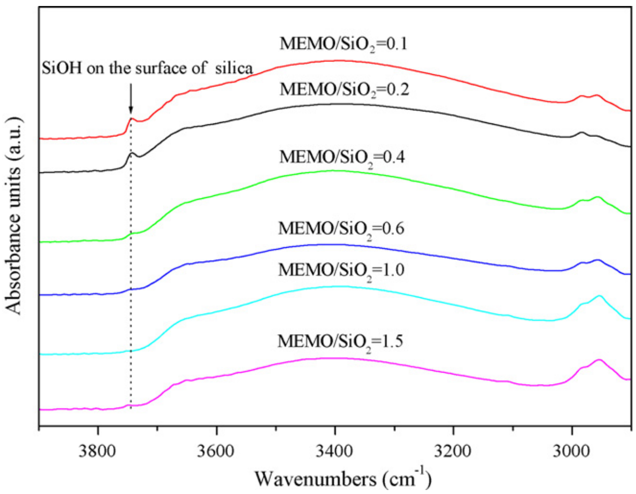

Fig. 1. FTIR spectra of the centrifuged samples in the 2900–3900 cm^{-1} region after the addition of various amounts of MEMO.

550, Haake, Germany). A Taber Abraser (Taber Industries, North Tonawanda, NY) was used to characterize the abrasion resistance of the coatings. Samples were abraded with alumina embedded rubber wheels (CS-10F, Taber Industries, North Tonawanda, NY). Each wheel was loaded with a 500 g weight. Abrasion was conducted for 500 cycles.

The transmittance spectra of the nano-composite coatings before and after abrasion testing in the 300–800 nm wavelength light range were measured using a UV–visible spectrophotometer (Agilent 8453, Palo Alto, CA).

3. Results and discussion

The FTIR spectra of the centrifuged samples in the 2900–3900 cm^{-1} region after the addition of various amounts of MEMO are shown in Fig. 1. The band at 3750 cm^{-1} resulting from the free silanol SiOH group was observed only for the samples with MEMO/SiO_2 weight ratio below 0.6 and the intensity decreased with increasing MEMO addition. The results indicate that the silanol groups on the SiO_2 surface, reactive sites for silylation play an important role in grafting MEMO onto the SiO_2 surface, are used up or covered by grafted MEMO for samples with MEMO/SiO_2 weight ratios larger than 0.6.

Figs. 2 and 3 shows the viscosity and shear stress as a function of applied shear rates for the SiO_2/HDDA solution with an MEMO/SiO_2 weight ratio of 0.6 at different solid contents. At low solid contents (≦11.66 vol.%), the shear stress appears to behave linearly proportional to the shear strain with a negligible yield stress, revealing a Newtonian fluid with a good dispersion quality. The suspensions with solid contents ≧14.71 vol.% exhibit shear thinning behavior in the low shear rate range, followed by near Newtonian plateaus. As the solid content is increased, the steric barriers built by the adsorbed silane on the surface of nano-sized SiO_2 particles will come into contact, interpenetrate or be compressed, which results in the loss of silane configurational entropy. This entropic effect will impose “structure” on the dispersion [7]. Shear thinning occurs due to the “structure” built up by the hydrodynamic interaction at rest, which is eventually broken down upon shearing, thereby reducing viscosity.

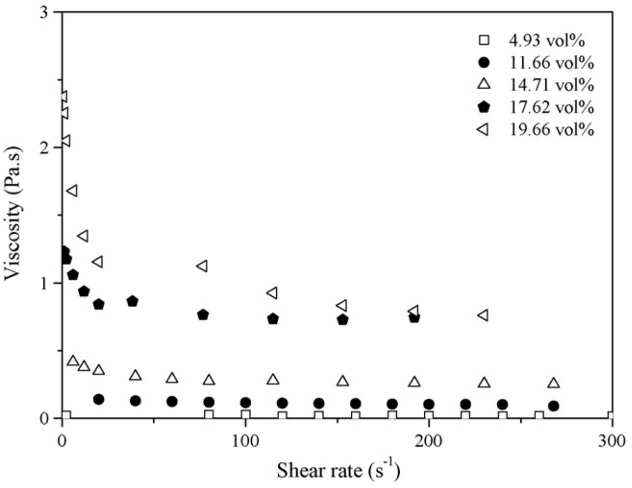

Fig. 2. Viscosity as a function of applied shear rates for the SiO_2/HDDA solution with an MEMO/SiO_2 weight ratio of 0.6 at different solid contents.

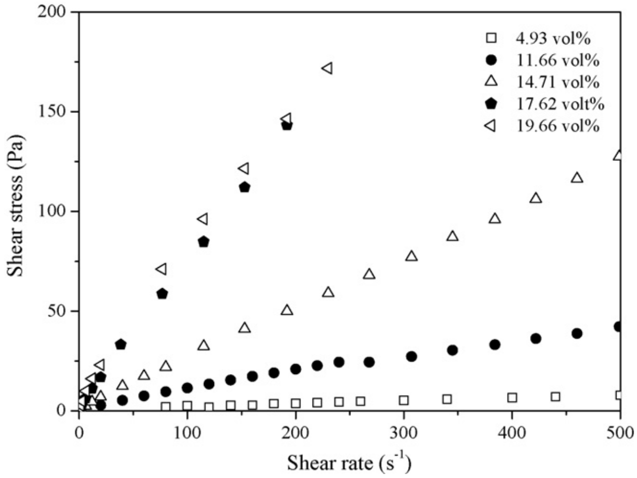

Fig. 3. Shear stress as a function of applied shear rates for the SiO_2/HDDA solution with an MEMO/SiO_2 weight ratio of 0.6 at different solid contents.

At higher concentration, hydrodynamic and Brownian many–body interactions affect rheological behavior. In this regime, a model proposed by Liu [8] can be used to describe this dependence and estimate the maximum solid concentration (Φ_m) attainable:

$$1-{\eta_r}^{-1/n}=a\phi+b \tag{1}$$

$$\eta_r=\frac{\eta}{\eta_0} \tag{2}$$

where η_r is the relative viscosity; φ is the solid concentration; η is the suspension viscosity; η_0 is the vehicle viscosity; n is a structure-dependent parameter and has a value between 2 and 3 for several suspension systems. Fig. 4 shows the resulting $(1-{\eta_r}^{-1/3})$ versus solid concentration curve. A linear relationship with a satisfactory correlation factor ($R^2=0.969$) is obtained. From Eq. (1), it is clear that when φ is close to Φ_m the relative viscosity (η_r) is becomes infinite, i.e. ${\eta_r}^{-1/3}=0$, and Eq. (1) is expressed as,

$$1=a\Phi_m+b \tag{3}$$

Therefore, the maximum solid concentration can be determined by extrapolating the value $1-{\eta_r}^{-1/3}$ to 1. This operation gives $\Phi_m=0.23$ for SiO_2/HDDA suspension, which is much lower than that of the random close packed ($\Phi_m=0.64$) mono-sized particles. This can be explained by the effective soft-sphere model. Most ceramic suspensions can be classified as soft-sphere system; i.e. repulsive interactions occur some characteristic distance away from the particle surface. For sterically stabilized SiO_2/HDDA suspension, the distance is determined by the adsorbed MEMO thickness. According to soft-sphere model the effective hydrodynamic size of a colloid particle is increased over its geometrical size by the increment h^* due to the steric repulsion [9]. Therefore, Φ_{eff}

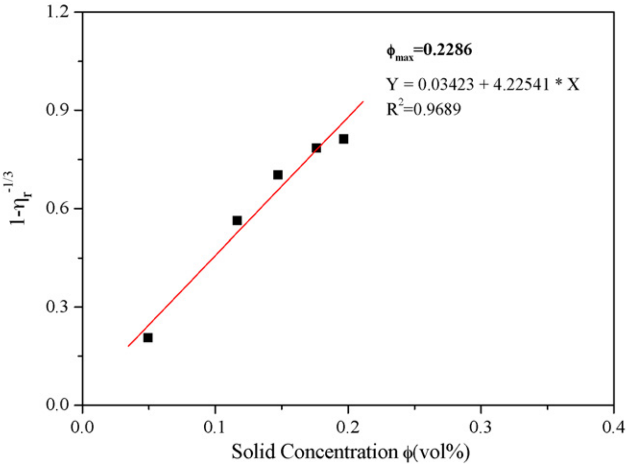

Fig. 4. Resulting $(1-\eta_r{}^{-1/3})$ versus solid concentration curve.

is enhanced by the volume occupied by the preferentially adsorbed MEMO around each particle, according to [10]:

$$\Phi_{eff} = \Phi_m \left(\frac{1+h^*}{a}\right)^3 \qquad (4)$$

By assuming $\Phi_{eff} = 0.64$, which corresponds to that of the random close packing of mono-sized particles, $h^*/a = 0.41$ can be obtained at $\Phi_m = 0.23$ (obtained from Fig. 4). This suggests that the effective particle size was increased by 41% for MEMO-modified SiO_2 due to the steric repulsion.

The above results suggest that the steric-hinderance and a higher proportion of free carbonyl groups on the grafted MEMO can effectively improve the dispersibility of nano-sized SiO_2 in HDDA suspensions.

Fig. 5 shows the FTIR spectra of the SiO_2 particle modified with different MEMO concentrations. An absorption peak at around 1640 cm^{-1} attributed to C=C stretching of MEMO were observed, indicating MEMO silane adsorbed on the SiO_2 surface. Fig. 6 demonstrates the FTIR spectra of the coatings after UV curing. It is found that the absorption peak at around 1640 cm^{-1} attributed to C=C stretching disappears after UV curing. It indicates that full conversion of C=C groups of HDDA and MEMO into polyacrylate chains has been achieved. Therefore, the MEMO-modified SiO_2 particles can crosslink with acrylate resin, which results in the formation of three dimensional networks.

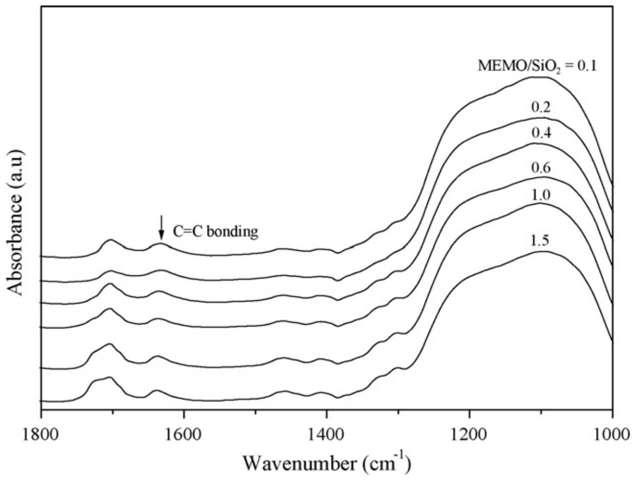

Fig. 5. FTIR spectra of the SiO_2 particle modified with different MEMO concentrations.

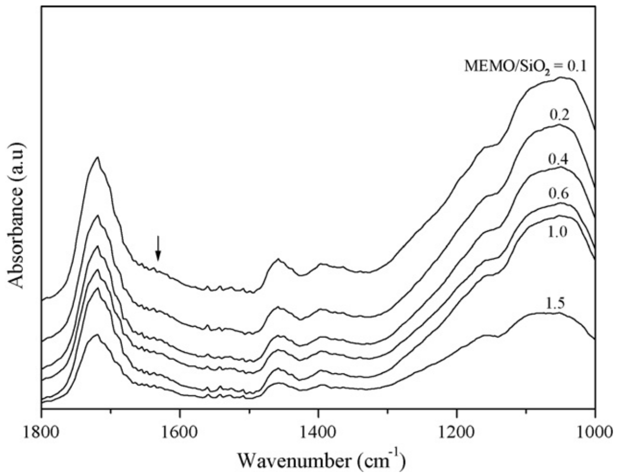

Fig. 6. FTIR spectra of the coatings after UV curing.

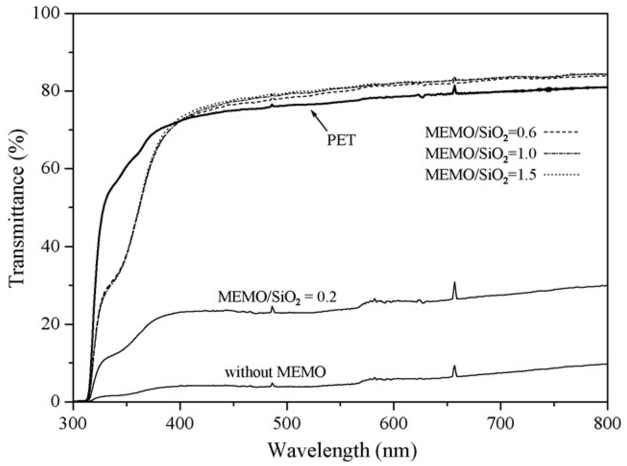

Fig. 7. UV–visible transmittance spectra of the PET film and coatings with different concentration of MEMO before abrasion test.

The UV–visible transmittance spectra of the PET film and coatings with different concentration of MEMO before and after abrasion test are shown in Figs. 7 and 8, respectively. After application of coating the transmission has been lowered for the coating with MEMO/SiO_2 weight ratio of 0.2 and increased for the

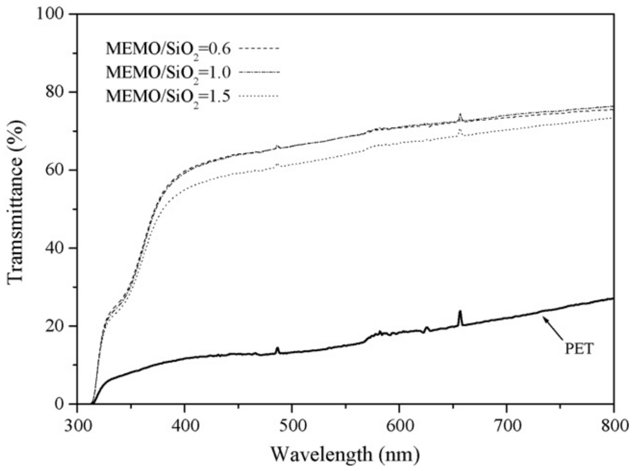

Fig. 8. UV–visible transmittance spectra of the PET film and coatings with different concentration of MEMO after abrasion test.

Table 1
Pencil hardness results for the coatings.

Sample	Pencil hardness
No-MEMO	4H
NOSI	4H
02C	4H
06C	6H
10C	6H
15C	6H

No-MEMO: coating with addition of 3 wt% unmodified SiO_2 particle.
NOSI: coating consisting of hydrolyzed MEMO, HDDA monomer, and commercial UV-curable acrylate resin without addition of SiO_2 particle.

MEMO/SiO_2 weight ratio above 0.6 compared to PET film (Fig. 7). Moreover, the abrasion resistance is improved as the MEMO/SiO_2 weight ratio increases above 0.6 (Fig. 8). The pencil hardness results for the coatings are shown in Table 1. The pencil hardness was improved as the MEMO/SiO_2 weight ratio was increased above 0.6. For the coating (NOSI) consisting of hydrolyzed MEMO, HDDA monomer, and commercial UV-curable acrylate resin without addition of SiO_2 particle, the pencil hardness is 4H. The coating with a high SiO_2 particle concentration (above 3 wt%) cannot be attainable for the sample added with unmodified SiO_2 particle due to too high viscosity of the suspension resulted from the occurrence of strongly flocculated SiO_2 particle in acrylate resin. Thus, the pencil hardness of the coating with addition of 3 wt% unmodified SiO_2 particle (No-MEMO) is only 4H. For the sample with addition of SiO_2 particle modified with MEMO/SiO_2 weight ratio of 0.2, the SiO_2 particle concentration can be increased above 12.5 wt%, yet the pencil hardness exhibits only 4H and the UV–visible transmission is low. It is due to the incomplete MEMO coverage on the SiO_2 surface, leading to poor dispersion of SiO_2 particle in acrylate resin. On the other hand, as the MEMO/SiO_2 weight ratio increases from 0.2 to above 0.6, the abrasion resistance is significantly improved (Fig. 8) and the pencil hardness increases from 4H to 6H, which may be attributed to the complete MEMO coverage on the SiO_2 surface, thereby enhancing the dispersion, compatibility, and cross-linking density between the MEMO-modified SiO_2 particles and acrylate resin.

4. Conclusion

The steric-hinderance established on the nano-sized SiO_2 surface due to the grafted MEMO can effectively improve the dispersibility of nano-sized SiO_2 in acrylate suspensions. Newtonian and shear thinning flow behaviors were found for the MEMO-modified nano-sized SiO_2 in acrylate solutions at low and high solid concentrations, respectively. Moreover, the maximum solid concentration was estimated to be 0.23. The abrasion resistance and pencil hardness of the MEMO-modified nano-sized SiO_2/acrylate coatings can be significantly improved as complete MEMO coverage existed on the SiO_2 surface.

Acknowledgment

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