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PREPARATION AND CHARACTERIZATION OF BIOMASS-BASED EPOXY ADHESIVES WITH SILANE-TREATED SILICAS

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ABSTRACT

In this work, we prepared biomass-based epoxy adhesives with silane-treated silicas. The effect of three types of silane-treated silicas on adhesive characterization of epoxidized soybean oil (ESO)/epoxy adhesives with different contents of ESO, i.e, 0.5, 1.0, and 2.0 wt.% was studied. As a result, the lap shear strength of the adhesives was increased as a polar component of surface free energy and oxygen functional groups of the silicas. The lap shear strength of the adhesives was also increased with increasing ESO content upto 2.0 wt.%. Consequently, ESO was one of the candidate materials for improvement of adhesives in bio-based epoxy adhesive system.

KEYWORDS: biomass-based epoxy adhesives, silane-treated silicas, epoxidized soybean oil (ESO), lap shear strength

INTRODUCTION

Epoxy resins are used widely as coatings, electronic materials, adhesives, and structural applications owing to their outstanding mechanical performance, good chemical and electrical resistance and superior dimensional stability. However, some of the properties of epoxy resins are non-beneficial, such as the inherent brittleness due to the high cross-linking density formed in curing, which limits their many end-use applications. Additions of inorganic particles has been performed to solve those problems [1-6].

As an inorganic filler, silica has been widely used to create high-performance or high-function materials over the last few decades. Silica particles can be used for reinforcement of polymer matrices to lower shrinkage upon curing, as well as for decreasing thermal expansion coeffcients and improving adhesion properties, abrasion resistance, and corrosion resistance [7-10].

Various methods used to modify the surface properties and dispersion of the silicas are largely introduced in terms of thermal, chemical, electrochemical, and coupling agent treatments. Among them, silane coupling treatment is known to be a very effective method for improving the interfacial adhesion between silicas and matrices [11-15].

Recently, epoxidized soybean oil (ESO) have attracted considerable attention due to the increasing emphasis on environmental issues and the Earth's limited petroleum reserves. ESO ploymers from renewable resources, such as vegetable oils-based polymers, replace of petroleum-based polymers, can be used as toughening agents in fabricating improved of resins [16-21].

In this work, ESO and silane-treated silicas were used as modifiers to increase the adhesion of epoxy resin. The biobased epoxy adhesives were characterized by Fourier transform infrared spectroscopy (FT-IR), N_2/77 K adsorption (BET), universal test machine (UTM), and scanning electron microscope (SEM) measurements.

MATERIALS AND METHODS

Materials

The epoxy resins used were the diglycidyl ether of bisphenol-A (DGEBA, EEW=184-190g/eq) supplied from Kukdo Chem. Co. Epoxidized soybean oil (ESO, Mn:1469 g/mol, Mw:1527 g/mol, 1H-NMR spectra 5.3 ppm, 2.9-3.1 ppm, 13C-NMR spectra

129.7-130.2 ppm, 54.0-54.3 ppm) [22] was prepared by a version of a previously reported method. 4,4'-diaminodiphenyl methane (DDM) was used a curing agent without further purification. Ultrasil silicas (Primary particle size 14 nm, specific surface area 180 m^2/g) were used as filler and reinforcement of cured networks from Degussa Co. γ-methacryloxy propyltrimethoxysilane (MPS, Shinetsu Co.), γ-glycidoxy propyl trimethoxy silane (GPS, Shinetsu Co.), and γ-mercapto propyl trimethoxysilane (MPTS, Sigma-Aldrich) were used as silane coupling agents. Fig.1 shows the chemical structures of the silane coupling agents and the synthesis route of ESO.

Preparation of silane-treated silica

All of the silane coupling agents were prepared under constant conditions for surface modification of silicas nanoparticles. In these solutions, a cosolvent of methanol (95 wt% in total solvent) and distilled water (5 wt% in total solvent) was used, and the silane concentration was fixed at 0.4 wt%. After the silane coupling agents were hydrolyzed for 1 h with acetic acid solution, the silicas were dipped in the hydrolyzed silane solution for 1 h and dried at 120°C for 3 h. The samples were named as as-received, γ -MPS, γ -GPS, and γ - MPTS.

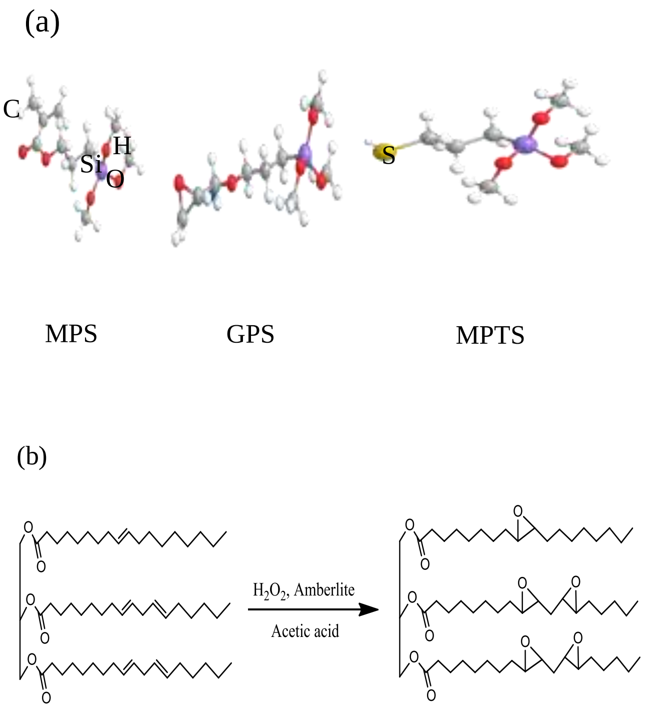


Fig. 1. (a) Chemical structures of the silane coupling agents (b) Synthesis route of ESO

Preparation of the adhesives

The ESO and silicas treated with three different coupling agents in epoxy resins were mixed under stirring after melting at 80°C. 10 wt% silane-treated silica and ESO were added from 0.5 to 2.0 wt% to the resin mixtures and then mixed via melt-mixing at 80°C. 20.3 wt% of the curing agents were added and mixed with the composites. Thereafter, the adhesives was applied to the each substrate materials, placed in a oven at 120°C for 3 h. The samples were named as non-specimens (non-spe), MPS-specimens (MP-spe), GP-specimens (GP-spe), and MPTS-specimens (MPTS-spe).

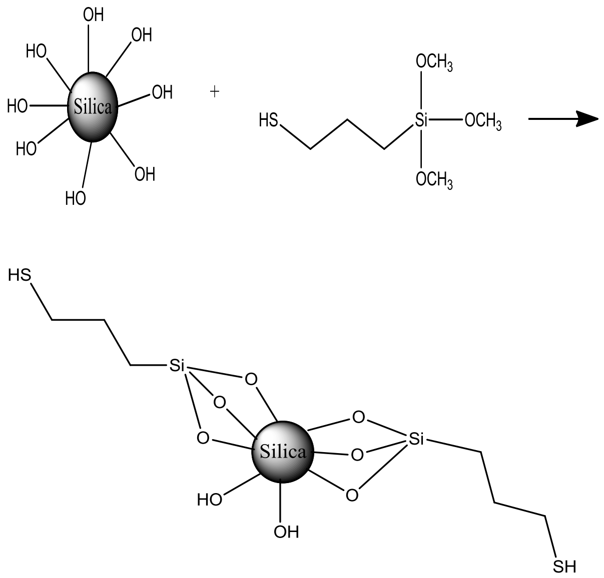


Fig. 2. Schematic diagram of the MPTS silane treatment mechanism on silica surface

Also, MPTS silane-treated silica-filled epoxy and ESO were blended to obtain the modified network at a weight ratio of 0.5, 1.0, and 2.0. A schematic diagram of the MPTS silane treatment mechanism was shown in Fig. 2. The samples were named silica-filled epoxy/ESO 10:0 (non-ESO), silica-filled epoxy/ESO 10:0.5 (ESO-0.5), silica-filled epoxy/ESO 10:1.0 (ESO-1.0), and silica-filled epoxy/ESO 10:2.0 (ESO-2.0).

Measurements

The surface funtional groups of silane-treated silicas were recorded using an FT-IR spectrophotometer (Nicolet-is10, Thermo). The equilibrium spreading pressure (π_e) of the silane-treated silicas were determined by gas adsorption. The physical adsorption of gased was measured using a Belsorp Max (BEL Japan) at 77 K. The samples were degassed at 298 K for 6 h to obtain a residual pressure of less than 10^{-3} torr. The amount of N_2 adsorbed on the samples was used to calculate the Brunauer-Emmett-Teller (BET) equation. The thermal stability of the adhesives was measured via a thermogravimetric analysis (TGA-50, SHIMADZU Co.) from 30 to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The lap shear test of the adhesives was measured according to ASTM D1002 [23] using a universal test machine (UTM). For each formulation, five specimens were tested at least. To investigate the phase morphology of the specimens, the surface of adhesives were examined by using a fied emission scanning electron microscope (FE-SEM, JEOL 6701F).

RESULTS AND DISCUSSION

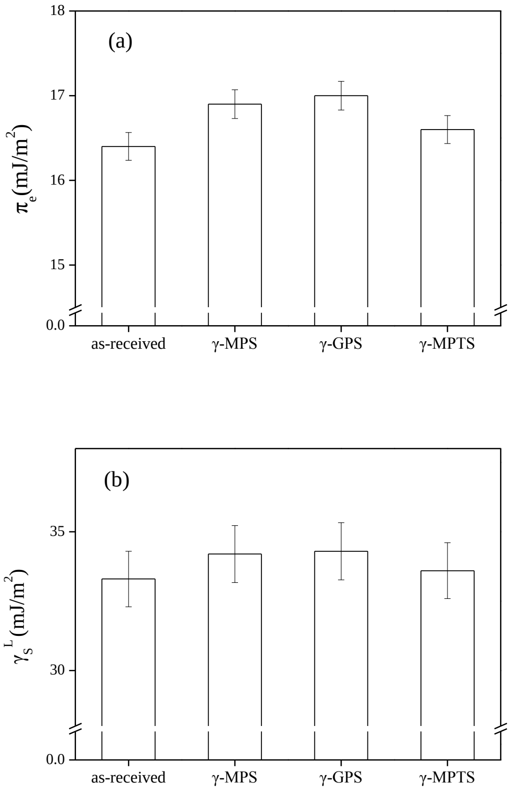


Fig. 3. (a) Equilibrium spreading pressure (π_e) and (b) London dispersive component of surface free energy (γ_s^L) of the silane-treated silica.

Fig. 3 shows the equilibrium spreading pressure and London dispersive component of surface free energy of the silane-treated silica. As an experimental result, the silane treatment leads to increases in both π_e and γ_s^L, which means that silane treatment is one of the effective methods in improving the stability of the dispersions of silica.

When the nitrogen adsorbate is considered in the adsorption studies, the equilibrium spreading pressure π_e can be determined by using the integrated form of the Gibbs equation [24, 25]:

$$-\Delta G_A(N_2) = RT\int_0^1 \frac{a}{a_0}\, d\left(In\frac{P}{P_0}\right) \qquad (1)$$
$$= N_A a_{N_2}\pi_e \qquad (2)$$

where R is the ideal gas constant, T the absolute temperature, a the amount adsorbed at a relative pressure P/P_0, a_o the amount adsorbed for filling a monolayer, N_A the Avogadro's number, and $a_N{}^2$ the cross-sectional area of the adsorbed nitrogen.

Therefore, π_e can be calculated according to Eqs. (1) , (2):

$$\pi_e = \frac{RT}{N_A a_{N_2}\pi_e}\int_0^1 a\, d(In\, P/P_0) \qquad (3)$$

From the values obtained for the nitrogen adsorbate, it is of interest to determine the London dispersive component, γ_s^L, of surface free energy of the silica studied at 77 K adsorption. The relationship between γ_s^L and π_e for a solid surface is given by the following equation [26];

$$\gamma_S^L = \frac{(\pi_e + 2\gamma_{N_2})}{4\gamma_{N_2}^L} \qquad (4)$$

Where subscript S and superscript L represent the solid state and London dispersive component of surface free energy, respectively, and $\gamma_S^L = \gamma_{N_2} = 10.5\ mJ/m^2$ [27].

The FT-IR spectra of MPTS silane-treated silica are shown in Fig. 4. The peaks at 794 cm^{-1} (Si-O-Si symmetric stretch), 963 cm^{-1} (Si-OH vibration), 1104 cm^{-1} (Si-O-Si asymmetric stretch), 1600-1800 cm^{-1} (-COOH, C=O groups), and 3450 cm^{-1} (-OH groups) are found in the silica surfaces. This indicates that the silane coupling treatment efficiently stimulated oxygen functional group formation on the silica surfaces [28,29].

Fig. 5 represents the lap shear strength values of the adhesives with different coupling agents. These adhesion strengths of the silane-treated silica are much higher than those of the as-received. And the adhesives treated by MPTS shows the superior interfacial adhesion in the present system. That is, the strong interaction between the distribution of the cross-linked aggregation on Cu substrate and the silicon wafer is attributed to the coupling agents resulting in increasing the adhesion of the adhesives [30, 31].

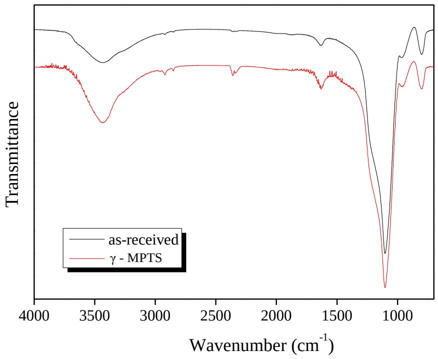


Fig. 4. FT-IR spectra of the MPTS silane-treated silica.

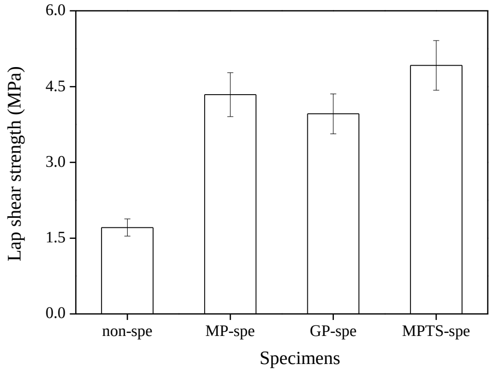
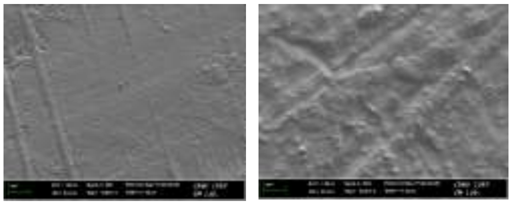


Fig. 5. Lap shear strength of the silicas-filled epoxy adhesives as a function of silane coupling

Fig. 6 shows the morphology of the specimens after lap shear tests [32,33]. It is observed that the surfaces of the silane-treated silica adhesives are smooth. However, non-spe were ununiform distribution of silica with rough surface was observed. It is seen that in the case of non-spe, the aggregated vary in shape from individual spheroidal particles, to clusters, but those of silane-treated silica are well dispersed. This indicates that some amount of toughness has been induced in the resin due to the incorporation of silica.

Good linearity between the London dispersive component of surface free energy and the resulting lap shear strength is shown in Fig. 7. The result indicates that the lap shear strength of the adhesives filled with MPS or MPTS treated silica is higher than that of the adhesives filled with as-received or GPS treated silica. Thus, we can recognize that the increasing γ_s^L (or π_e) of silane-treated silica is important for improving the degree of adhesion between the epoxy resins and the silane-treated silica [34].



(a) (b)

Fig. 6. SEM images of the silicas-filled epoxy adhesives; (a) non-spe and (b) MPTS-spe

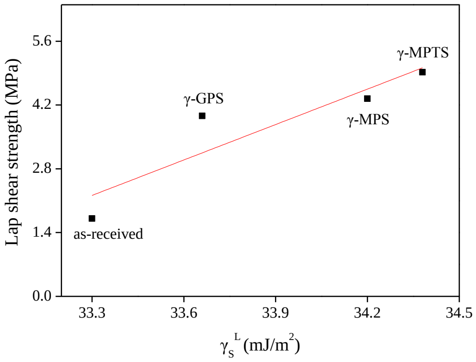


Fig. 7. Dependence of lap shear strength on the London dispersive component of surface free energy of the silicas-filled epoxy composite adhesives (R=0.91)

The thermal degradation behaviors of Epoxy/ESO blends is studied with TGA at a heating rate of 10 °C/min in a nitrogen atmosphere and the TGA thermograms of the blends are shown in Fig. 8. Thermal stability factors, including initial decomposed temperature (IDT) and temperatures of maximum rate of degradation (T_{max}) of the blends can be determined from the TGA thermograms.

The results of the IDT and T_{max} of the blends are listed in Table 1. As a results, it is confirmed that the decomposition of the blends commences near at 269 °C and rapidly continues until 389 °C. From which, it can be confirmed that the blends have excellent thermal stability. Whereas, the IDT of the blends is little decreased from 271 to 269 °C with increasing the ESO content, this is attributed to the reduced cross-linking density of the epoxy network, due to the incompletely curing reaction [35,36].

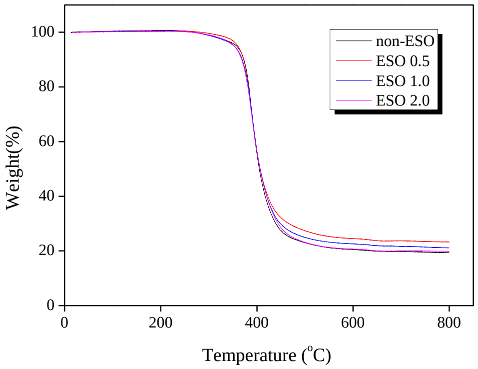


Fig. 8. TGA thermogram of Epoxy/ESO blends

Table 1. Thermal stabilities of cured Epoxy/ESO blends

	IDT (°C)	T_{max} (°C)
Non-ESO	271	390
ESO 0.5	284	387
ESO 1.0	267	389
ESO 2.0	269	389

Fig. 9 shows the effects of the ESO content on the lap shear strength values of the adhesives with MPTS coupling agents. It can be seen that the lap shear strength values of the specimen increased with increasing ESO content to 2.0 wt%. The introduction of the flexible aliphatic chain of ESO into the epoxy matrix leads to a decrease of the internal stress of the network structure, resulting in an improved bonding strength in the DGEBA/ESO blends [13].

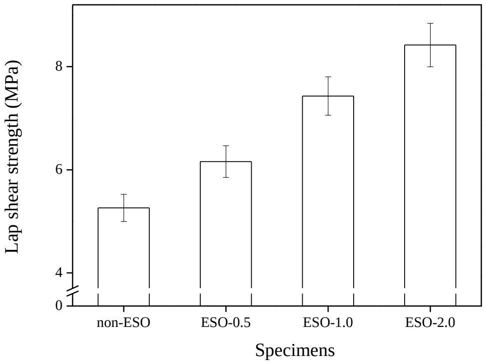


Fig. 9. Lap shear strength of the MPTS silane-treated silicas-filled epoxy adhesives as a function of ESO content.

CONCLUSIONS

In this study, the additions of silane-treated silica and epoxidized soybean oil (ESO) were carried out to improve the adhesion properties of epoxy adhesives. The experimental results showed that the lap shear strength of the adhesives was increased as the polar component of surface free energy and oxygen functional groups of the silica, which led to an improvement of the adhesion force of the adhesives. Consequently, the surface treatment of silica with silane coupling agents was a good method to improve the adhesions in the silica-filled adhesives. The lap shear strength of the adhesives was increased with increasing ESO content upto 2.0 wt% ESO. The lap shear strength and thermal stability at low ESO contents showed similar values to those of the neat epoxy resin. The results confirmed that ESO was one of the candidates for use as biomass-based adhesives.

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