

Epoxy Coatings Physically Cured with Hydroxyl-contained Silica Nanospheres and Halloysite Nanotubes

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ABSTRACT

Epoxy coatings are usually reinforced by the use of nanofillers, but reactive nanofillers having physical tendency towards epoxide ring opening are preferable. In this work, nanosilica (SiO₂) and halloysite nanotubes (HNTs) known for their hydroxyl-contained surface are used and their effects on the curing behavior of an epoxy/amine coating is compared. The spherical and tubular nanoparticles used in epoxy led to somewhat different crosslinking. Epoxy/amine systems containing equivalent amount of silica spherical and halloysite nanotube particles were compared for their cure characteristics, i.e. temperatures of starting and ending of curing reaction (T_{ONSET} and T_{ENDSET}), the exothermal peak temperature (T_p), the temperature range among which curing reaction was completed ($\Delta T = T_{ENDSET} - T_{ONSET}$) and the total heat of curing reaction (ΔH). Fourier-transform infrared spectrophotometry and scanning electron microscopy analyses were used to assess formation of SiO₂. Nonisothermal differential scanning calorimetry was performed at different heating rates and cure characteristics together with values of glass transition temperature of two kinds of systems containing SiO₂ and HNTs were calculated, where both nanofillers revealed accelerating role in epoxy curing reaction. Prog. Color Colorants Coat. 11 (2018), 199-207 © Institute for Color Science and Technology.

1. Introduction

Epoxy resins have been used for formulating high performance coating because of properties such as light weight, good wettability and formation of strong bonds with many polar high-energy substrates, low shrinkage during cure, superior mechanical strength, remarkable chemical/corrosion resistance, and ease of processability [1-5]. The properties of polymers can be strongly affected by nanomaterials even at low contents because of their special properties like tendency to reaction with polymers with their surface functional groups and the large surface to volume ratio which

results to enter to a domain that quantum effects are predominated [6-11]. Thus, in recent years it has become popular areas to use different kind of nanomaterials such as alumina [12], silica [13, 14], clay [15], carbon nanotube [16], and graphene oxide [17], to improve the properties of epoxy resins.

Along with the importance of nanomaterials size, their properties such as high surface area and high surface energy, are also shape-dependent [18]. Also, physical and chemical properties of nanoparticles like thermal stability, selectivity, activity, electrical and optical properties, are depends on the actual shape of

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nanoparticles and their surface chemistry [19]. Typically, in addition to relation of final properties of polymers to the nanomaterial shape and size their interaction with polymers by the chemical functionalities on their surface is effective. It is found that not only the type of chemical groups on the surface of nanoparticles but their relative arrangement and number of functional groups also plays a key role in their interaction with polymers. Recent research has demonstrated that the use of different forms of nanoparticles can greatly affect the properties of epoxy resins [20, 21]. In our research group effect of various types of micro/nanoparticles with different surface chemistry such as carbon nanotube [22], magnetic nanoparticles [23-26], silica and alumina [27], zinc oxide [28, 29] and graphene oxide [30-32] on properties and cure behavior/kinetics of epoxy resin was investigated.

Among zero-dimensional nanostructures (also known as nanoparticles) silica has been widely used as reinforcement in epoxy resin to make appropriate properties [33, 34]. Through the second type of nanostructures it means one-dimensional or nanotubes the interest in the study of halloysite nanotubes (HNTs) with very advantageous features such as high ratio of length to diameter (L/D), acceptable level of porosity, and large surface area, in epoxy resins is enriched in recent years [35, 36]. HNTs are clay minerals that occur naturally in the form of nanotubes resemble to that of multi-wall CNTs with a 1:1 Al:Si ratio and a structural formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ [37].

Final properties of epoxy nanocomposites highly impressed by 3D cross-linked microstructure that formed through the curing reaction. Therefore, investigation of the potential of new developed epoxy/nanoparticle composites to achieve highest possible conversion is an essential requirement. So, a key factor for understanding structure–property relationships of epoxy nanocomposites is exact tracing of the cure process in order to control curing reactions to optimize the properties of the final product.

Regards to wide range of type, shape and surface chemistry of nanoparticles there is still a long way to go to distinguish the exact role of nanomaterial in formation of epoxies cross-linked microstructures. In the current study the effect of individual HNT and silica on epoxy cure behavior were discussed based on calorimetric analyses. Dynamic differential scanning calorimetry (DSC) was performed to measure cure characteristic of epoxy nanocomposites such as heat of

cure, onset, peak and endset temperature.

2. Experimental

2.1. Materials

Epoxy resin used in the current work was semisolid polyfunctional phenol novolak glycidyl ether (Araldite EPN 1180) with epoxide equivalent weight of 175–182 geq^{-1} which was provided by Huntsman. The curing agent used was EPIKURE F205 (Hexion). Halloysite nanotube (HNT) was supplied from Hunan Province, China. According to the supplier data, this material had the length of 100–3000 nm, external diameter of 50–200 nm, internal diameter of 15–70 nm, specific surface area of 26.29 m^2g^{-1} and pore volume of 0.122 cm^3g^{-1} . Ammonium hydroxide (32%), Tetraethyl orthosilicate (TEOS), ethanol, and dimethylformamide (DMF) were purchased from Merck.

2.2. Preparation of silica nanoparticles

Silica nanoparticles were prepared through Stober method [13]. First, ethanol (25 mL) and 32% aqueous ammonia solution (1.5 mL) were mixed under stirring for 10 min. Then, TEOS (2 mL) was added to the mixture and stirred mechanically at room temperature for 24 h. The portion of nano-scale powders was collected utilizing centrifugation (6000 rpm, 10 min) and washed four times with ethanol. The samples were subsequently dried at 80 °C for 5 h under vacuum.

2.3. Preparation of epoxy nanocomposites

Epoxy nanocomposites comprising 1 wt% silica and HNT nanoparticles were prepared through the following procedure. Firstly, different nanoparticles were dispersed in ethanol under sonication for 10 min then the mixture were homogenized by high speed homogenizer at 12000 rpm for 20 min. Then, The resulting mixture was added in EPN1180 with 20 wt% DMF as solvent and sonicated (50% duty cycle) for 15 min and then the mixture was mixed by a mechanical mixer working at 3000 rpm at 80 °C for further 30 min. Eventually, The resulting composite was degassed at 80 °C for 5 h in a vacuum oven.

2.4. Characterization methods

The synthesized silica nanoparticle was performed on a FT-IR instrument (Spectrum one, PerkinElmer Inc., Boston, MA). FT-IR spectra were collected using a

KBr pellet in a transmission mode in the wavenumber range of 4000-400 cm^{-1} with resolution of 4 cm^{-1} .

The particle size and morphology of the resulting silica particles were visualized by a scanning electron microscopy (Zeiss model Supra 25). The samples were dispersed in ethanol by 15 minutes of sonication. The disc was pasted with copper tape, and the sample dispersed over the tape or an aluminum foil. Then, disc was coated with gold in an ionization chamber.

Cure behavior of epoxy, epoxy/1HNT and epoxy/1silica nanocomposites was investigated in non-isothermal condition on a calorimeter (NETZSCH 200F3 Maia, Netherland) under nitrogen atmosphere varying the heating rate (5, 10, 15, and 20 $^{\circ}\text{C}/\text{min}$).

3. Results and Discussions

3.1. Fourier-transform infrared spectroscopy (FT-IR)

The FT-IR spectra (Figure 1) of the silica colloidal nanoparticles shows absorption bands arising from

asymmetric vibration of Si-O (1095 cm^{-1}), asymmetric vibration of Si-OH (952 cm^{-1}), and symmetric vibration of Si-O (799 cm^{-1}). The broad peak between 3300 cm^{-1} and 3500 cm^{-1} was related to stretching vibration bonds of hydroxyl group (O-H). Also this band can be cross checked through the 1632 cm^{-1} band due to scissor bending vibration of molecular water [38].

3.2. Scanning electron microscope (SEM)

SEM micrograph of synthesized silica nanoparticles are shown in Figure 2. As apparent, silica nanoparticles were successfully synthesized in spherical shape. The mean size of silica particles are 188.63 nanometer and standard deviation of 43.65.

3.3. Cure behavior

The effect of HNT and silica nanoparticles on cure characteristics of the epoxy resin was studied by non-isothermal DSC experiments. The cure behavior of neat epoxy, epoxy/1HNT and epoxy/1silica in different

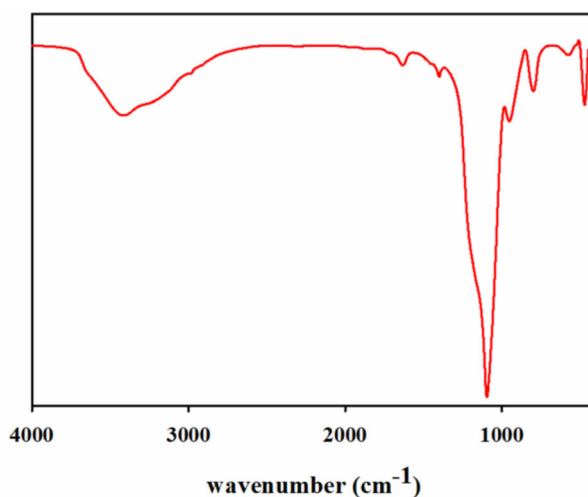


Figure 1: FT-IR spectra of Silica nano particles.

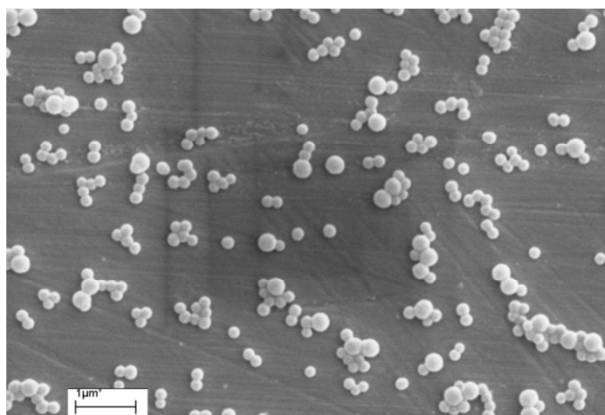


Figure 2: Electron micrograph of synthesized silica spheres.

heating rates ($\beta = 5, 10, 15$ and $20\text{ }^{\circ}\text{C min}^{-1}$) are shown in Figure 3. Also, the maximum exothermal peak temperature (T_p), heat of reaction (ΔH), which is calculated as the total area under the exothermic curve,

based on the extrapolated baseline at the end of the reaction, and the initial and final cure temperature (T_{ONSET} and T_{ENDSET}) of samples at different β are presented in Table 1.

Table 1: Curing characteristics of prepared samples evaluated from DSC thermograms recorded at different heating rates.

Designation	B ($^{\circ}\text{C/min}$)	T_{ONSET} ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_{ENDSET} ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)	ΔH_{∞} (J/g)
Epoxy	5	24.710	86.014	230.913	206.203	331.043
	10	30.540	97.314	272.818	242.278	375.118
	15	40.547	104.470	287.713	247.166	380.465
	20	41.387	110.389	295.947	254.560	430.947
Epoxy/1HNT	5	18.864	85.952	217.289	198.425	347.935
	10	29.219	98.603	243.699	214.480	393.901
	15	32.075	106.060	260.033	227.958	365.064
	20	40.417	111.697	260.010	219.593	363.395
Epoxy/1Silica	5	16.771	85.863	215.166	198.395	380.745
	10	28.707	97.898	243.497	214.790	386.727
	15	32.550	105.532	250.961	218.411	386.273
	20	39.715	111.354	275.239	235.524	383.199

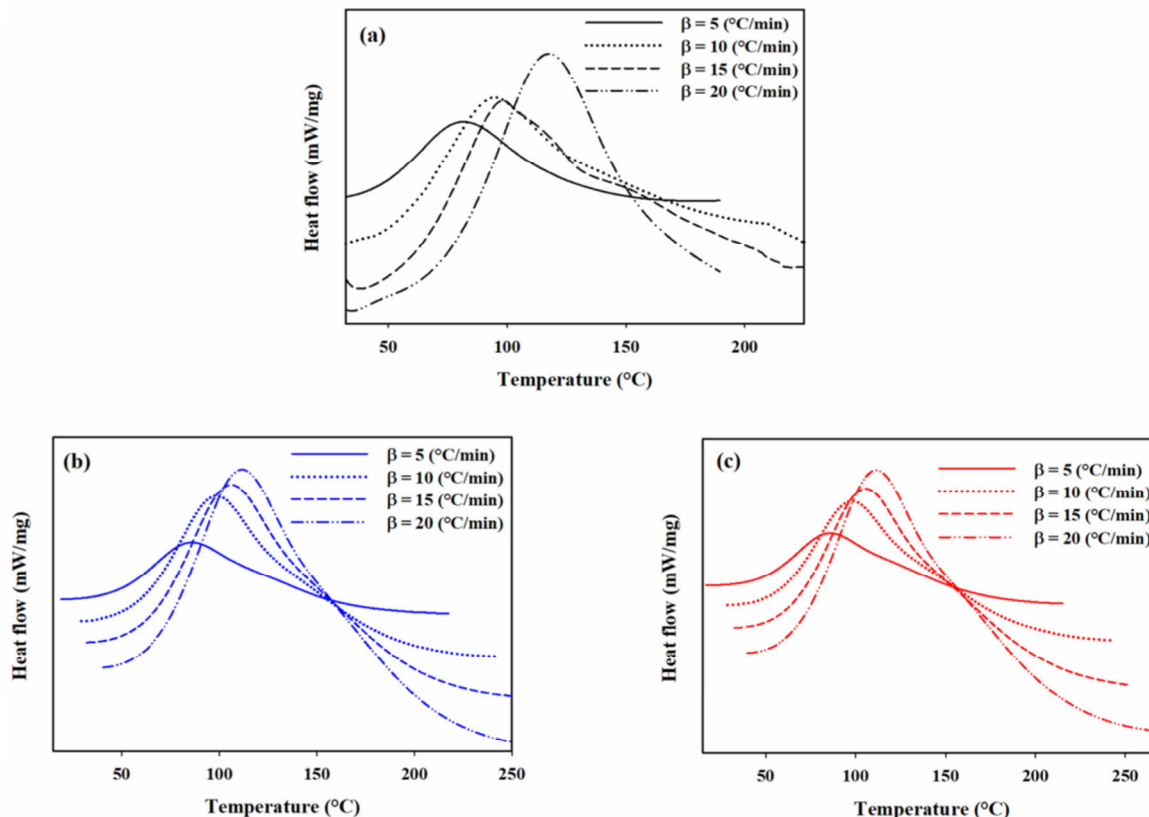


Figure 3: Dynamic DSC thermograms of epoxy-amine systems at different β of 5, 10, 15, and $20\text{ }^{\circ}\text{C min}^{-1}$ (a) neat epoxy, (b) epoxy/1HNT and (c) epoxy/1silica.

As can be observed from Figure 3, a single exothermic peak is appeared in the thermograms irrespective of heating rate. This suggests that the presence of HNT and silica nanoparticles in the epoxy resin does not change the cure reaction mechanism. Therefore, it is supposed that the cure reaction in all samples proceeds mainly with the epoxy-amine ring opening reaction [39].

By increasing heating rate which leads to increase of the kinetic energy of the system per molecule both T_p and T_{ONSET} shifted to higher temperature for neat epoxy and its nanocomposites containing HNT and silica (Table 1). This result can be ascribed that lower heating rates offered longer time for the reaction of chemical groups. However, at higher heating rates, due to lack of appropriate time DSC curves shifted to a higher temperature to compensate for the reduced time [40].

Comparing results of unfilled epoxy and filled epoxy nanocomposites reveals that T_{ONSET} decreases while a small increase can be seen in T_p at presence of nanoparticles. HNT and silica nanoparticles due to their hydroxyl-rich structure which can participate in epoxy ring opening leads to a fall in T_{ONSET} and ΔT . Less decrease in T_{ONSET} of epoxy/HNT in comparison with epoxy/silica was attributed to the low number of OH groups in outer surface of HNT nanotubes compared with silica nanoparticles which have large number of hydroxyl groups. Occurrence of this autocatalytic reaction at early stage of cure accelerates the gelation phenomenon and increases the viscosity of the system which leads to increase in T_p .

Furthermore, total heat of reaction (ΔH) for epoxy/HNT and epoxy/silica increase compared to the values calculated for the unfilled epoxy-hardener system in at lower heating rates where there is longer time for the reaction of chemical groups. At $\beta=5\text{ }^{\circ}\text{C min}^{-1}$ the total heat released during curing reaction increased from 331 Jg^{-1} for neat epoxy to 380 Jg^{-1} for epoxy/silica due to facilitation of curing reaction because of hydroxyl-rich structure of silica nanoparticles. In comparison with epoxy/silica, epoxy containing HNT shows lower ΔH due to the lower number of OH groups in outer surface of HNTs. Moreover, effect of these two kinds of nanoparticles with different OH number on their surface on cross-linking of epoxy/amine system is schematically illustrated in Figure 4. By contrast, ΔH of the epoxy at presence of both HNT and silica nanoparticles decreased at high β . At higher heating rate due to lack of adequate time the completion of reaction is prevented by restriction of mobility of reactants and molecular diffusion [40].

According to direct correlation between heat of reaction and extent of reaction, consequently the final extent of reaction (α) can be calculated using the following equation [40].

$$\alpha = \frac{\Delta H_T}{\Delta H_{\infty}} \quad (1)$$

where ΔH_T is the heat released during the curing reaction of epoxy at a specific temperature T .

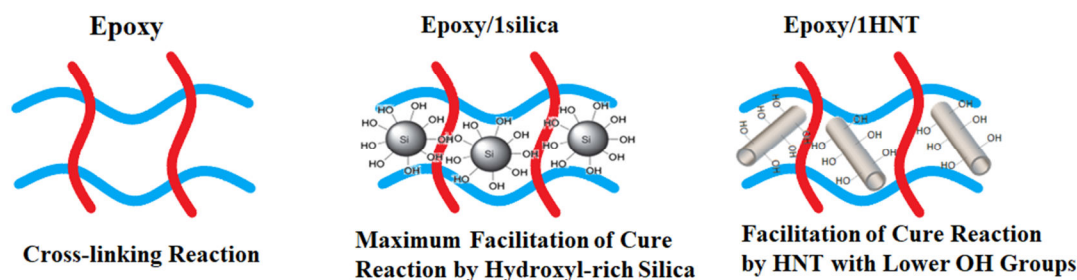


Figure 4: Schematic illustration of hydrogen-rich silica nanosphere and halloysite nanotubes on cross-linking of epoxy/amine system.

Figure 5 demonstrates the fractional extent of conversion vs. time for neat epoxy, epoxy/1HNT and epoxy/1silica at different β . As apparent, HNT and silica nanoparticles could accelerate curing reaction of epoxy-amine after vitrification it means these nanoparticles accelerate diffusion controlled mechanisms regardless of heating rate. These spherical and tubular nanosize particles can diffuse through epoxy conjunction in cross-linked network and participate in ring opening of unreacted oxirane rings which led to accelerating the reaction. As HNT exhibited more acceleration role on the cure reaction of epoxy resin compared to silica, it can be speculated that the steric hindrance is less effective in the HNT filled epoxy resin possibly due to the tubular shape of HNT.

Glass transition temperature (T_g) of cured epoxy-

amine, epoxy/1HNT and epoxy/1silica was listed in Table 2 and obtained from DSC analysis performed at the heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ during the third scan. Epoxy nanocomposites reinforced with both HNT and silica nanoparticles exhibit higher T_g compared with neat epoxy. This enhancement in T_g of epoxy at presence of HNT and silica nanoparticles is due to homogeneous dispersion of these nanoparticles in epoxy matrix as well as interactions between the OH groups on their surface and epoxy rings [41]. In comparison with neat epoxy, 1 wt% silica caused $19\text{ }^{\circ}\text{C}$ rise in T_g which is attribute to increase in the interfacial area between the silica and the epoxy and consequently crosslinking density which mentioned earlier in Table 1. Similar to the results of ΔH , T_g values of epoxy/1HNT less increased compared to epoxy/silica due to lower OH groups on HNT surface.

Table 2: Glass transition temperature (T_g) of the neat epoxy-amine and prepared nanocomposites.

Sample name	T_g ($^{\circ}\text{C}$)
Epoxy	128
Epoxy/1HNT	144
Epoxy/1silica	147

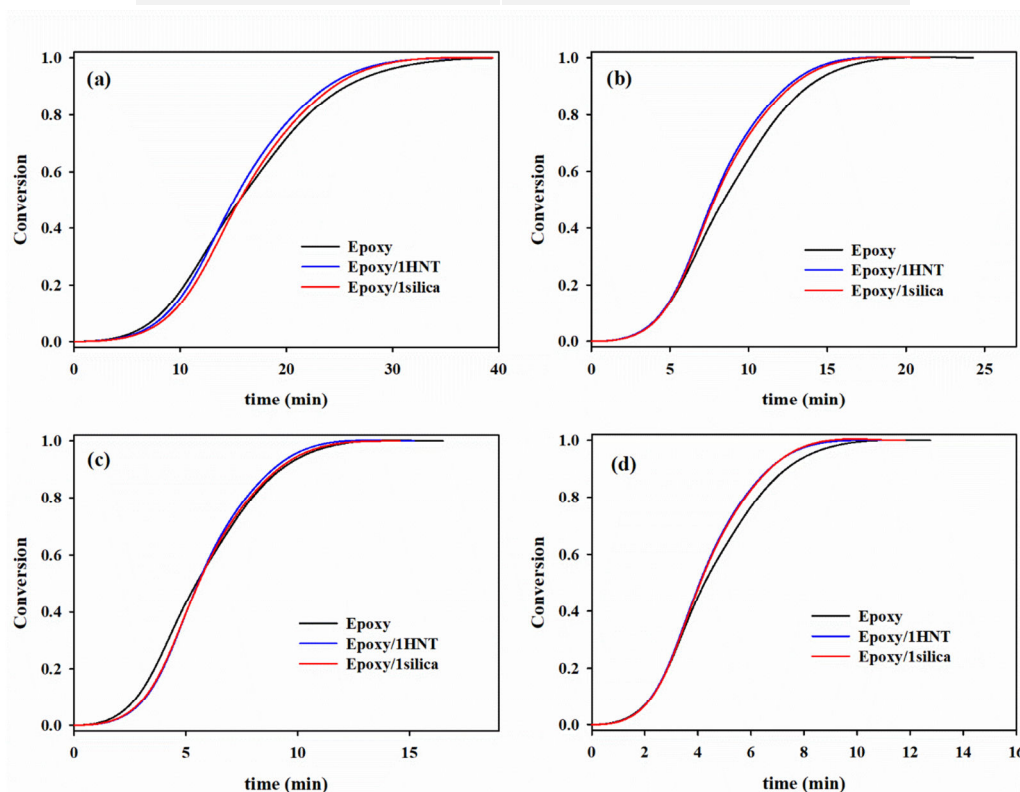


Figure 5: Fractional extent of conversion vs. time for neat epoxy, epoxy/1HNT and epoxy/1silica at four different heating rates (β) of (a) 5, (b) 10, (c) 15 and (d) $20\text{ }^{\circ}\text{Cmin}^{-1}$.

4. Conclusion

Epoxy-amine composites containing spherical silica nanoparticles and tubular HNT was prepared in order to investigate the curing potential of these different shaped nanoparticles for curing epoxy. For this purpose, silica nanoparticle was synthesized via a Stober method. It was confirmed by FT-IR and SEM analyses that the spherical silica nanoparticles were successfully synthesized. From DSC results it was found that the both HNT and silica nanoparticles have the potential increase cross-linking of epoxy resin especially at low heating rates where there is adequate time for curing precursors for reaction. Adding 1 wt%

hydroxyl-rich silica nanospheres significantly increased the heat of cure from 331 J g^{-1} for neat epoxy to 380 J g^{-1} at $\beta=5 \text{ }^{\circ}\text{C min}^{-1}$. This increase in ΔH is less for epoxy/1HNT because of low hydroxyl groups on the surface of HNT. Regardless of heating rate, HNT and silica nanoparticles accelerated curing of epoxy when reaction is under diffusion controlled. The T_g of nanocomposites was found to be higher than the neat epoxy which indicate strong interlocking of OH groups of nanoparticles and epoxy resin. Presence and interaction of HNT and silica nanoparticles with epoxy were able to increase T_g from $128 \text{ }^{\circ}\text{C}$ for neat epoxy to $143 \text{ }^{\circ}\text{C}$ for epoxy/1HNT and $147 \text{ }^{\circ}\text{C}$ for epoxy/1silica.

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