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PROCESSING AND CHARACTERIZATION OF EPOXY NANOCOMPOSITES WITH MWCNT'S/CNF'S USING THINKY AND 3-ROLL SHEAR MIXING TECHNIQUES

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In this work, thinky mixing method was used to disperse multi-walled carbon nanotubes (MWCNT's) and carbon nanofibers (CNF's) in SC-1 epoxy either in isolation or in combination with 3-roll shear mixing. To achieve better dispersion, MWCNT mixing with SC-1 resin directly or pre-mixed with a solvent and then mixed with SC-1 resin after evaporating the solvent. Dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), flexural tests, electrical conductivity tests and micrographic analysis were performed on neat, 0.2 and 0.4wt% MWCNT/CNF infused SC-1 epoxy to observe the loading effect on thermo-mechanical properties of composites. DMA results indicated improvement on storage modulus and glass transition temperature, Tg, while flexural results exhibited enhanced flexural strength and modulus with up to 0.4wt% MWCNT/CNF infused epoxy resin over neat. TGA results revealed improved residue content but almost constant decomposition temperature for nanophased resin compared to neat. However, these enhancements were observed only up to 0.2 wt. % loading after which the properties were seen to either reduce or not significantly improve. These results indicate that the methods used for dispersion is suitable for low weight percent loading only.

Key Words: Nanocomposites, Carbon Nanotubes/Nanofibers, Flexure, Thermo-mechanical properties.

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Introduction

Epoxy resin based materials have superior mechanical, thermal and electrical properties [1] and the use of inorganic fillers to enhance the properties of epoxy resin is a common practice [2]. Multi walled carbon nano tubes (MWCNT's), are becoming excellent nano reinforcing agents for thermosetting polymers for their high strength, thermal and electrical conductivity, stiffness and thermal stability[3] whereas, vapor grown carbon nano fibers (VGCNF's), are also attracting attention for the same purpose due to their high tensile strength, modulus and relatively low cost [4]. However, enhanced properties of the nanophased polymers are possible only when nanoparticle disperses uniformly in the polymers. In order to disperse MWCNT's in polymers, different dispersion techniques have been used. These include; high speed mixing [5, 6], sonication and solution evaporation processing [7-10] and calendaring method [11-14]. Sonication method was effectively used to disperse MWCNT's in epoxy [3]. Although the thermo-mechanical properties of MWCNT infused polymers were improved, some agglomerated CNT's on the fractured surfaces were observed. This was caused by re-agglomeration of MWCNT's during degasification of resins in VARTM [5]. But sonication method reduces the vibrational energy extremely with increasing distance from the sonicator probe. Moreover, local energy input causes the rupture of the CNT's which results in reduction of the effective tube length of MWCNT's [11]. Calendering method indicated to be effective regarding achieved dispersion and signifies to up-scale the capacity to solve the dispersion problem of nano particles for resin systems [13]. But Wichman *et al.* [15] found increased viscosity of the matrix during the degasification of the resin and hardener complicating the RTM processing. To investigate the effective dispersion of MWCNTs in epoxy, a relatively new technique, thinky defoam mixing was employed in isolation/combination with calendaring method in this study. Moreover, a solvent based method was also introduced to investigate any thermo-mechanical and morphological improvement of MWCNT infused epoxy systems. Thinky mixing in isolation/combination was also adopted for VGCNF's to investigate their thermo-mechanical properties of VGCNF infused epoxy resins.

Experiments

SC-1 epoxy resin was purchased from Applied Poleramic Inc. SC-1 and is a two component (Part A: Resin- Diglycidylether of bisphenol A, aliphatic diglycidylether and epoxy toughener, Part B: Hardener- Tetra aliphatic amine blend) room temperature curing epoxy. Unfunctionalized MWCNT's were purchased from Cheaptubes.com, and were of 8-15 nm outer diameter and 10- 50 µm length. PR-24 HHT- High Heat Treated VGCNF's were procured from Applied Science, Inc, and were of 60-100 nm OD and 30-100 µm length. EXAKT 80E type 3-Roll Shear mixing machine from EXAKT Technologies, Inc and Thinky Planetary Vacuum Mixer ARV 310 were used for the dispersing these nanoparticles in the epoxy system (Figure 1). For the isolation method of mixing, pre calculated amounts of MWCNT's and Part A of SC-1 epoxy were carefully weighed and mixed together in a thinky beaker. Thinky mixing machine was used to disperse CNT into Part A. After that, the solution was degasification for one hour. Part B of SC-1 epoxy was mixed with CNT dispersed Part A by a mechanical stirrer for about 3

to 5 min, followed by degasification for 30 min. Then, the mixture was placed on a metal rectangular mold for 12 hrs at room temp, 25° C and subsequently, post cured at 80° C for two hours. For the combination method, 3-roll shear mixing machine was used with gap settings (40/30/20/10 µm) after completing thinky mixing keeping all other procedures as same as before. For the solvent based method, CNT was mixed with 50 gm of Acetone and mixed with a thinky mixing machine for one hour. Then the beaker was placed on a magnetic stirrer to evaporate all the solvent. A magnetic bar was placed inside the beaker with rotation of the magnetic bar fixed at 600 rpm and 70° C. When, all the acetone was evaporated thinky mixing machine was again used to disperse CNT into Part A. After that, 3-roll shear mixing machine was used with gap settings (40/30/20/10 µm) keeping all procedures same as the isolation method.


Fig.1: Thinky defoam mixer and 3-roll shear mixing machine.

Thermogravimetric analysis was performed using TGA module TGA/SDTA 851e from Mettler- Toledo, Inc in nitrogen gas at a heat rate of 10° C/min. from ambient to 700° C. Weight of TGA samples ranged between 10-15mg. Dynamic mechanical analysis was performed on a TA Instruments Q800, operated with three point bending mode at an oscillation frequency of 1 Hz. The sample dimensions were maintained at 60×12.5×3 mm. Data was collected from 35° C to 160° C at a scanning rate of 10° C/min. Flexural results were performed according to ASTM D790-07 under three point bending configuration using Zwick Roell testing machine with 2.5 KN load cell and 2mm/min crosshead speed. The sample dimensions were 60×12.5×3 mm. Microstructure of neat and nanophased samples was examined under JEOL JSM 5800 Scanning Electron Microscope with Hummer 6.2 sputtering system.

Results and discussion

1. Flexural response

To identify the optimum mixing conditions of MWCNT and CNF, the weight fraction of nanoparticles in epoxy was varied from 0 to 0.4%. Stress-strain curves obtained from the flexural tests are shown in Fig.2. Both stress- strain curves showed considerable non-linearity before reaching the ultimate strength. Most of the samples failed

immediately after reaching their ultimate strength. Five to eight specimens were tested for each mixing conditions.

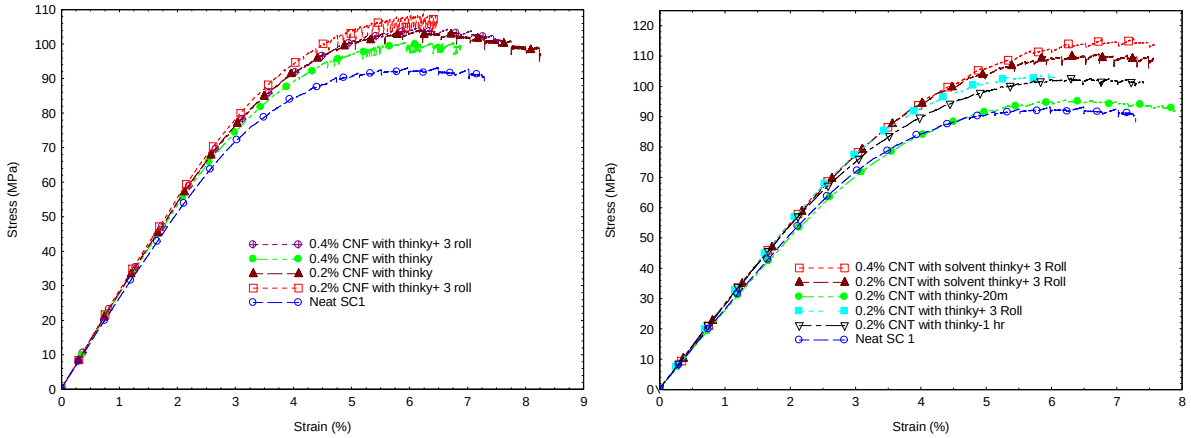


Fig.2: Stress- strain curves of epoxy and CNF/epoxy (left) and MWCNT/epoxy (right).

Table 1: Mechanical properties of neat and MWCNT infused epoxy

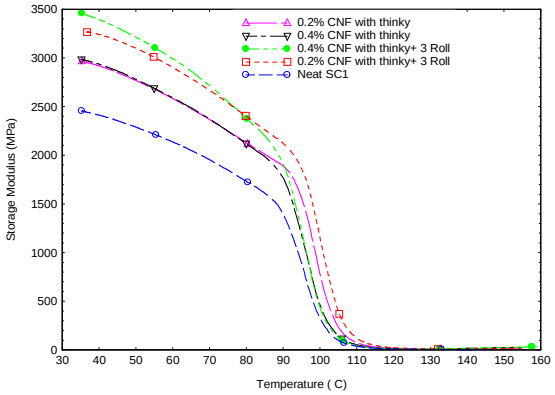
	Strength (MPa)	% change	Modulus (GPa)	% change	Maximum Strain (%)	% change
Neat epoxy	93.15±1.35		2.59±0.03		5.73±0.07	
0.2% t-20m	95.90±1.92	2.95	2.62±0.06	1.16	6.17±0.22	7.68
0.2% t-60m	102.35±1.28	9.88	2.76±0.12	6.56	6.33±0.14	10.47
0.2% t-60m+3R	103.28±2.0	10.87	2.81±0.09	8.49	5.98±0.16	4.36
0.4% t-60m	85.13±2.68	-8.61	2.94±0.13	13.51	3.25±0.19	-43.28
0.4% t-60m+3R	103.35±7.34	10.94	2.80±0.06	7.92	6.50±0.53	13.35
0.2% s-t-60m+3R	107.46±3.99	15.36	2.82±0.05	8.88	6.47±0.32	12.91
0.4% s-t-60m+3R	111.48±3.82	19.68	2.65±0.08	2.32	6.76±0.54	17.98
t=thinky, s=solvent						

Table 2: Mechanical properties of neat and VGCNF infused epoxy

	Strength (MPa)	% change	Modulus (GPa)	% change	Maximum Strain (%)	% change
Neat epoxy	93.15±1.35		2.59±0.03		5.73±0.07	
0.2% t-60m	104.6±3.63	12.29	2.78±0.11	7.34	6.17±0.18	7.68
0.2% t-60m+3R	108.51±1.38	16.48	2.81±0.04	8.49	6.27±0.29	9.42
0.4% t-60m	101.77±1.96	9.25	2.77±0.05	6.95	5.87±0.3	2.44
0.4% t- 60m+3R	103.35±2.42	10.95	2.69±0.04	3.86	6.26±0.25	9.25

Average and standard deviation values of flexural strength, flexural modulus and maximum strain obtained from these tests are listed in Tables 1 and 2. It can be observed in Table 1 that 0.2 wt% CNT infused epoxy with thinky mixing showed maximum strain values compared to same loading conditions with thinky+ 3 roll mixing; whereas later condition showed better strength and modulus values over former condition. Solvent treated 0.2 wt% CNT with thinky+ 3 roll mixing showed better modulus, whereas solvent treated 0.4 wt% CNT with thinky+ 3roll mixing showed best

strength and maximum strain values compared to all sets of data. These results indicate that mixing the MWCNTs with acetone helps to break the agglomeration of MWCNTs



which affects the overall mechanical properties. It can be observed from Table 2 that 0.2 wt% CNF with thinky+ 3roll mixing showed best strength, modulus and maximum strain values compared to all sets of data.

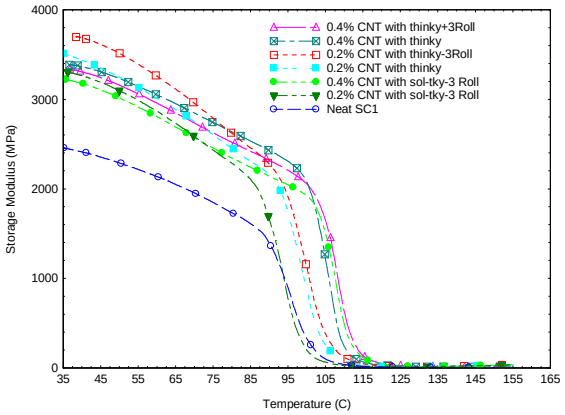
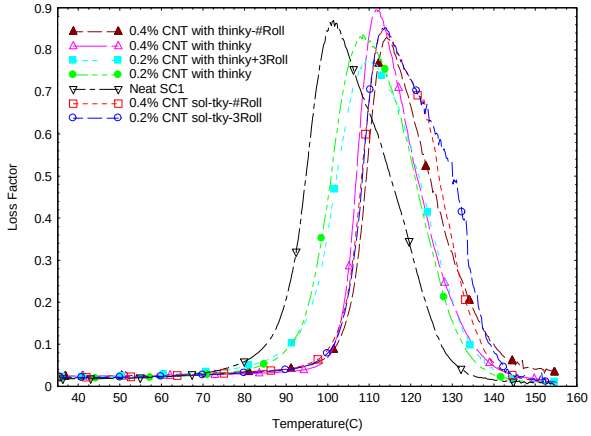


Fig.3: Storage modulus vs. temperature curves of epoxy and MWCNT/epoxy (left) and CNF/epoxy (right).

2. Thermo-meachnical properties

Fig. 3 shows the DMA graphs of storage modulus vs. temperature in different mixing conditions with different loadings of MWCNT and CNF. Among them, 0.2wt% CNT and 0.4wt% CNF infused epoxy resins yielded 50.37% and 40.72% increase in storage modulus at 35° C, respectively over the neat epoxy.



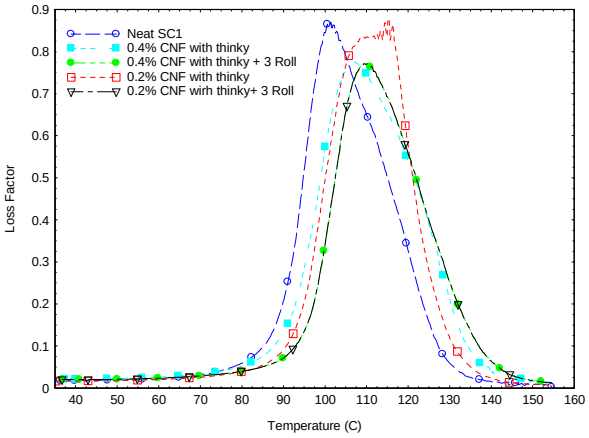


Fig.4: Tan δ vs. temperature curves of epoxy and MWCNT/epoxy (left) and CNF/epoxy (right).

The loss factor, tanδ vs. temperature curve for different mixing conditions with different loadings of MWCNT and CNF measured by DMA are shown in Fig. 3. The peak position temperature of tanδ curve, T_g, increased from 7.89° C to 12.37° C with different mixing conditions of CNT and from 4.38° C to 13.65° C with different mixing conditions of CNF, respectively. Most of the curves with different mixing conditions showed lower peak height compared to the neat epoxy specimen. To evaluate the homogeneity of epoxy network, the peak factor, *Γ*, ratio of full width at half maximum of the loss factor peak to its peak height, can be used qualitatively. MWCNT and VGCNF infused epoxy showed higher peak factor which signifies higher heterogeneity in their epoxy network compared to neat epoxy. Neat epoxy specimen showed lower peak factor which indicates their homogeneity in their polymer network.

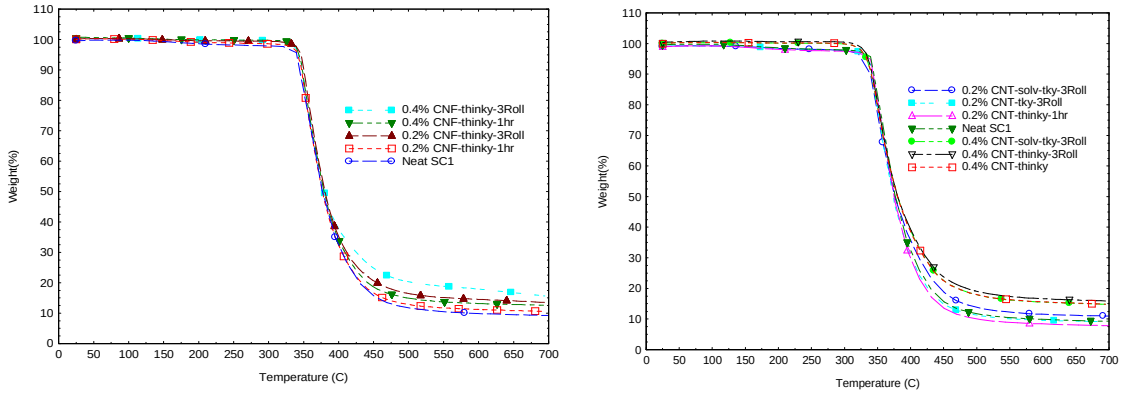


Fig.5: Weight (%) vs. temperature curves of epoxy and MWCNT/epoxy (left) and CNF/epoxy.

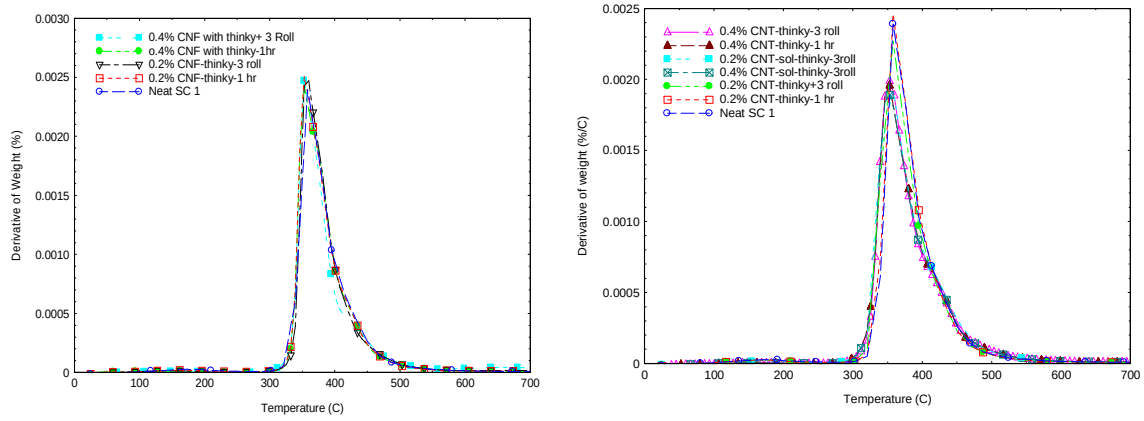


Fig. 6. Derivative of weight vs. temperature curve for MWCNT/epoxy & CNF/epoxy.

TGA of both MWCNT and CNF infused epoxy specimens are shown in Fig. 5 with respect to normalized weights vs. temperature. Most of the samples started to decompose at around 350° C and completed decomposition at around 475° C. Except 0.2wt% CNT infused epoxy samples with one hour thinky mixing, all samples of MWCNT and CNF infused samples showed higher residue content than neat epoxy; whereas residue content of neat epoxy was 4.39%. Thinky with 3 roll mixing samples of 0.4wt % MWCNT and CNF infused epoxy showed highest residue content of 15.90% and 15.49%, respectively. Fig. 6 shows the derivative peaks of weight vs. temperature curve, which indicates their Decomposition temperatures. Decomposition temperatures of MWCNT and CNF infused epoxy samples varies within ±5° C and ±1.5° C respectively, in compared to neat decomposition temperature, 349.84° C. which is not really significant.

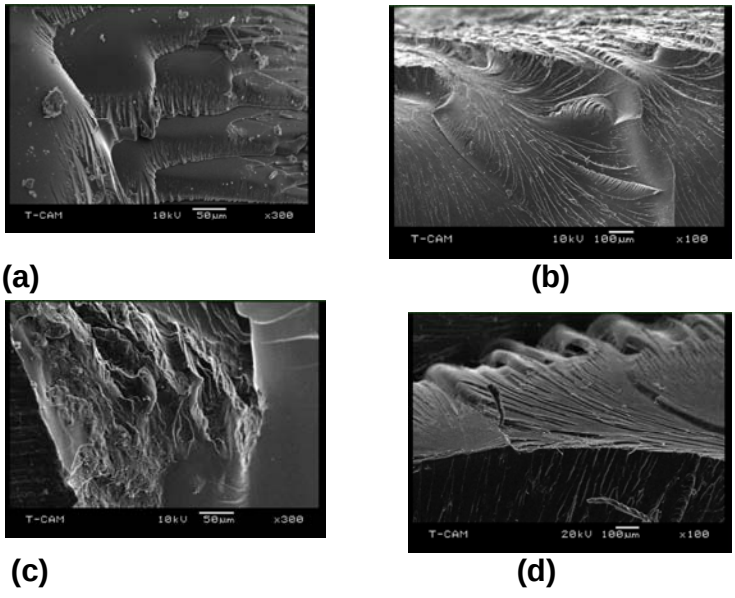
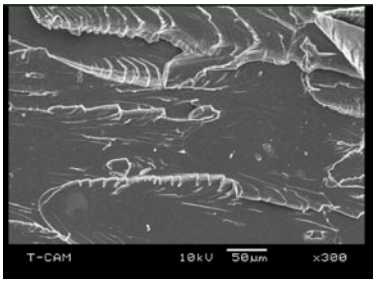
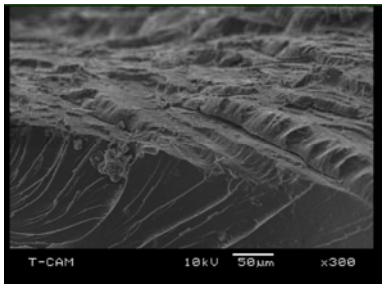


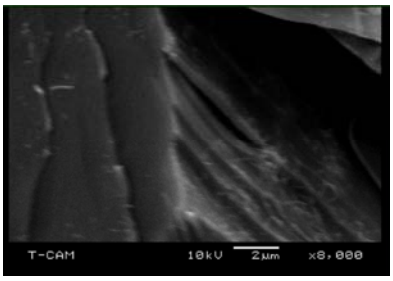
Fig.7. Micrograph of (a) neat and (b,c,d) 0.2wt% MWCNT infused epoxy with thinky+ 3Roll mixing.



(a)



(b)



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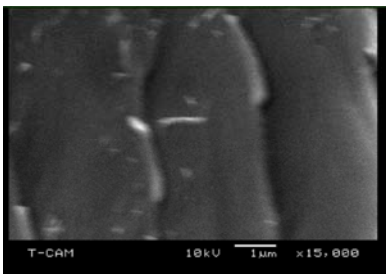

(d)

Fig.8. Micrograph of 0.4wt% MWCNT infused epoxy with thinky+ 3Roll mixing at higher magnification.

4. Fracture Surface

The fractured surfaces of the neat and 0.2wt% MWCNT infused epoxy specimens were observed by using SEM. Neat epoxy (Fig.7a) exhibits relatively smooth fractured surface, unlike the nanophased samples (Fig.7b,c,d), where rough fractured surface indicates brittle fracture behavior. River like patterns are distinctly observable in 0.4wt% MWCNT infused epoxy specimens (Fig.8a) along with rougher fracture surface which indicates that they exhibit brittle fracture behavior. Higher magnification images of 0.4wt% MWCNT infused epoxy (Fig.8c,d) neither exhibit any distinct images of MWCNT nor their dispersion with epoxy but fig 8d shows a few white, somehow cylindrical objects which might be MWCNT's and their dispersion with epoxy can't be described from this image.

Conclusion

Thermal and Mechanical tests were performed on MWCNT's and VGCNF's infused SC-1 epoxy resin. Solvent treated 0.2 wt% CNT with thinky+ 3roll mixing showed 8.88% improvement in modulus values over neat, whereas solvent treated 0.4 wt% CNT with thinky+ 3roll mixing showed 19.68% and 17.98% improvement on strength and maximum strain values, respectively compared to neat. 0.2 wt% CNF with thinky+ 3roll mixing showed 16.48%, 8.49% and 9.42% improvement on strength, modulus and maximum strain values over neat. 0.2 wt% CNT with thinky+3 Roll and 0.4wt% CNF with thinky+3 roll infused epoxy resins yielded 50.37% and 40.72% increase in storage modulus at 35° C, respectively over the neat. Tg values increased up to 13.65° C with

different mixing conditions of CNF and CNT. TGA showed nominal improvement on decomposition temperature and residue content. Solvent treated 0.2 wt% CNT with thinky+ 3roll mixing showed highest electrical conductivity among 0.2wt% MWCNT infused SC-1 resin samples.

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