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Microfluidization, time-effective and solvent free processing of nanoparticle containing thermosetting matrix resin suspensions for producing composites with enhanced thermal properties

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ABSTRACT

Dispersion of low content (0.1 wt.%) of multi walled carbon nanotubes (MWCNTs) in an epoxy resin through microfluidization was brought under spotlight as a case study. For the sake of performance comparison, epoxy resin suspension with the same MWCNT content was also produced through sonication, and the energy consumed to disperse MWCNTs in the epoxy resin remained the same for the both processes. At the equal energy consumption level, preparing the resin suspension through microfluidization was determined to take approximately 4.5 min, which is about 9 times lower than it takes for the same suspension to be prepared through sonication. Following cure of the prepared suspensions, thermal and thermo-mechanical properties of the resulting composites were systematically investigated. As a result, glass transition temperature (T_g) of the neat epoxy and its composites produced by sonication and microfluidization were determined to be 78 ± 3, 83 ± 5 and 88 ± 4 °C, respectively. Moreover, thermal expansion coefficient (CTE) of the epoxy resin was reduced by 7% when it was blended with MWCNTs through microfluidization, while no significant change was observed in the corresponding CTE value when through sonication. Thermomechanical testing findings implied about 5% and 10% improvement in storage and loss modulus values of the composites produced by microfluidization over by sonication. Transmission electron microscopy (TEM) examination showed that MWCNTs were more homogenously and individually dispersed in the epoxy resin by retaining their initial aspect ratio through microfluidization. Scanning electron microscopy (SEM) examination revealed that composite fracture surface morphology significantly varied, depending to large extent on the type of the process used. Based on the results obtained, it was proposed that microfluidization might pave the way for cost-and-time effective solvent-free processing of nanoparticle modified thermosetting resin suspensions, especially including those that could be promisingly used as matrix constituent for manufacturing fabric reinforced composites with multi-functional properties.

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1. Introduction

Thermosetting polymers have aroused great interest among the scientific community over the last three decades due to their relatively low cost and ease of processing. They are network-forming polymers and include epoxy, phenolic, unsaturated polyester, polyurethane, cyanate ester, bismaleimide, acrylate and many others. They have been in majority used as matrix materials for the manufacture of fiber reinforced composites. However, thermosetting polymers exhibit poor damage tolerance combined with low strength and stiffness relative to other engineering materials, such as metals [1–8]. Most thermosetting polymers therefore incorporate various types of particulate fillers to reduce cost, to modify thermal and mechanical properties, or to reduce shrinkage during cure. Nanotechnology has very recently made it possible to look at thermosetting polymers from a different perspective, when it comes to creating new application areas in composite manufacturing industry. With this respect, the use of nanoparticles of high strength and modulus as filler constituent for thermosetting polymers has been believed to pave the path to producing novel multi-functional composites of extraordinary versatility [3–7]. As a very recent example, carbon nanotubes (CNTs) have emerged as one of the most promising nanofiller candidates and have been therefore utilized for various types of polymers to manufacture electrically conductive composites with at least retained or improved thermal and mechanical properties [8,9]. In fact, a CNT is a tube-shaped material, made of carbon, having a diameter as thin as a few nanometers yet exhibiting a length as long as hundreds of microns. They are unique because the bonding between the atoms is very strong and they can have huge aspect ratios [4]. CNTs are usually categorized as either single-walled (SWCNT) which is just like a regular straw composed of only one wall, or multi-walled nanotubes (MWCNTs), a collection of nested tubes of continuously increasing diameters, held together by interatomic forces. Unlike the use of traditional micro-sized filler particles, such as carbon black (CB), that usually end up compromising among polymer mechanical properties, leading to high strength combined with low toughness, the use of CNTs is expected to provide a synchronized increase in polymer composite mechanical and thermal properties [10]. However, the studies in the literature reported up to date showed that CNT modified polymer composites demonstrated mechanical strength and thermal properties very far below the theoretical predictions [7–9]. Specifically speaking, it is required that the two major problems be solved prior to putting theoretical predictions into practical use. The former is weak interfacial bonding between CNTs and the surrounding polymer matrix, a struggle arising from very inert surfaces of CNTs, while the latter is a strong tendency of CNTs to form agglomerates because of their huge surface area and aspect ratio [3–8]. Those problems are not just only limited to the use of CNTs, but also to the use of most of the fiber-like fillers at nanoscale, too. To alleviate the first challenge, two different strategies are adopted, one of which is the covalent functionalization, while the other is the non-covalent functionalization. The covalent functionalization has been most commonly used to graft chemical functional groups that are compatible with the matrix resin onto CNT surfaces to promote the interfacial interactions in between [2,4]. Strong acids, such as nitric and sulfuric, or their mixture at different specified weight ratios are used to oxidize CNT surface followed by imparting the desired functional groups onto them to ease their processing when blended with polymers. Nevertheless, incorporation of functional groups into a conjugated π-electron system, as in the case of such graphite structures as CNTs, causes formation of sp^3-carbons which carry the functional groups. Thus, the chemical modification interrupts the conjugation, hence inducing a shape distortion in the graphitic layer structure, which is detrimental to final mechanical, thermal, and electrical properties of CNTs [6]. That stands for the reason why application of any covalent functionalization reported in the literature up to date brought about an uncontrolled length reduction in CNTs along with significant surface flaws in their structure [10]. To overcome these drawbacks, the non-covalent functionalization of CNTs has been lately adopted [3]. It is believed to help better preserve the CNT conjugated double bonds than does the covalent functionalization. The non-covalent functionalization has been several times shown to result in more stable and concentrated dispersions of CNTs both in organic and in aqueous solvents than it would be possible with the covalent functionalization [2–6]. Once agglomerated CNTs are properly disentangled and the strong van der Waals forces among the adjacent bunches are gotten rid of with application of high shear, CNT dispersions could be achieved as a means of polar and π-stacking interaction of CNTs in company of a suitable solvent, with their structures mainly intact remaining [2,3,6]. Another non-covalent functionalization approach to favoring CNT dispersion in organic solvents is to cover the CNT surface with a thin layer of a dispersant phase, a molecule characterized by a high affinity towards CNT sidewalls, which is also to be predominantly soluble in the solvent of choice [3,4]. Both small molecules and high weight polymers have been utilized as dispersant phases for this purpose.

As for the second challenge, the huge surface area of CNTs leads to strong attractive forces to occur among the bunch of CNTs, which ends up with formation of agglomerated clusters. The extent of agglomeration is highly critical to the mechanical properties of resulting CNT modified polymer composites [7–10]. In the literature, a number of different techniques, including high speed mechanical stirring, magnetic stirring, reflux, shear mixing, 3-roll milling, or, most commonly, ultrasonication, either mild sonication in a water bath, or high-power sonication using a metal tip have been employed for proper dispersion of CNTs in thermosetting polymers [1–13]. As a result, high-power sonication has been cited as the most promising among all [5–8]. During high-power sonication, a pulsed ultrasound with certain amplitude is applied in an effort to divide large agglomerates into relatively small or individual CNTs. However, the magnitude of applied vibration energy is limited to distance from the sonicator tip. Sonication is therefore claimed to shorten the length of CNTs uncontrollably by applying a high local energy input nearby the sonicator tip, which might be detrimental to some extent to the thermal, electrical, and mechanical characteristics of CNTs [4,6,8]. In our early studies, 3-roll milling turned out to be more promising approach than high-power sonication to produce CNT modified vinyl-ester epoxy composites [4]. However, when it comes to scaling it up, it remains lacking in terms of processing dwell time and labor cost. In brief, any methods used to de-agglomerate and homogenously disperse CNTs with or without functional groups within thermosetting polymers for large volume applications require to be efficient, economical, and scalable. At this point, microfluidization could be considered a promising alternative to sonication and 3-roll milling. Generally speaking, microfluidization is a dynamic high-pressure homogenization process based on accelerating liquid to velocities of up to several hundreds of meters per second through a specially designed fixed interaction chamber wherein several orders of magnitude higher shear rates are created than are obtainable by any conventional mixing equipment [14–19]. The process pressure and the channel geometry control the velocities inside the channels, and therefore the energy dissipation during the process [17–19]. A distinct advantage is that the amount of shear applied on liquids can be easily adjustable, which might suppress the possibility of having an uncontrolled and undesired length reduction in CNTs during processing [18]. Regardless of chemical functionalization, whether covalent or non-covalent, the common point for processing of CNTs involves using an appropriate solvent before they are brought in contact with the polymer matrix resin of choice to produce functional composites.

The major motivation behind this study lies in taking advantage of a cost and time effective solvent-free processing of thermosetting suspensions which is also up-scalable at the need of large volume applications. As a case study, an epoxy resin and MWCNTs were, respectively, utilized as matrix and filler constituents. The major emphasis was placed on thermal and thermo-mechanical properties of the resulting epoxy matrix composites, which is critical for the prepared suspension when it is especially intended to be used as matrix material for manufacture of fiber reinforced composites. The identical suspensions were also produced through sonication. To convincingly compare their working efficiencies, the total energy consumed to disperse MWCNTs was kept the same during the both processes. Glass transition temperature (T_g) of the composites was measured using Dynamic Scanning Calorimetry (DSC). A facile method based on the use of Dynamic Mechanical Analyzer (DMA) was utilized to measure thermal expansion coefficient (CTE) of the resulting composites. Thermomechanical properties of the composites including storage and loss modulus, and tangent loss factor were also measured by using DMA, too. Scanning electron microscopy (SEM) was then employed to examine the fracture surfaces of the composites to visualize the morphology and the dispersion state of MWCNTs. Transmission electron microscopy (TEM) was used to check the aspect ratio of CNTs after blended with the epoxy through sonication and microfluidization. The findings obtained were then evaluated and discussed in a concise manner.

2. Experimental

2.1. Materials

High conductive grade of MWCNTs (NC-7000) produced by catalytic chemical vapor deposition were obtained from NANOCYL, Namur Belgium. MWCNTs with a length of several micrometers up to 50 μm have average outer and inner diameters of 3.2 and 2.8 nm, respectively. The bisphenol-A based epoxy matrix (L-160) and its aromatic hardener (H-163) were purchased from the Hexion resin. They were used in this study as matrix constituent after mixed with each other at the specified weight ratio (100:28 w/w).

2.2. Principles of preparation of epoxy suspensions through microfluidization

Fig. 1 gives the working principle schematic of microfluidization process together with the details of the methodology used in this study for preparing MWCNT modified suspensions through microfluidization. Generally speaking, regardless of type of liquids or suspensions, process begins once the product enters the system by means of the inlet reservoir, as seen in the figure in the middle of the illustration. An intensifier pump that generates extremely high pressures (up to 276 MPa) accelerates the liquid product into the interaction chamber at velocities up to 500 m/s, thus exposing it to very high shear stresses. Within the interaction chamber, the product stream separates into micro channels of various geometries as narrow as the cross section of a human hair. The product stream is then forced to collide upon itself, which creates incredible forces of impact and shear which are several orders of magnitude greater than the forces of impact and shear obtained when using other technologies including homogenization, sonication, 3-roll milling, and high-shear mechanical stirring [14–17]. In the last part, the finished product is effectively cooled and collected in the outlet reservoir. The energy dissipation during the process is highly related to the process pressure as well as to the channel geometry which regulate the velocities inside the channels. In addition, many experimental parameters are also influential in accomplishing the desired final dispersion quality. These include process pressure, number of circulation passes at the specified process pressure, orifice geometry in the chamber type, which are mainly related to the magnitude of shear impact. Moreover, temperature, which is interrelated to the viscosity of the dispersion, is also important parameter to be taken into account, especially, under exceptional conditions in which its adjustment is indispensable and inevitable for the sake of the stability of the liquid of interest.

Dispersion of MWCNTs within epoxy was performed with a commercially available processor (M-110P, Microfluidics Corp.) equipped with two Z type interaction chambers which consists of sharp turns and a very narrow rectangular cross-section, as small as 50 μm. As it is certain, as stated by the producer, that microfluidization is capable to reduce the CNT length significantly when the suspension is allowed to pass through the channels many several times, we preferred

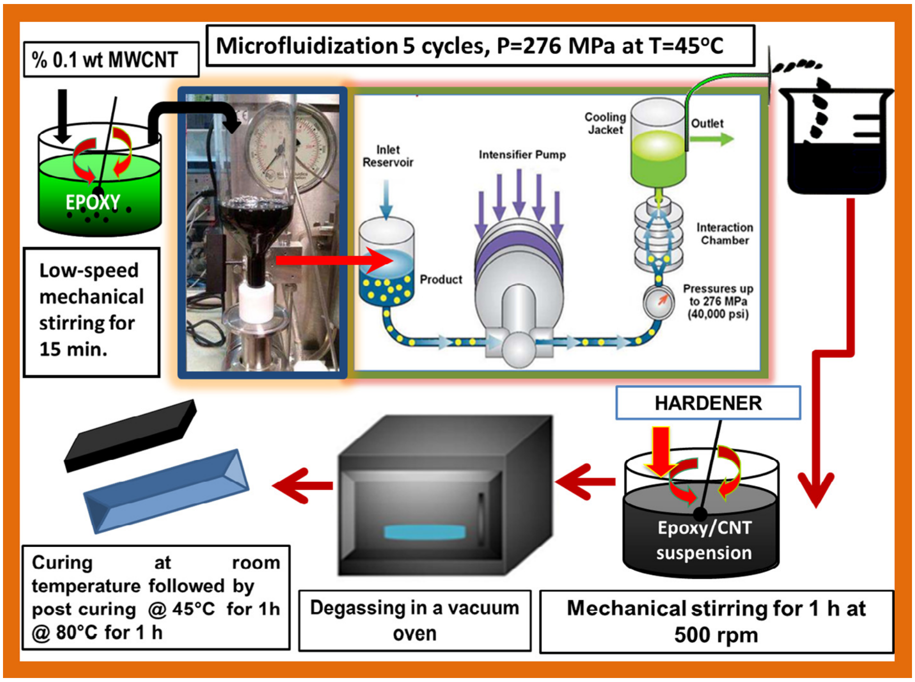

Fig. 1. Working principle schematic of a microfluidizer and the illustration of preparation of MWCNT modified epoxy suspensions through microfluidization.

subjecting the suspension to just 5 passes for the sake of the CNT aspect ratio. We observed that, after 5 passes, any additional pass caused a significant reduction in the length of CNTs. On the other hand, to check the effect of microchannel diameter and pump pressure, chambers with different microchannel diameters (100 and 200 μm) were employed either separately or together at a time at three different pressure levels (150, 200, and 276 MPa). At the end, we concluded that the best dispersion was accomplished when the two chambers were lined up in series when the pressure level was adjusted to maximum 276 MPa. In consequence, shear stress applied on the resin suspensions was optimized, executing a constant intensifier pump pressure of 276 MPa in a series chamber combination of H30Z (200 μm) and H10Z (100 μm). Moreover, prior to the process, to prevent any MWCNT clusters from clogging up the micro channels under high shear, very low content of MWCNTs (0.1 wt.%) was first mixed by a low-speed mechanical stirrer with epoxy resin without hardener for 15 min. The viscosity of the suspension was then lowered to ease the flow process by placing it in a vacuum oven at 45 °C for 30 min. Temperature was kept constant at around 45 °C through the use of a flexible water-cooled jacket that is wrapped around the interaction chamber section in an effort to avoid superfluous increase in the resin temperature caused by very high shear applied inside the chamber. After subjected to very high shear forces, the suspension obtained was then blended with the curing agent by a jiffy mixer for 1 h at 500 rpm, followed by degassing in a vacuum oven once again for 30 min. The degassed catalyzed resin mixtures obtained were then allowed to cure at room temperature for 24 h followed by post curing at 45 °C for 1 h and 80 °C for 1 h, respectively.

Note that very low content of MWCNTs (0.1 wt.%) was intentionally aimed for in this study. This is because the final suspension obtained sounds to be highly promising polymer matrix candidate for the manufacture of fiber reinforced composites that can eliminate any MWCNT induced filtering effects among the fiber tows during resin infusion, whether in-plane or through-the-thickness directions, at the same time, irrespective of the manufacturing method used, either vacuum infusion (VI) or resin transfer molding (RTM). In fact, mechanical enhancements at various low loading rates of MWCNTs ranging from 0.05 to 1 wt.% were in detail addressed in the literature for neat epoxy resins and their use in fabric reinforced composites in different studies [18–27]. In our earlier study [27] where the resin suspension was prepared by 3-roll milling, MWCNT modified composite laminates (0.1 wt.%) were found to exhibit 8% and 11% high mode II interlaminar fracture toughness and interlaminar shear strength values (ILSS), respectively, as compared to the base laminates.

2.3. Preparation of epoxy suspensions through sonication

Another suspension with the same MWCNT content was also prepared using a horn type sonicator (SONICS 750 VCF). For this purpose, MWCNTs were first mixed with epoxy resin without hardener by a low speed mechanical stirrer for 15 min in the same manner as in microfludization. The prepared suspension was then placed in a water cooled-mug which acted as a heat sink to escape extreme heat accumulation in the sonication container. Suspension was subjected to sonication at frequency of 20 kHz with amplitude of 40%, operating in a pulse operation mode (on 10 s, off 30 s) with the power set at 750 W. Note that temperature of the suspension remained the same as in micro fluidization (45 °C) to eliminate any temperature induced noise on the results found. The suspension obtained was first allowed to cool down to room temperature and placed in a vacuum oven afterwards. It was then blended with the curing agent by a jiffy mixer for 1 h at 500 rpm, followed by degassing in a vacuum oven once again for 30 min. The degassed catalyzed resin mixtures obtained were then allowed to cure at room temperature for 24 h followed by post curing at 45 °C for 1 h and 80 °C for 1 h, respectively, as in microfluidization.

2.4. Comparison of energy consumption level

In this study, the energy consumed to disperse MWCNTs in epoxy remained the same for sonication and microfluidization in an attempt to compare their working efficiencies. With this respect, the total energy consumed to disperse 0.1 wt.% of MWCNT within epoxy through sonication was estimated by the following equation [6,7].

$$E_{sonication} = 750 \times t \tag{1}$$

where (t) is the active sonication duration time in seconds. The total energy consumed in dispersing 100 ml MWCNT suspension by microfluidization was estimated as follows on the other hand [14,15].

$$E_{microfluidization} = \in \times \frac{V_{batch} \times \rho}{1000} \times \left(\frac{V_{batch}}{V_{processor}} \times t \times N \right) \tag{2}$$

where ε (1.0×10^{7} W/kg) refers to the turbulent energy dissipation rate attainable in the interaction chamber of M-110P, which has a volume of 1.0×10^{-6} ml, referring to V processor in this configuration. The density of the solution (ρ) was taken as 1.2 g/cm^3. In the above equation, t and N refer to, respectively, the residence time of dispersion in the interaction chamber and the number of circulation pass. In this study, the residence time of dispersion was taken as 1.0×10^{-6} s. Please note that the numerical values of, V processor and t were taken as disclosed by the processor manufacturer [15,16]. Following the calculations, it was found that it takes 0.9 min for 100 ml suspension to complete one pass. In this study, the number of circulation passes was taken as 5 to optimize the shear stress, as explained before. On the other hand, the more number of circulation passes is applied, the more possible it is for temperature to uncontrollably ramp up through the interaction chamber walls, which causes the thermal degradation of the suspensions to some extent where their degree of cure is adversely affected. This is in fact the reason why we paid our utmost attention to keeping temperature the same as possible as we can, as elucidated in detail. Putting the numerical values in the Eq. (2), the energy consumed to disperse MWCNTs within epoxy by microfluidization was calculated to be 550 kJ. This value is then used as input to compute the required active sonication time with the Eq. (1). Providing the energy consumption level remain the same for each process, microfluidization seemed to be by far superior over sonication in the total processing time, such that it takes 4.5 min to prepare the suspension by microfluidization, which is about 9.3 times less than the processing time required to prepare the same suspension using sonication (48 min and 54 s with 12.2 min active sonication duration time involved).

2.5. Microscopic characterization

To reveal processed induced effects on failure modes and morphology of the composites, fracture surfaces of the samples were examined, conducting a Schottky emitter field emission gun (FEG)-SEM (SEM-Zeiss SUPRA 50 VP) at an acceleration voltage of 5 kV. Samples were crushed in liquid nitrogen. Furthermore, TEM was used to visualize the dispersion state of MWCNTs within epoxy matrix. TEM sample films with a thickness of 70 nm were prepared at room temperature by using an ultra-microtome. TEM studies were performed by conducting FEG-TEM (TEM-Jeol 2100F).

2.6. DSC measurements

Dynamic scanning calorimetry (DSC) measurements were performed using a TA instrument DSC Q-2000 to investigate MWCNT induced effect on T_g of the epoxy resin, depending on the process used. All the samples were heated to 150 °C with a heating rate of 3 °C/min and were held in the molten state for 5 min. to reset their thermal history followed by cooling down to room temperature at a rate of 3 °C/min. The samples were then reheated to 150 °C to properly detect their T_g values. All operations were carried out under nitrogen environment with a flow rate of 50 ml/min. At least, three specimens were tested for the sake of statistical assessment of the results obtained.

2.7. DMA measurements

Dynamic mechanical properties of the samples that were obtained by the cure of the resin suspensions were investigated by using a dynamic mechanical thermal analyzer, (DMA, METRAVIB + 450 N). For the measurements, rectangular specimens of 50 mm in length, 5 mm in width and 2 mm in thickness were sectioned from larger samples. The tests were performed in tensile mode at frequency of 1 Hz with a static strain of 0.6% and dynamic strain of 0.1%, in a temperature range from 50 to

200 °C with heating rate of 3 °C/min. The storage modulus (E'), loss modulus (E'') and the loss tangent (tan δ) of the resulting solid samples were experimentally determined as a function of temperature.

The coefficient of thermal expansion (CTE) of the samples with and without MWCNTs was also measured using DMA in thermo-mechanical analyzer (TMA) mode. Generally speaking, DMA normally works by applying an oscillating force onto a material and the resultant displacement of the sample is measured. When determining CTE by means of a DMA, the oscillating force function is switched off. The static displacement of the sample is measured, as it expands or contracts as a function of temperature. By plotting the displacement against temperature, CTE can be calculated. The method used in this study involves placing a sample in tension mode and monitoring the displacement to specify how the geometry of the sample changes over the given temperature ranges. To compensate for the expansion of the driveshaft and clamps, a calibration of the DMA with a known standard material is required prior to the core experiment. This calibration data needs subtracting from the sample data to acquire an expansion curve just belonging to the sample alone. For this purpose, the sample of aluminum in rectangular shape (30 × 5 × 2 mm.) was selected as reference material. The composite samples with identical geometry were mounted in the same way as aluminum. All the measurements were performed at constant frequency of 1 Hz with heating rate of 3 °C/min. Note that only data before the T_g was presented for purposes of this study, as this method works for polymer based materials as long as they are in the glassy region, otherwise shape distortion or conformational changes that would occur across the sample could lead to data misinterpretation. At least, three specimens were tested for statistical evaluation of the results found. CTE of the samples was then calculated using the following equation.

$$\alpha_s = (S_S - S_R + L_R \cdot \alpha_R) \cdot \frac{1}{L_S} \tag{3}$$

where (α_s) is expansion coefficient of the sample of interest, (S_s) is slope of the curve obtained from specimen, (S_r) is the slope of the curve obtained from aluminum, (L_R) is the length of the aluminum, (α_R) is the expansion coefficient of aluminum, (L_s) is the length of the sample of interest at room temperature.

3. Results and discussion

3.1. Dispersion state of MWCNTs

Fig. 2a–c depict typical TEM images captured from the samples produced through microfluidization where MWCNTs appear to be homogenously and individually distributed within epoxy, with their initial aspect ratio almost intact remaining. This can be thought of as ample evidence that the number of the passes, the processing pressure, and the chambers were properly optimized and selected in light of the preliminary findings of the experimental trials that were carried out at the very beginning, as described in detail in the experimental part. On the other hand, Fig. 2d and e depict typical images captured from the samples produced through sonication. As gotten clearly, typical dispersion of MWCNTs within epoxy

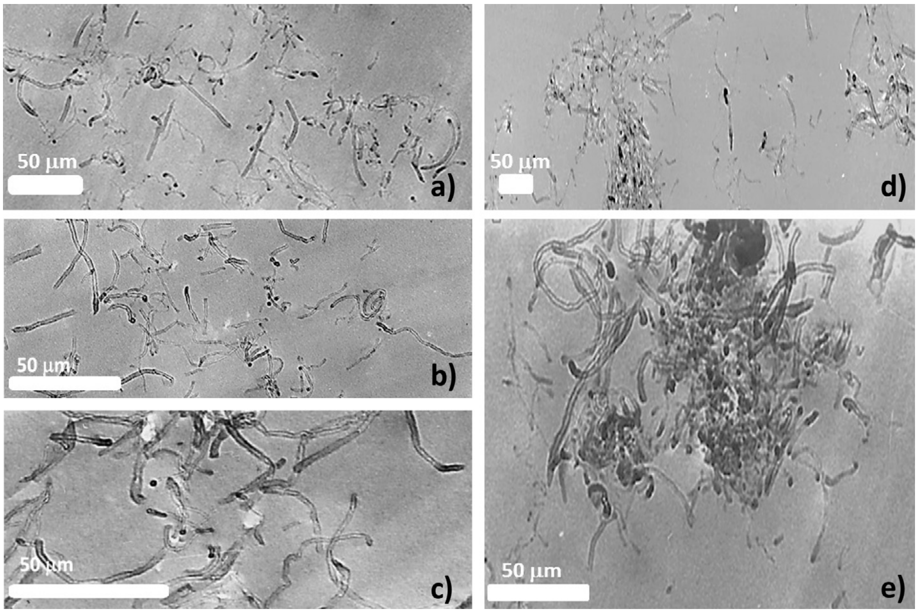

Fig. 2. TEM images of the samples produced by microfluidization (a, b, and c) and sonication (d and e).

was in the form of tiny clusters in majority. At a first glance, it seems that microfluidization works better in the way it is supposed to, as initially acknowledged, than sonication.

3.2. Fracture surface morphology

Fig. 3a–e depict SEM fracture surface images of the samples produced by microfluidization at different magnifications. Overall speaking, in each figure, a number of individual MWCNTs highlighted by red arrows are remarkably noticeable to the naked eye between the adjacent co-existing fracture bands lying by one another on vertically aligned parallel planes. Moreover, MWCNTs seemed to absolutely retain their aspect ratio, following 5 circulation passes, as confirmed by the image in Fig. 3d which was recorded at a higher magnification of the zone highlighted by dashed red circle in Fig. 3b. This can be considered ample evidence as to how good a microfluidizer could be at producing almost agglomerate-free resin suspensions with nanofiller even on large volume basis. Fig. 4a–e give the SEM fracture surface images of the samples produced by sonication at different magnifications. Unlike the dispersion state of MWCNTs in the composites through microfluidization, no

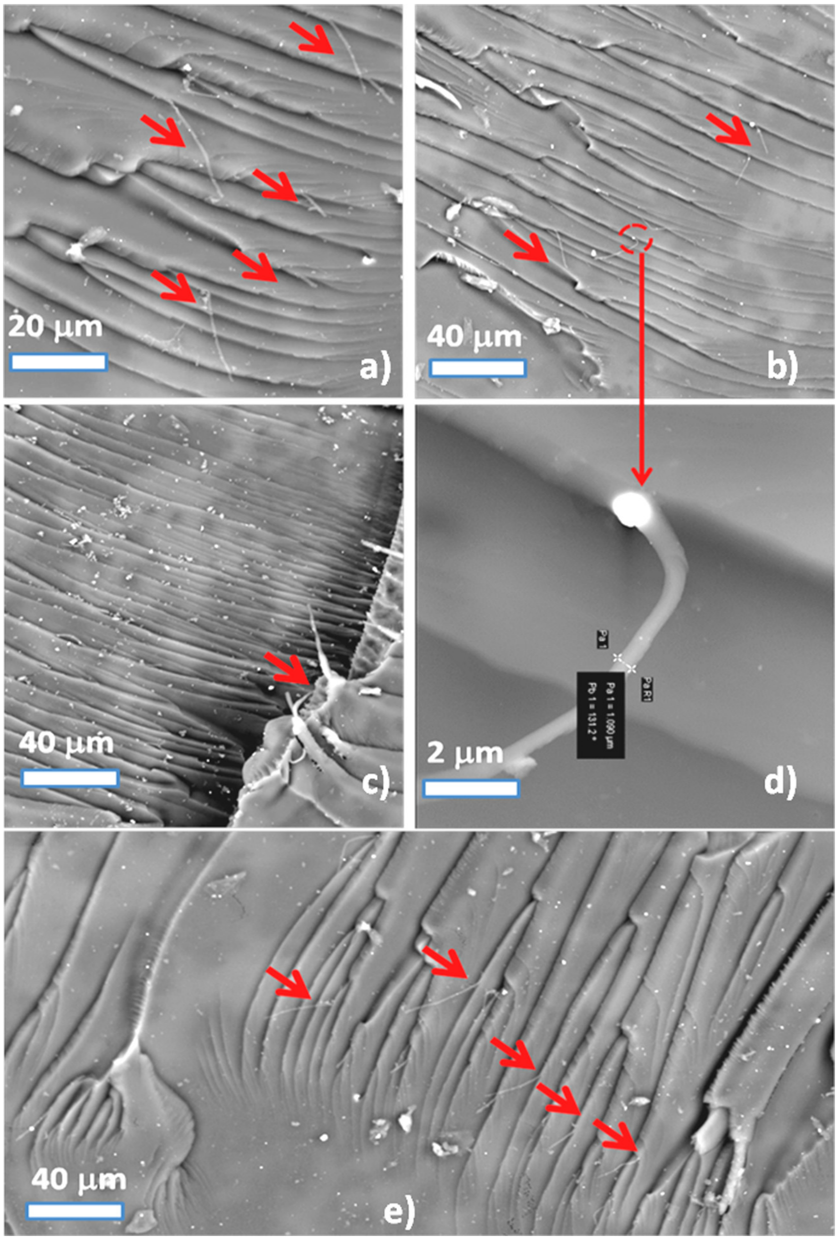

Fig. 3. SEM fracture surface images of the samples at different magnifications produced by microfluidization after 5 cycles.

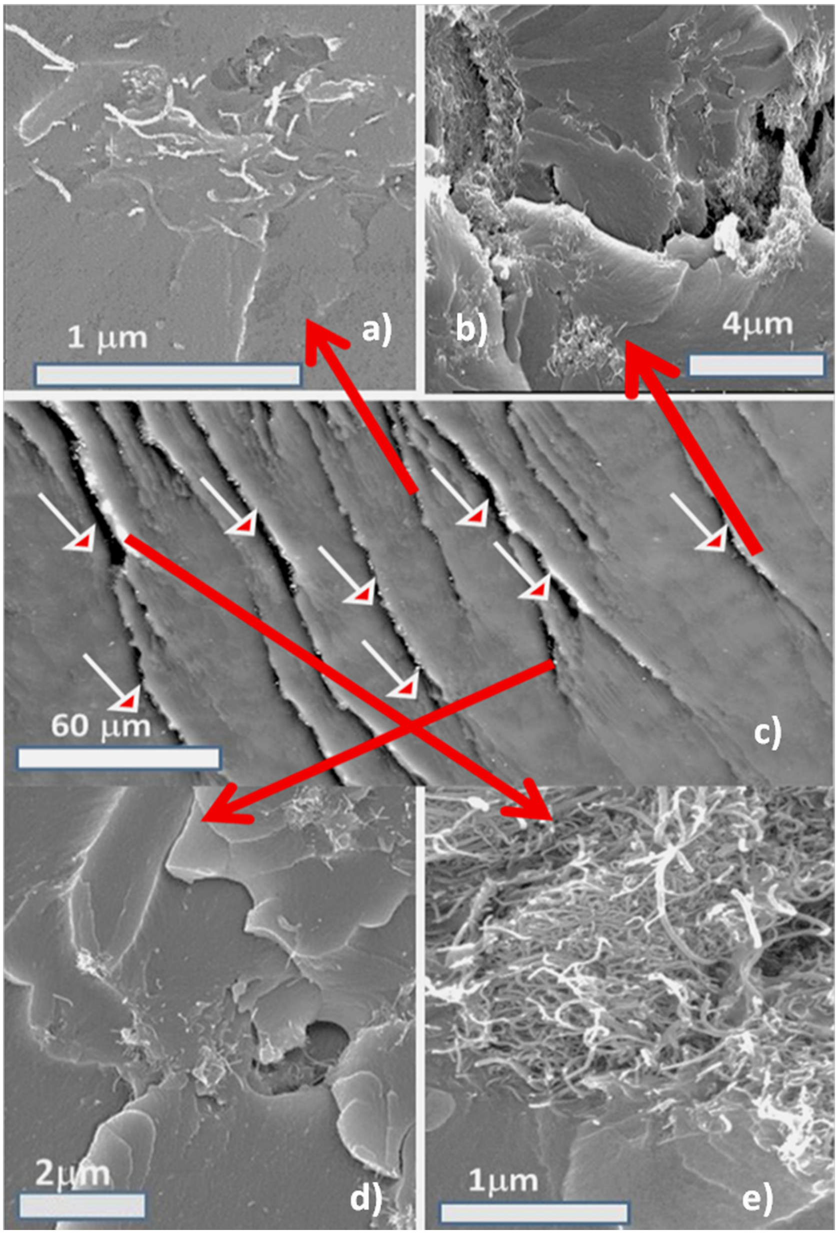

Fig. 4. SEM fracture surface images of the samples produced by sonication at different magnifications.

individual or separate, but a number of tiny MWCNT clusters are apparently located entrapped between and within the deep down of the sigmoidal-shaped vast fracture bands, as seen in Fig. 4c. When looked closer into the cavity of the corresponding vast fracture bands at very high magnifications, MWCNTs were found hosted, appearing not individually, but in agglomerated form, as seen in Fig. 4a, b, d, and e where tiny MWCNT clusters were indicated by red arrows. In addition to this, what deserves special mention is that, in terms of fracture surface morphology, huge differences ensued in between the composites, depending on the process used. This may be due to application of a high local energy input nearby the sonicator tip, hence leading to a graded heat release rate through the depth of the water-cooled mug. On the other hand, another major reason for the observed differences might arise from the distinct flow fields of the dispersion medium. In microfluidization, shear flow governs, whereas, in sonication, extensional flow does in majority [5,6]. In other words, in microfluidization, the flow characteristics coupled with high viscous dissipation which results from the heat evolved under very high shear rates in tiny micro channels of the interaction chamber might pose a more-than expected influence on the fracture surface morphology alteration in the resulting composites, favoring the individual MWCNT dispersion. As for sonication, in a similar manner, temperature gradient within the suspension arising from the vibration energy nearby the sonicator tip might be of more importance than presumed at a first glance. However, it would be most probably anybody's guess how much of the observed differences is the result of distinctly diverse local energy level distribution in each corresponding process and how much of is the result of the flow field differences between the processing types. This suggests that, in our case, given the same energy consumption rate, the principles of the flow field could affect more distinctly the characteristics of the resulting suspensions as well as of their resulting composites, too. As you can see from the foregoing argument, processing type used is of fundamental importance in dispersion state of nanofiller in the resin as well as in thermal response of the resulting composites. On the basis of the discussion made here, thermal and thermo-mechanical properties of the composites were further evaluated in the next section to further back up and delve into the approach.

3.3. Glass transition temperature of the samples

Fig. 5 gives typical DSC thermograms of the neat epoxy and its composites produced by microfluidization and sonication. Generally speaking, regardless of the type of the process used, addition of very low content of MWCNTs gave rise to the T_g of the epoxy resin by most probably aiding in restricting molecular motion mobility of epoxy networks while at the same time they are being cross-linked. The degree of molecular restriction depends, however, to large extent on the manner in which MWCNTs interact with each other in the epoxy matrix.

Once T_g values of the samples were statistically evaluated, it was found that the neat epoxy and its composites produced by sonication and microfluidization exhibited values of 78 ± 3, 83 ± 5 and 88 ± 4 °C, respectively. This is most likely because MWCNTs were dispersed more individually by microfluidization than by sonication, as approved by SEM and TEM studies so far. In addition to this, as MWCNTs keep their dimensions almost intact at the end of microfluidization, relatively high T_g value was obtained from the composites produced by microfluidization. Overall speaking, microfluidization is capable of providing nearly agglomerate free-nanofiller modified thermosetting suspensions with enhanced properties at low loading rates. On the other hand, given that fluctuations in T_g value of each corresponding sample differ from each other by what seems to be a modest amount, it might be inaccurate to conclude that the difference in between the values is large enough to imply that microfluidization resulted in composites possessing better thermal response. In the following sections, more evidences were therefore brought into the light to put the approach on a more reliable ground.

3.4. Thermomechanical properties of the samples

Fig. 6 gives typical storage and loss modulus values with respect to temperature for neat epoxy and its composites produced by sonication and microfluidization. Regardless of type of the process used, it is obvious that the addition of MWCNTs affected the storage modulus of epoxy in both glassy and rubbery regions. When the modulus values of different samples at 30 °C were statistically evaluated, the results were found to be, respectively, 3080 ± 51, 3130 ± 310 and 3260 ± 62 MPa for neat epoxy and its composites produced by sonication and microfludization. However, as temperature ramps up till around at 70 °C, some deviations took place from the trend, which is certainly apparent at the beginning, such that composites produced by microfluidization started exhibiting more thermal resistance at any temperatures above 70 °C until it ramps down to the baseline. This suggests that the load was more successfully transferred from the epoxy matrix to MWCNTs when epoxy was blended with MWCNTs, using the micro-processor, even though no chemical functional groups were attached onto MWCNT surface to tailor interfacial adhesion. As for the composites produced by sonication, obtaining a relatively high

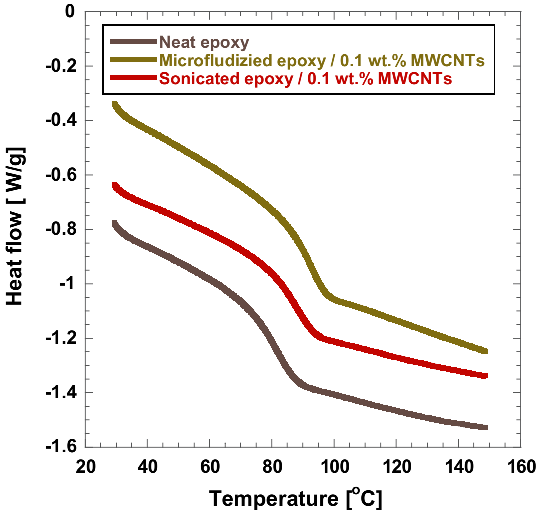

Fig. 5. Typical DSC thermograms of neat epoxy resin and its composites produced by sonication and microfluidization.

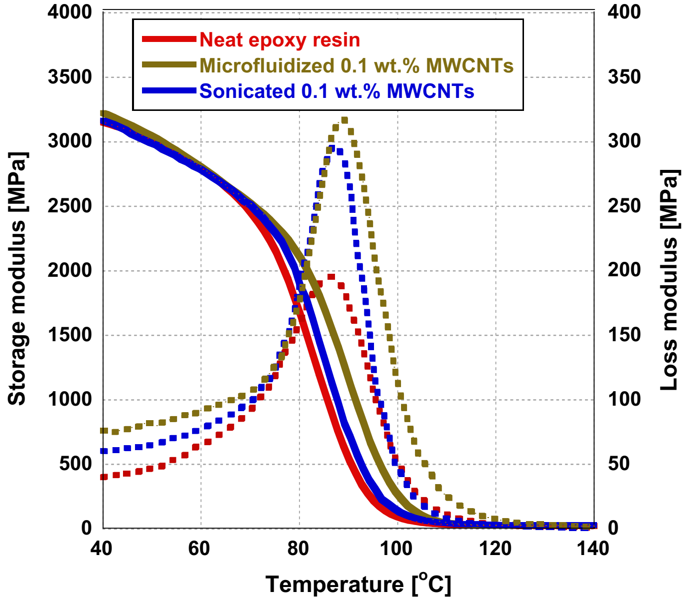

Fig. 6. Typical storage and loss modulus values with respect to temperature for neat epoxy and its composites produced by sonication and microfluidization.

frequency of the standard deviation in the modulus values indicates that the data points spread out over a large range of values. Actually, the results obtained are highly consistent with the findings obtained from SEM and TEM examinations, which were discussed earlier. The more individually dispersed MWCNTs existing in the epoxy, the lower standard deviation is supposed to have a hand in the results obtained, which would assure at least retained or improved final composites properties. In addition to this, it also means that, from a statistical point of view, the processor provides more reliable outcomes than sonication, which is of definitive significance when preparing suspensions for large volume applications. Moreover, regardless of the samples with and without MWCNTs, T_g values were found to scatter more or less around the same value (82 °C) with a statistically insignificant standard deviation, when they were obtained from the tangent slope of the storage modulus of the samples. It is known that interactions at the interface between CNTs and epoxy reduces the mobility of the epoxy matrix around the CNTs and helps increase the thermal and mechanical stability of the resulting composites [8–13]. This effect becomes indeed more pronounced when the distribution of CNTs within polymer matrix is more uniform. From this standpoint, it can be concluded that microfluidization works for dispersing CNTs more separately and individually than sonication. On the other hand, loss modulus values (neat epoxy: 196 ± 15 MPa) tend to increase with MWCNTs (composite produced by sonication: 291 ± 33 MPa) and the highest value was obtained from the composites produced by microfluidization (323 ± 17 MPa). Generally speaking, the more individually CNTs are dispersed within polymers, the more energy is supposed to be dissipated as a consequence of their conformational resistance against viscoelastic deformation of the surrounding polymer matrix resin [9–12]. With this respect, the significant increase in the loss modulus value of the corresponding composite can be reasonably attributed to the existence of fewer amounts of MWCNT agglomerates within epoxy resin. As a result, high energy dissipation takes place in the composite when it is gone under viscoelastic deformation [10–13]. In our case, using microfluidization gave good matching of the above-mentioned theoretical presumptions with the experimentally determined values, as it makes possible more uniform distribution of individually dispersed MWCNTs across the produced composites, which was approved by SEM and TEM findings, besides DSC results.

Fig. 7 gives typical loss factor values with respect to temperature for neat epoxy and its composites produced by sonication and microfluidization. The loss factor, the ratio of loss modulus to storage modulus, is a measure of the energy lost in terms of the recoverable energy, and denotes mechanical damping or internal friction in a viscoelastic system. As it gets higher, material is supposed to have a high non-elastic strain component. When it gets lower, material is assumed to be more elastic. As seen in the figure, the lowest value is obtained from the composite produced by microfluidization, indicating that it is more elastic than neat epoxy and its composites produced by sonication. In other words, the more properly dispersed MWCNTs, the more they would assist in dissipating energy under viscoelastic deformation of the matrix polymer in which they are embedded. This is also consistent with the SEM and TEM findings.

3.5. Thermal expansion coefficient of the samples

CTE is an important property of polymers because, during their service life, they are frequently exposed to temperature gradients in different circumstances, under which they either expand or contract. When used as matrix in fabric reinforced

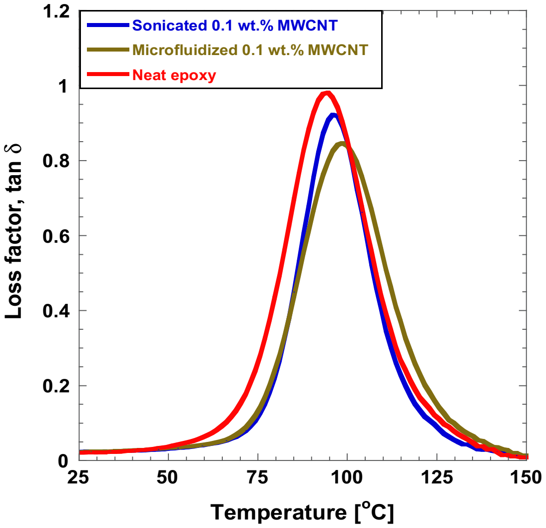

Fig. 7. Typical loss factor values with respect to temperature for neat epoxy and its composites produced by sonication and microfluidization.

composites, large CTE mismatches between polymer matrix and fibers lead to thermal stresses to accumulate at contact interfaces, which may significantly trigger mechanical shear forces, resulting in component failure by interfacial microdebonding [8–14]. In addition to this, it is also important to keep CTE as low as possible to avoid delamination propagation due to occurrence of cure-induced residual thermal stresses across fiber reinforced composite parts. Since the prepared suspensions herein are anticipated to be favorable matrix materials for fiber reinforced composites, it is worth investigating how the processing type affects the evolution of the CTE of epoxy with MWCNTs. Fig. 8 gives typical measured static displacements with respect to temperature obtained from the neat epoxy and its composites produced by sonication and microfluidization. The CTE of aluminum is taken as $2.4 \times 10^{-5}\,\mathrm{K}^{-1}$ in calculations. As discussed earlier, the expansion becomes non-linear above the T_g due to conformational distortion and thus any CTE values taken beyond glassy region become unreliable. It is for this reason that only the data gathered when the samples were in the glassy region were plotted. The CTE of the samples was calculated from the slope of the linear portion of the data. To improve the calculation accuracy, linear regression analysis was executed. The equation given earlier in the experimental section was then used to calculate the CTE of the samples. The CTE of neat epoxy and its composites produced by sonication and microfluidization were found to be $1.042 \times 10^{-4} \pm 0.02 \times 10^{-4}$, $1.040 \times 10^{-4} \pm 0.05 \times 10^{-4}$ and $0.972 \times 10^{-4} \pm 0.01 \times 10^{-4}\,\mathrm{K}^{-1}$, respectively. This implies that the CTE of the epoxy resin was lowered by around 7% when blended with MWCNTs through microfluidization, whereas

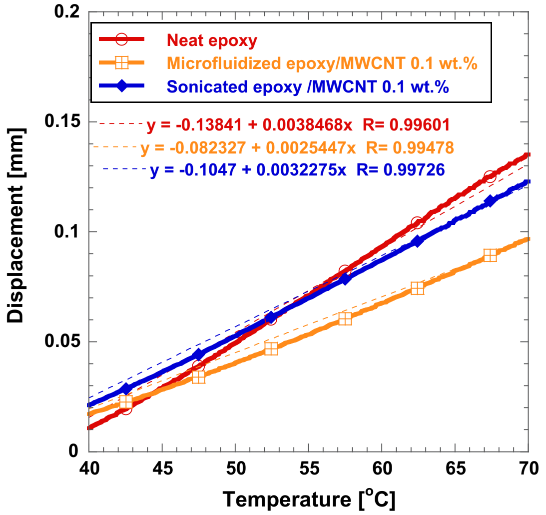

Fig. 8. Typical measured static displacements with respect to temperature obtained from the neat epoxy and its composites produced through microfluidization and sonication.

CTE of the epoxy scattered more or less around the same value when blended with MWCNTs through sonication. In addition to this, one can also gain qualitative insights into how stiff the tested samples are in comparison to each other. For example, in the corresponding graph, the lowest slope (0.00257) is obtained from the composites produced by microfluidization, indicating that relatively high stiffness is accomplished compared to neat epoxy (0.0038) and the composites produced by sonication (0.0032). This trend is valid for the other measured samples in a manner which is consistent with the trend in the graph. In brief, these findings are also proportional to the earlier reported findings (SEM, DSC, and DMA findings) and backs up our approach that microfluidization is effective in processing CNT modified epoxy suspensions even for large volume applications in a short dwell time when compared to any other widely used traditional processing techniques.

4. Conclusions

Microfluidization was proposed as a highly promising method to prepare low content-MWCNT modified epoxy suspensions with enhanced thermal properties. Sonication was conducted for the same purpose for the sake of performance comparison. To compare the working efficiencies of sonication and microfluidization, the energy consumed to disperse MWCNTs was set to the same value. It was found that microfluidization has ability to disperse MWCNTs homogenously compared to sonication, thus enhancing final composite thermal properties. At the same energy consumption level, it was determined that it facilities dispersion of MWCNTs in epoxy in a relatively short time. It takes 4.5 min to prepare the suspension by microfluidization, which is about 9.3 times less than the processing time required to prepare the same suspension by sonication. It was also determined that neat epoxy and its composites produced by sonication and microfluidization exhibited T_g values of 78 ± 3, 83 ± 5 and 88 ± 4 °C, respectively. CTE of the epoxy resin was reduced by 7% even at very low loading rate of MWCNTs when processed through microfluidization, whereas it remained almost to be the same when processed through sonication. Relatively high storage and loss modulus values were also obtained from the composites produced through microfluidization. In brief, microfluidics technology with almost spontaneous flow field characteristics in mind can be carefully utilized for various applications of any nanofiller modified thermosetting polymers which call for very high quality requirements in terms of particle size of the dispersed phase, particle size distributions and the resulting suspension stability. In most cases where alternative processing technologies stay insufficient to fulfil the requirements of low energy input and short processing times accompanied with some processing drawbacks, it would sound more encouraging. In the next study, MWCNT modified epoxy suspensions to be produced by microfluidization will be used as matrix material for manufacture of fiber reinforced composites and matrix dominant mechanical properties of resulting reinforced composites will be systematically investigated.

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