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Critical aspects related to processing of carbon nanotube/unsaturated thermoset polyester nanocomposites

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Abstract

Carbon nanotubes (CNTs) have outstanding mechanical, thermal and electrical properties. As a result, particular interest has been recently given in exploiting these properties by incorporating carbon nanotubes into some form of matrix. Although unsaturated polyesters with styrene have widespread use in the industrial applications, surprisingly there is no study in the literature about CNT/thermoset polyester nanocomposite systems. In the present paper, we underline some important issues and limitations during the processing of unsaturated polyester resins with different types of carbon nanotubes. In that manner, 3-roll mill and sonication techniques were comparatively evaluated to process nanocomposites made of CNTs with and without amine (NH_2) functional groups and polyesters. It was found that styrene evaporation from the polyester resin system was a critical issue for nanocomposite processing. Rheological behaviour of the suspensions containing CNTs and tensile strengths of their resulting nanocomposites were characterized. CNT/polyester suspensions exhibited a shear thinning behaviour, while polyester resin blends act as a Newtonian fluid. It was also found that nanotubes with amine functional groups have better tensile strength, as compared to those with untreated CNTs. Transmission electron microscopy (TEM) was also employed to reveal the degree of dispersion of CNTs in the matrix.
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1. Introduction

Scientific and industrial efforts have been recently focused on nanotechnology and nanomaterials. Nanomaterials are exhibiting some superior properties, as compared to their micro or macro size counterparts. Carbon nanotubes (CNTs) are composed of thin tubes with diameters of only a few nanometers, but a length of few microns. They exhibit higher aspect ratio, extraordinary mechanical, thermal and electrical properties, which make them prime candidates as reinforcing constituents in various polymers for the production of nanocomposites. Although there is a number of work published [1–5] on CNT reinforced polymer composites, realization of the expected enhancement in the properties of the composites, such as mechanical properties has not entirely been established so far. This is because of

the fact that nanotubes have strong tendency to exist in agglomerated form via their huge surface area, which leads to non-homogeneous dispersion and random distribution of the nanotubes inside the resin. Therefore, homogeneous dispersion of CNTs in the polymer matrix is one of the key factors to enhance mechanical properties of the composites [1–9]. The common dispersion techniques for processing CNT/polymer composites have been direct mixing and sonication [1–15]. In addition, Gojny et al. [6] showed that the utilization of 3-roll-milling, which applies intensive shear forces on the processed compounds, is an appropriate technique to exfoliate and disperse carbon nanotubes in an epoxy resin. They also concluded that 3-roll-milling technique provided a better dispersion of CNTs in the epoxy resin resulting in higher mechanical properties, as compared to those prepared by sonication. Furthermore, besides the physical approaches for the CNT dispersion, some other attempts including the use of surfactants and chemical functionalization of the CNT-surfaces have been made in order to alter the degree of dispersion and to tailor the interface between the matrix and carbon nanotubes. In the near future, the further development in chemical functionalization of nanotubes may be the key challenge for advanced nanocomposites with the desired properties. Consequently, it is obvious that a better understanding of the relationship between processing, interfacial optimization, surface chemistry and composite properties is necessary for the potential future applications of CNTs in polymer matrices.

Unsaturated polyesters (UP) with good cost/property relation have been the most commonly employed matrix materials for glass fiber reinforced polymer composite parts. UP based materials have been utilized in many applications including automotive, construction, transportation, storage tanks and piping industry. Unsaturated polyesters become insoluble and infusible by crosslinking with a monomer, which is usually styrene. The miscibility of the resin and the styrene depends on the resin composition. Commercial polyester resins contain about 30–40% by mass of styrene. Polyester resins are versatile, quick curing, and have a long shelf life at room temperature. The disadvantages of these thermoset resins are self-polymerization at higher temperatures and significantly higher cure shrinkage, as compared to epoxy. Despite the fact that polyester resins have been commonly employed in many industrial applications, to our knowledge, there is

no reported work in the literature on the processing and properties of CNT/polyester systems. Thus, CNTs have a great potential to improve the properties of a low cost resin like polyester at very low filler content and to induce new characteristics such as electrical conductivity. In this paper, we address some critical aspects on the processing of CNT/polyester nanocomposites prepared with the use of 3-roll-milling and also sonication techniques. Transmission electron microscopy (TEM) was employed to reveal the degree of dispersion of carbon nanotubes with and without functional groups in the involved resin. Some rheological and mechanical properties of the composites are also discussed.

2. Experimental details

An isophtalic commercial unsaturated polyester resin Cam Elyaf 266 with 35 wt.% of styrene was obtained from CAM ELYAF Inc, Turkey. Also, special polyester resin blends, composed of an allylic based polyester resin Poliya 240 with negligible amount of styrene and Poliya 420 without any styrene were obtained from POLİYA POLYESTER Corp., Turkey. Double-wall carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT) with and without amine functional group (NH_2) produced by chemical vapor deposition (CVD) were obtained from Nanocyl (Namur/Belgium) and used as additives in the involved resin systems. DWCNTs and MWCNTs have average diameters of 2.8 and 15 nm, respectively, with a length of approximately 50 μm. Cobalt naphthanate (CoNAP) and methyl ethyl ketone peroxide (MEKP) were used as an accelerator and initiator, respectively, to polymerize the resin suspensions that contain various amounts of CNTs.

To prepare CNT/polyester nanocomposites, the first approach was the utilization of the 3-roll-milling process, successfully employed to process epoxy resins, employing to a commercial unsaturated polyester resin. In this manner, the samples were prepared under excessive shear forces for the dispersion of 0.1, 0.3, and 0.5 wt.% of carbon nanotubes in Cam Elyaf 266 resin, setting the dwell time of CNTs/polyester suspension on the rolls for about 2 min. The resin suspensions were polymerized with the addition of 0.3 wt.% of CoNAP and 1 wt.% of MEKP into the system. During the application of this technique, we have experienced some difficulties. The major concern was the styrene evaporation from the polyester resin during the processes, which

caused a dramatic increase of the viscosity. Styrene evaporation was accelerated due to heat occurred on the rolling mills due to higher shear effect. The polyester resin with high viscosity stacked on the rolls and it caused some difficulties for the collection of the resin, due to the uncontrolled styrene evaporation, and thus the final styrene compositions within the resin blends were unknown. Alternatively, the sonication method was employed with the same CNT/resin systems. Some problems with the sonication method similar to 3-roll-milling process were observed. Even though the sonication bath was cooled by water, the local heating due to energy created within the resin system, caused styrene evaporation from the polymer suspension, leading to a more viscous resin. In addition, it was observed that nanotubes were agglomerated in the volumes closer to the tip of the sonicator. Van der Waals attractive forces between the CNT-surfaces are known to be sensitive to heat, so increasing agglomeration occurred [2,6]. To overcome the difficulties associated with styrene evaporation, we switched to a resin system, containing negligible amount of styrene (Poliya 240) and non styrene (Poliya 420).

With the corresponding novel polyester resin systems nanocomposites were prepared by setting the appropriate gelation time and viscosity for the 3-roll-milling processing. The styrene was added to the system after 3-roll-milling. After some experimental trials, polyester resin blends were formulated based on 45 wt.% of Poliya 420, 30 wt.% of Poliya 240 and 25 wt.% of styrene with the presence of 0.2 wt.% of CoNAP and 1.5 wt.% of MEKP. The polymer mixture to be used during 3-roll-milling process was prepared by hand-mixing of two types of the polyester resin at the given ratio for 10 min. Nanocomposite samples were prepared by the dispersion of the 0.1, 0.3, and 0.5 wt.% of the carbon nanotubes within the polyester resin blend. After collecting the CNT containing polyester suspension by spatula from the 3-roll-milling, 25 wt.% of styrene was added to the involved resin system. The whole system was then subjected to the intensive mixing for half an hour using magnetic stirrer and finally poured down into an aluminum mold and cured at room temperature followed by post curing in an oven at 110 °C for 2 h. Although Poliya 240 with a lower amount of styrene was introduced to 3-roll-milling, comparable viscosity increase of the resin, and problems due to the stacking of the high viscosity resin on the rolls were observed. However,

note that in this second approach, we diminished difficulties with styrene evaporation and unknown styrene content in the final product by using low styrene containing resin. For that reason, in our further experimental investigations, we focused just on investigating the properties of the nanomaterials prepared by the second approach.

The dispersion of the CNTs within the composites was characterized by transmission electron microscopy (TEM) using a Philips EM 400 at 120 kV acceleration voltages. The ultra thin TEM samples with a thickness of 50 nm were prepared by ultramicrotome cutting at room temperature.

TA Instruments RDA III with parallel plate rheometer geometry (500 μm gap, and 50 mm plate diameter) was used to analyze the rheological behaviour of the polyester suspensions with different carbon nanotubes loadings. Tests were performed in steady state modes at room temperature in order to avoid styrene evaporation during the measurements. For that reason, liquid samples were taken from the collected resin suspension from the 3-roll-mill. Steady shear rates (SSS) were used to investigate the flow properties of the polyester suspensions by considering the viscosity as a function of increasing shear rates.

Mechanical tensile properties of the composites were determined according to DIN EN ISO 527.1. Dog bone specimens were prepared by countersinking using a Mutronic Dear Drive 2000. The tensile samples were tested using a Zwick Z010 Universal tensile testing machine at a cross head speed of 1 mm/min. The elongation of the specimens during the test was also measured.

3. Results and discussion

The 3-roll-milling process via intensive shear forces seems to be more convenient technique than traditional ones such as sonication and direct mixing for the dispersion of carbon nanotubes within a liquid polymer resin. Fig. 1 shows the TEM micrographs of MWCNTs and DWCNTs with and without functional groups in the polyester resin blend for 0.3 wt.% of loading. MWCNTs with functional groups exhibited better local dispersion in the polyester matrix, as compared to DWCNTs with and without treatment. In general, DWCNTs were observed to be more agglomerated form caused by their pronounced higher surface area. In the literature, rheological behaviour of the polymer suspension was associated with the prediction state of
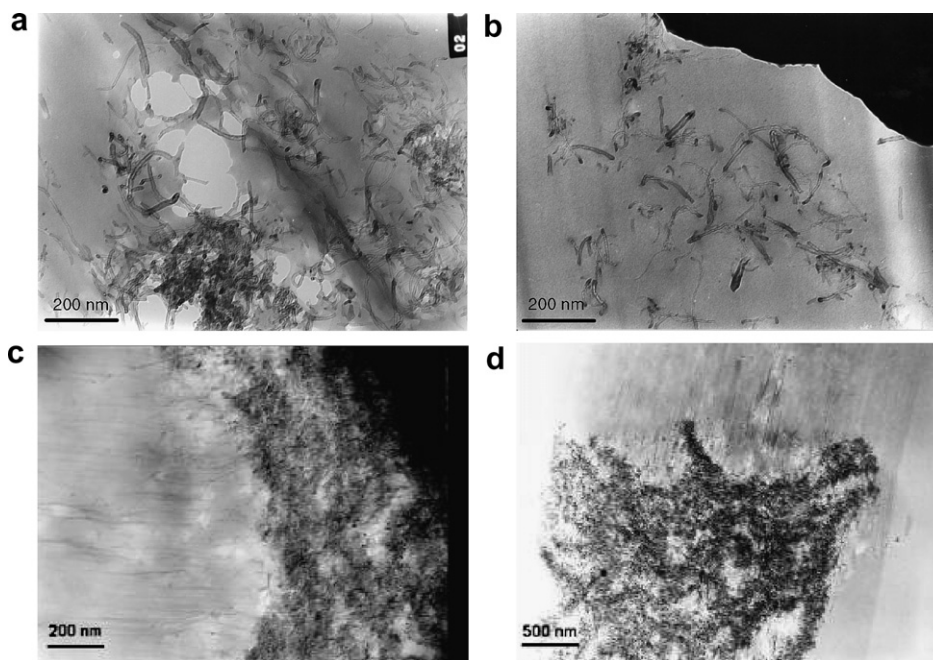
Fig. 1. TEM micrographs of nanocomposites prepared from POLIYA™ polyester at 0.3 wt.% loading of (a) MWCNT, (b) MWCNT–NH$_2$, (c) DWCNT (d) DWCNT–NH$_2$.

CNTs dispersion within the corresponding resin [11]. Figs. 2 and 3 give the viscosity as a function of shear rate for the Poliya polyester based suspensions containing MWCNTs, MWCNT–NH$_2$, respectively at different loading rates. As seen in the figures, shear thinning beha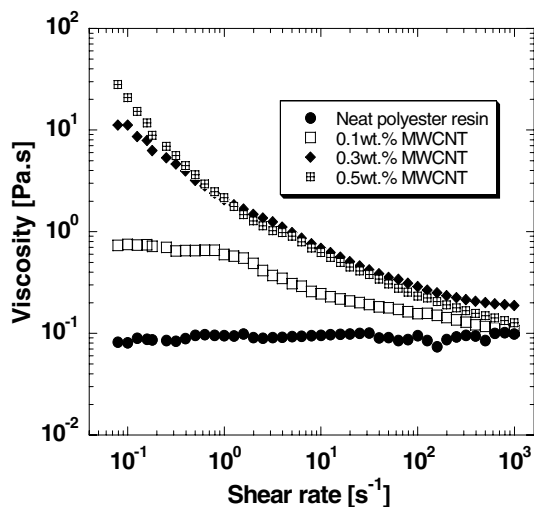vior was observed for the samples containing either MWCNT or MWCNT–NH$_2$, such that viscosity is reducing with the increase of shear rates. The viscosity of polyester suspensions with MWCNT decreases sharply at 0.1 wt%, but MWCNT–NH$_2$ has not the same behavior. This might be due to the fact that nanotubes with amine functional groups reveal better compatibility or chemical interaction with the polyester chains within the system. Carbon nanotubes

Fig. 3. Viscosity of the polyester suspension with MWCNT–NH$_2$ as a function of shear rate.

Fig. 2. Viscosity of the polyester suspension with MWCNTs as a function of shear rate.

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have a high aspect ratio, which alters significantly the flow characteristics of involved polymer suspension.

In order to investigate the nanofiller effect with and without chemical functional groups on the mechanical properties of the composites, tensile tests were conducted. The tensile properties of Poliya polyester blend were much lower, as compared to a common commercial polyester resin in the market. Note that both of the components of Poliya were specially snythesized and their individual mechanical properties were lower than those of a commercial polyester resin. The Figs. 4 and 5 show
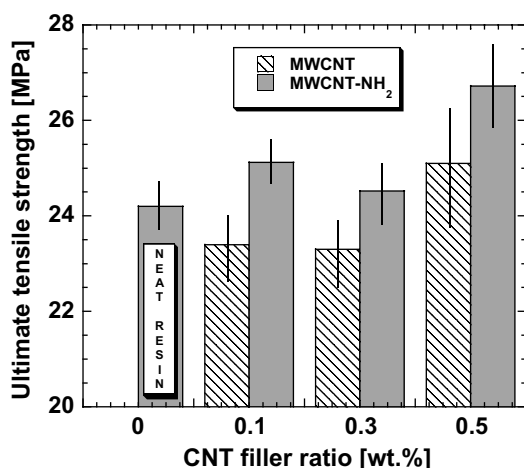

Fig. 4. Ultimate tensile strength (UTS) of the CNT/polyester nanocomposites with MWCNT and MWCNT–NH$_2$ as a function of CNT filler ratio.
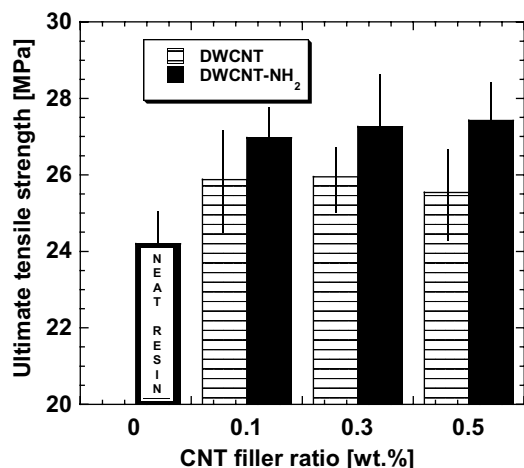

Fig. 5. Ultimate tensile strength (UTS) of the CNT/polyester nanocomposites with DWCNT and DWCNT–NH$_2$ as a function of filler ratio.

the tensile strength of the resulting nanomaterials. As it can be seen in the figures, there are some differences between the MWCNT reinforced nanocomposites with and without amine functional groups, as compared to neat polyester resin. Moreover, at each loading rate, composite specimens containing MWCNTs with amine functional group have higher values than those with MWCNTs without any functional group. For instance, the nanocomposites with 0.5 wt.% of MWCNT–NH$_2$ have about 6% and 15% higher strength than those with the same loading rate of MWCNTs and the neat resin, respectively. The same findings were also valid for the composites with DWCNTs and DWCNT–NH$_2$. The nanocomposites with DWCNT–NH$_2$ at 0.5 wt.% loading ratio have about 17% and 5% of higher strength values than the neat resin and the ones with DWCNTs. Note that nanocomposites with DWCNTs with either functional group or not have higher strengths than those with MWCNTs or MWCNT–NH$_2$ at each loading rate. This can be explained by the higher surface area of the double wall carbon nanotubes, which may result in a better load transfer efficiency at the interface region as well as amine functional groups over CNTs which is supposed to promote the dispersion and pronounced covalent bonding to some extent.

4. Conclusion

In this paper, we have focused principally on investigating three common key issues (i) availability of blending of polyester resin with very low amount of carbon nanotubes, highlighting some critical aspects and some limitations for the process, (ii) dispersion state of carbon nanotubes within the corresponding resin, (iii) interfacial adhesion/interactions of carbon nanotubes with the polyester resin system. We have concluded that the styrene evaporation and self-polymerization via too much heat occurred are the two major issues to be considered, when a thermoset polyester resin is blended with carbon nanotubes by employing 3-roll-milling and sonication techniques. We also revealed that 3-roll-milling method is more adequate technique for the dispersion of CNTs within a thermoset polyester resin blend, as compared to methods such as sonication and direct mixing. Furthermore, the fact that CNTs with amine functional groups exhibited relatively enhanced dispersion state within the polyester resin blend, resulting in better tensile mechanical properties is evidence for that appropriate

chemical functionalization of carbon nanotubes would be the key for the potential future applications. In the further studies, we are going to concentrate on developing CNT/polyester master batches by means of different types of functional groups and without styrene in order to obtain desired microstructure and mechanical properties of the nanocomposites.

Acknowledgement

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