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Microwave-induced rapid nanocomposite synthesis using dispersed single-wall carbon nanotubes as the nuclei

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Abstract Single-wall carbon nanotubes (SWNTs) provide a reactive environment in presence of microwave radiation because they absorb the energy that leads to fast, direct heating. This makes composite formation in a microwave reactor highly feasible where the SWNTs serve as the nuclei for polymerization. In this article, we demonstrate rapid, in situ synthesis of poly(methyl methacrylate) (PMMA) and polyvinylpyrrolidone (PVP) nanocomposites using their respective monomers. The key to their success was the use of the highly dispersible SWNTs, which had strong interactions with the monomer and the polymer. Rapid synthesis within a few minutes was possible, which led to remarkable nanoscale dispersion of nanotubes in polymer matrix by encapsulation of the already dispersed SWNTs before the latter could agglomerate. The molecular weight and polydispersity of the polymers remained unchanged in the presence of the SWNTs. The addition of 0.5 wt% SWNT to PMMA enhanced its thermal stability (as measured by the initial degradation temperature) by 37 °C and the hardness by around 50%. On the other hand, with the addition of up to 4 wt% SWNT, the PVP showed no enhancement in thermal stability but its hardness increased by 250–300%. Finally, this technique is practical because it reduces time, cost, and energy requirements.

Introduction

The incorporation of carbon nanotubes (CNTs) [1, 2] of high aspect ratio into various polymers [3–5] has been studied as an effective means to enhance mechanical, physical, electrical, and thermal properties of polymer nanocomposites [6–8]. Potential applications of this include telecommunications [9], field emission [10], radiation shielding [11], actuators [12], photovoltaic cells [13], light-emitting diodes [14], and structural materials [15]. Several theoretical and experimental investigations have clearly demonstrated that the incorporation of CNT in polymer enhances both the physical and mechanical properties [16–20]. On the other hand, others have shown insignificant improvements [21–23]. However, the use of nanotube reinforcement in polymer has been a challenge [24, 25] because of the difficulties in optimizing the processing conditions to achieve good dispersion. Several techniques including the use of surfactants [26], emulsion polymerization [27], judicial sonication-induced polymerization [28], melt mixing [29, 30] solvent-based method with surfactants [26, 31, 32], and in situ polymerization [22] have been attempted to overcome this problem. Other approaches include chemical functionalization [33], doping [34], polymer coating [35], and the use of compatibilizer like amine-terminated poly(ethylene oxide) [36]. However, significant challenges on the dispersion issue still remain. Moreover, the above-mentioned conventional methods require complicated instrumentations, time, and energy. We report a convenient and economic process which has great potential to produce polymer nanocomposites (nanoscale dispersion of CNT) with various polymers in few minutes (15–20 min) in a microwave reactor. The fast polymer formation is essential in encapsulating the single-wall carbon nanotubes (SWNTs) before they can agglomerate.

Chemistry under microwave radiation is known to be significantly different, eco-friendly, faster, and more efficient [37–39] than under conventional chemical processing

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conditions. It has been exploited in a variety of organic syntheses with reported advantages like high yields, rapid reaction under controlled temperature and pressure (especially in a closed system), and high-purity products due to short residence times.

Recently, we have reported the microwave-induced functionalization of CNTs [40, 41], where after rapid microwave treatment in specific reagents, it was possible to heavily functionalize the SWNTs to the point that they dispersed into different solvents without the addition of water-soluble polymers or surfactants. We have also demonstrated the in situ growth of ceramics on CNT under microwave radiation to form CNT–silicon carbide composites [42]. The CNTs provide a reactive environment in presence of microwave radiation because they absorb energy leading to fast heating along with some local superheating. These make composites formation in a microwave reactor highly feasible where the CNTs serve as the nuclei. The key to the success of this process would be the dispersion of the CNTs in the monomer followed by rapid polymerization before the CNTs agglomerate. The objective of this article is to demonstrate the microwave-induced rapid nanocomposite synthesis using dispersed CNTs as the nuclei using methyl methacrylate (MMA) and vinylpyrrolidone (VP) as the monomers.

Experimental

Materials

The starting SWNTs, which were synthesized by high-pressure CO conversion, were purchased from CNI Inc. Carboxylated SWNTs were also purchased from Cheap Tubes Inc. All other chemicals including MMA, VP, 2,2′-azobisisobutyronitrile (AIBN), and ethanol were purchased from Sigma–Aldrich Chemicals.

Functionalization of SWNT

The functionalization of SWNTs and in situ polymerization were carried out in CEM MARS microwave reactor with a 100 mL closed Green Chem Plus (Teflon) vessel. The microwave system was placed inside a fume hood for safety reasons. Both as-received and dispersible nanotubes were used to make PMMA and PVP composites. SWNT functionalization was carried out as follows [40]. Approximately 15 mg of as-received SWNTs were added to 20 mL of a 1:1 mixture of 70% nitric acid and 97% sulfuric acid mixture in the reaction chamber. Reaction vessel was then subjected to microwave radiation at 100 °C for 10 min applying 90% of 1600 W microwave power and 20 psi. The mixture was then diluted with deionized water (DI) and filtered through 10-μm poly(tetrafluoroethylene) (PTFE) filter paper, and the filtrate was transferred to a dialysis bag with nominal molecular weight cutoff of 12,000–14,000. The bag was placed in a beaker containing DI water. The DI water was continually replaced till the pH reached 7. The filtrate was then removed and concentrated in a vacuum evaporator. The final solvent dispersible SWNT was referred to as SWNT-D.

Synthesis of PMMA nanocomposites

Twenty mg of the SWNT-D was dispersed in 10 mL distilled water by 30 min sonication. Six mg of free radical initiator, AIBN and 4 g of MMA were dissolved in different beakers containing 10 mL ethanol by 30 min sonication. Finally, the three ingredients were mixed together by 15 min of sonication. The microwave-induced reaction was carried out for 20 min at 30 psi and 90 °C using 60% of 1600 W microwave power. The composite precipitated out of the reaction mixture, which was then separated and washed with ethanol. Pure PMMA synthesis was carried out using the same reagents and under the same conditions without the addition of SWNT-D. PMMA and its SWNT composites were solvent cast into films/sheets from toluene solutions. These were dried under controlled pressure and temperature in a vacuum oven to avoid bubble formation. To compare the effectiveness of the microwave process, composites were also made by solution blending of PMMA and SWNT-D, and by in situ polymerization under the same condition with unfunctionalized SWNT.

Synthesis of PVP–SWNT nanocomposites

One hundred and sixty milligram of functionalized SWNT (referred to as SWNT-D2), which was purchased from Cheap Tubes Inc., was dispersed in distilled water by sonication for 1 h in presence of 1 wt% sodium dodecyl sulfate (SDS). In a separate container, 4 g of VP was dissolved in water, which was mixed with the dispersed SWNT-D2 and subjected to 1 h sonication. Six milligram of AIBN was dissolved in 10 mL of ethanol and added into the monomer/SWNT-D2 mixture and further sonicated for 30 min. This mixture was placed in the microwave reactor and the polymerization was carried out for 15 min at 30 psi and 90 °C, using 60% of 1600 W microwave power. The composite was precipitated out in acetone solution, filtered, and evaporated in a vacuum oven. A concentrated water solution of the composite was used for solvent casting a sheet of polymer. Pure PVP was synthesized using the same reagents and under the same conditions without the addition of SWNT-D2.

Characterization

The composite was characterized by various techniques. Molecular weight and polydispersity were measured by gel permeation chromatography (GPC). The analysis was carried out in tetrahydrofuran (THF) against a polystyrene standard using RI detector. Field emission scanning electron microscopy (SEM) images were taken using a LEO 1530 electron microscope. FTIR measurements were made on the thin films, made by compression molding, using a Perkin Elmer spectrometer. The thermogravimetric analysis (TGA) was performed by a TA Q50 thermal analyzer in nitrogen and at a heating rate of 10 °C/min. LECO Microhardness Tester (Model LM 700) equipped with a VICKERS and KNOOPS indenter was used for Microhardness measurements. Indentations were made using 10 g and 100 g loads, and the dwell time was 20 s. KNOOP hardness was based on average length of the imprint made from the indenter, and the VICKERS hardness was based on the average diagonal length of the imprint made from the indenter. Both diagonals were measured for each indentation for VICKERS and lengths were measured for KNOOPS. The hardness numbers reported were based on an average of ten measurements. Shore hardness of PMMA and its composites were measured by Shore Scale Durometer Hardness Tester, Analogue D.

Results and discussion

PMMA and PVP nanocomposites were formed with dispersible SWNTs, where the dispersion was possible via appropriate functionalization. PMMA and PVP are commercially important polymers with desirable properties such as good mechanical strength, dimensional stability, etc. The dielectric constants and loss tangents (tan δ) of MMA, PMMA, VP, and PVP are in the microwave processible range making the composite synthesis highly feasible. Microwave-induced functionalization and composite formation of CNT was facilitated by the fact that it absorbed microwave energy leading to fast and efficient heating probably with some local superheating.

The fast polymerization of monomers on the surface of SWNT-D prevented the tubes from agglomerating. This can be seen in the series of SEM images presented in Fig. 1a–d, which shows the progression of the PMMA composite formation. Figure 1a shows the state of the reaction mixture at the end of 5 min. The SWNT-D was well dispersed in the matrix, but the PMMA polymerization was incomplete; therefore, much of the background is from monomers and oligomers. After 10 min, the polymer formation progressed and is shown in Fig. 1b. Here the SWNT-D was well covered with the polymer. At the end of 20 min, the composite formed into a solid bulk. The SEM of the fractured surface (not shown here) showed that the tube bundles were completely encapsulated in PMMA. When this composite was washed with toluene, part of the PMMA was washed out, showing a skeleton of SWNT-D covered with polymer. From the SEM (Fig. 1c), the dimension of nanotube bundles were clearly in nano scale (<100 nm). So it was concluded that a nanocomposite was formed overcoming the difficulty of SWNT dispersion. In another set of experiments, a composite was made with unfunctionalized SWNTs, and in this case the PMMA and the nanotubes separated into two phases with poor dispersion. Composites were also made via solution blending of PMMA and SWNT-D. The process in the absence of microwave-induced reaction showed unsatisfactory dispersion as shown in Fig. 1d. Therefore, good dispersion is attributed to the combined effects of rapid in situ polymerization and appropriate derivatization of the nanotubes. The results with the PVP–SWNT composite were similar and not all data are presented here for brevity. Figure 1e shows the SEM of this composite containing 4 wt% of SWNT-D2. From Fig. 1e it is evident that SWNT bundles were well dispersed in the polymer, and again this was possible only because of rapid polymer formation on the surface of already dispersed tubes.

The PMMA–SWNT nanocomposites were formed within 20 min at high yield. Typical sheets made of these composites are shown in Fig. 2. The PMMA–SWNT (0.5 wt%) (Fig. 2a) showed a homogeneous dispersion of SWNTs forming a transparent sheet, while a composite formed with as-received SWNT showed poor, nonuniform dispersion (Fig. 2b). Compared to the pure PMMA (Fig. 2c), the PMMA–SWNT was slightly colored. The molecular weight of pure PMMA and that of the composite were measured by GPC. This was done in THF against polystyrene standard using a RI detector. The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity (PDI) of pure PMMA were found to be 79,348, 39,892, and 1.99, respectively, while for PMMA in PMMA–SWNT the respective numbers were 81,803, 42,176, and 1.94. So, it was clear that the presence of nanotubes did not hinder polymerization. It was possible to incorporate nanotubes in a polymer matrix by this method while maintaining the molecular weight and polydispersity of the original polymer.

The FTIR spectra of pure PMMA and PMMA–SWNT-D are shown in Fig. 3. The interaction between PMMA and SWNT-D was evident. Most distinct features of the PMMA spectra were present in the PMMA–SWNT-D composite, demonstrating the chemical similarity between the two. The peak around 1730 cm^{-1} was attributed to C=O stretching frequency and the peaks around 2995 and

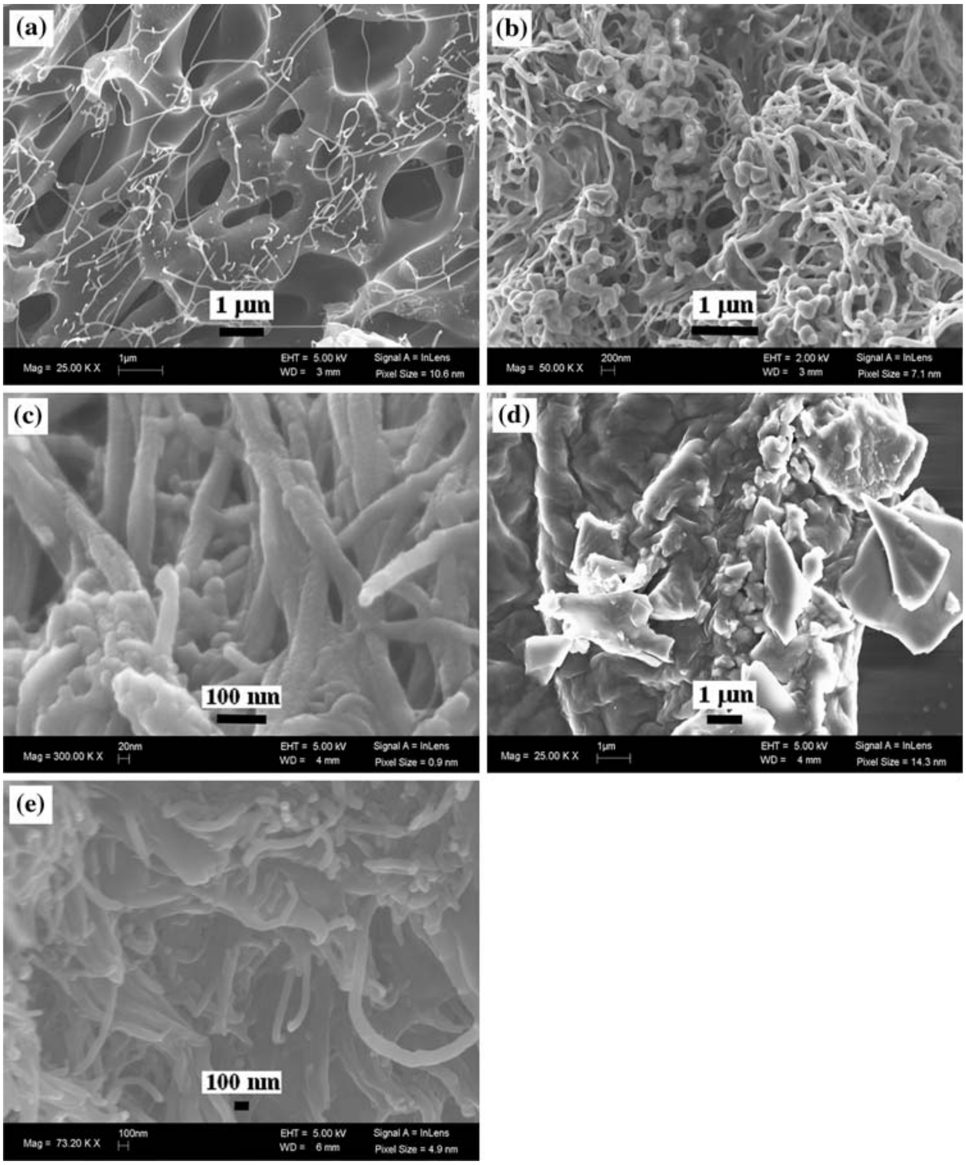

Fig. 1 SEM images of (**a**) PMMA–SWNT-D composites, after 5 min of polymerization; (**b**) SWNT well covered by PMMA after 10 min of reaction; (**c**) Carbon nanotube bundles after washing PMMA by toluene; (**d**) Surface of PMMA composites made by solution blending showing no evidence of nanocomposites formation; (**e**) PVP–SWNT nanocomposites showing PVP-coated nanotubes. SEM scale bar: (**a**, **b**, **d**) are 1 µm; (**c**, **e**) are 100 nm

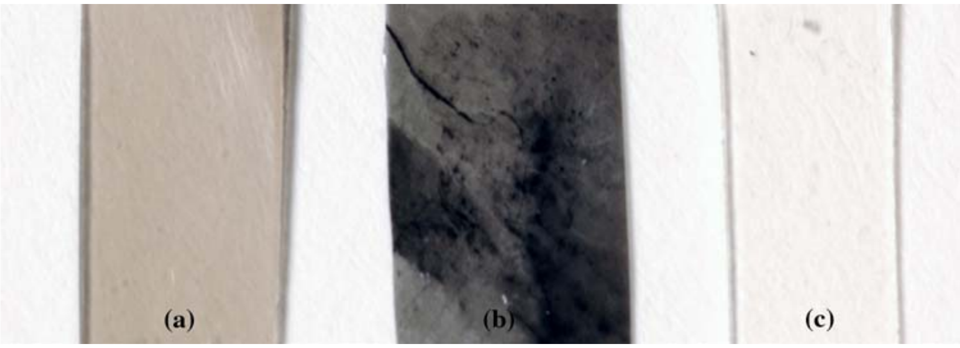

Fig. 2 **a** PMMA–SWNT-D composite made by microwave technique. **b** SWNT-D solution blended with PMMA. **c** Pure PMMA without any SWNT

2944 cm^{-1} were attributed to CH$_2$, and CH$_3$ vibration.[1] In the region of 3100 to 3700 cm^{-1}, a prominent difference was observed. This broad band around 3450 cm^{-1} was assigned to the –OH stretching mode of the –COOH group originating from the SWNT-D. The band at 1641 cm^{-1} in the nanocomposite was assigned to the C=C graphitic stretching from the SWNT. This is known to occur in

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[1] FTIR data of PMMA product (average M_w 93,000 and average M_n 46,000) from Sigma-Aldrich website.

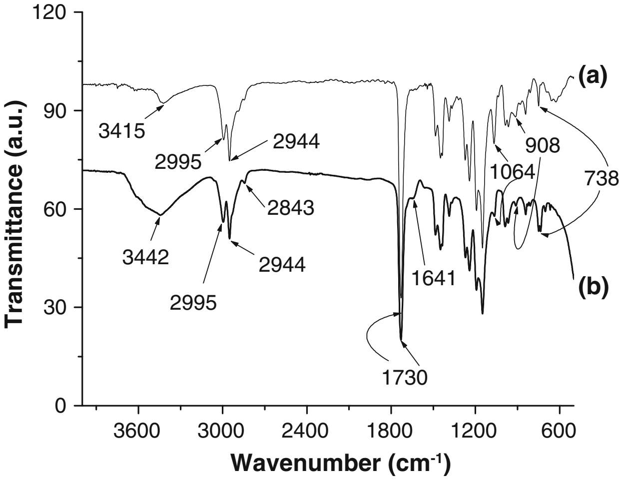


Fig. 3 FTIR of PMMA (a) and PMMA–SWNT-D composite (b)

functionalized nanotubes. Interestingly, another additional peak appeared in the composite at 2842 cm^{-1}. The relative intensities of some peaks, such as the ones at 738, 908, and 1064 cm^{-1} increased in the nanocomposites. While, the chemical linkage between SWNTs and PMMA are not clear, the differences in the two spectra show some interactions between PMMA and SWNT-D.

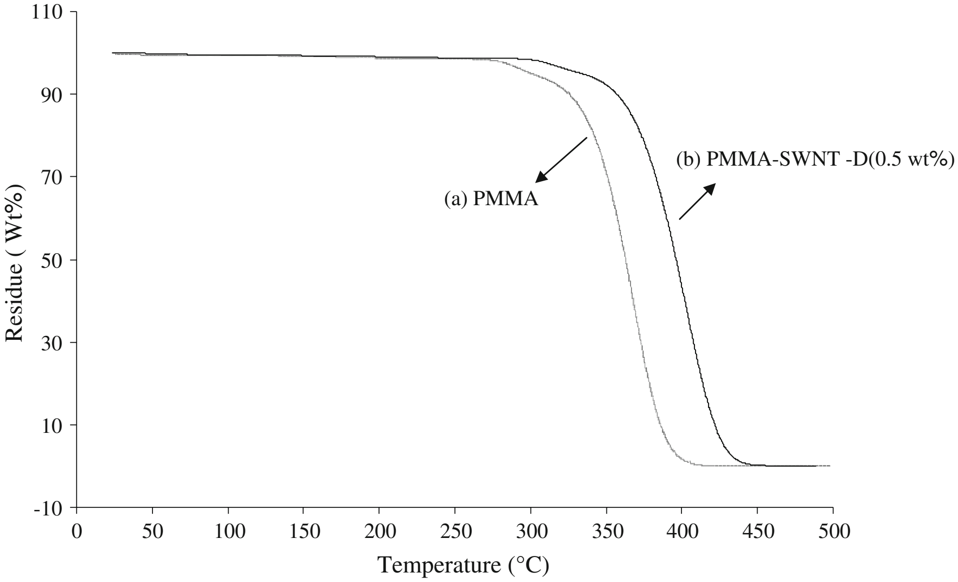
The reinforcement of PMMA by SWNT was reflected in the data from TGA presented in Fig. 4. Initial degradation onset of pure PMMA and PMMA-SWNT are at 322 and 359 °C, respectively. So, relatively a small amount (0.5 wt%) of SWNT thermally stabilized the PMMA by around 37 °C. The process of degradation of composite was delayed all the way starting from 100 wt% residue to complete burning. The T_{50} (the temperature at which 50% degradation took place) increased by 35 °C from 362 °C for PMMA to 397 °C for the composites suggesting a considerable increase in thermal stability. However, this enhancement in thermal stability was not observed for the PVP–SWNT nanocomposites.

The reinforcement was also evident from the microhardness measurements. The microhardness for PMMA and PMMA–SWNT were found to be 10.11 and 15.63 HV, respectively with a 100 g test load. The KNOOPS number for PMMA and PMMA–SWNT were found to be 11.82 and 17.52 HK, respectively with 100 g test load. Using a 10 g test load, the values were 11.89 and 17.96 HK for PMMA and PMMA-SWNT, respectively, while the corresponding numbers in VICKERS scale were 12.20 and 18.13 HV. The improvement of mechanical property was also evident by Shore D durometer, which showed 60 and 95 for PMMA and PMMA–SWNT, respectively. On an average, it was estimated that the addition of 0.5 wt% of functionalized SWNT led to approximately 50% improvement of microhardness. As shown in Table 1, for the PVP–SWNT nanocomposite containing 4 wt% SWNT, the improvements were significantly higher of the order of 250–300%.

Table 1 Microhardness of the PMMA and PVP and their composites

Sample	KNOOPS hardness (HK)	VICKERS hardness (HV)	Applied force (g)
PMMA	11.82	10.11	100
	11.89	12.20	10
PMMA–SWNT (0.5 wt%)	17.52	15.63	100
	17.96	18.13	10
PVP	7.7	7.1	100
	8.3	7.9	10
PVP–SWNT (4 wt%)	27.21	28.34	100
	29.01	30.41	10

Fig. 4 TGA of PMMA (a) and PMMA–SWNT-D (0.5 wt%) (b)



Conclusions

Microwave-assisted in situ synthesis of CNT-based PMMA and PVP nanocomposites is presented. Underivatized SWNTs showed poor dispersion in the composite. Appropriate derivatization and prior solvent dispersion of the SWNTs were key to the success of this approach. Reinforcement by the SWNTs was evident from the significant improvements in thermal stability and mechanical strength with the addition of as little as 0.5 wt% nanotubes. In summary, this is a fast and energy-efficient process and can be used to synthesize other nanocomposites as well.

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