

Impact of Functional Groups in MWCNT on Surface Hydrophilicity, Mechanical and Thermal Properties of Polystyrene/CNT Composites

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Abstract. We prepared nanocomposites of MWCNTs/polystyrene via a solution casting method, and DI water was used as coagulation bath. The influence of pristine and two functionalized MWCNTs on surface morphology, thermal properties and mechanical properties of MWCNT/polystyrene composites were extensively discussed. Analysis of SEM shows that the porous structures with narrow size distribution from micro- to nano-size appear in all composites, which decrease the tensile strength of the composites. Despite the glass transition temperatures (T_g) of all the composites lower compared with T_g of pure polystyrene, which increase with the loading of MWCNTs. The mechanical properties of the composite with 5 wt.% MWCNTs are enhanced greatly, and the phenomenon is especially pronounced for the addition of the MWCNT-OH.

1. Introduction

Polymer composite materials have been applied in different industrial fields due to their light weight, flexibility in process, high durability and strength[1,2]. The selection of nanofillers can significantly improve the strength, toughness, durability of the resulted composites[3]. Comparing with the conventional fillers as carbon nanofibers and spherical particles, carbon nanotubes (CNTs) are regarded as an ideal filler in preparing polymer/inorganic composites due to their outstanding electrical, thermal[4], and mechanical properties[5]. Therefore, polymers/CNTs with diverse functional and structural properties have found many applications[1,5], one of which is to produce CNTs-reinforced composite materials[6]. Nowadays, polymer materials as polystyrene[4], polymethylmethacrylate[6], and polyethylene[7] were commonly chosen as polymer matrices for producing polymers/CNTs composites. Several methods as melt mixing[8], solution casting technique[9], and in situ polymerization[10] were generally adopted for the synthesis of polymers/CNTs composites. However, the applications of these composites in different fields have been limited by poor interfacial interaction between polymer and CNTs, having the strong tendency to self-aggregate of CNTs. Two approaches as mixing process and surface treatment of pristine CNTs are generally used either for disentangling CNTs by mechanical force or for altering the surface functionality with -OH or -COOH. Surfactant such as sodium dodecyl sulfonate, sodium dodecylbenzene sulfonate, and Triton-X has been successfully applied to improve the dispersibility of CNTs in polymer matrix. The content of surfactant was also found to be a critical effect in dominating the surface morphologies caused by phase separation. Up to now, the combination effects of surfactant and pore structures on the composite properties have rarely been mentioned.

In this study, pristine and two functionalized MWCNTs on the various properties of PS based



composites were investigated. The influences of type and content of MWCNTs, and presence of surfactant on the performance of composites were analyzed. The chemical component, thermal properties, as well as surface hydrophilicity of composite materials are systematically studied.

2. Experimental

0.2g polystyrene (Goodfellow, U.K.), a certain amount of pristine MWCNTs (p-MWCNT, length 10-30 μm), or hydroxylated MWCNTs (MWCNT-OH, hydroxyl content 5.58 wt.%, length 10-30 μm), or carboxylated MWCNTs (MWCNT-COOH, carboxyl content 0.49 wt.%), obtained from Beijing DK Nanotechnology Co. Ltd, 0.1 ml surfactant (Triton X-100) and 10 ml Tetrahydrofuran (THF) were mixed together and stirred until PS completely dissolved. Then the mixture was ultrasonicated for 2 h and then cast into a specific container. After 20 min, the gasket was immersed into DI water to obtain a stable membrane. The morphologies of composite surface and cross-section were studied through FESEM (Hitachi-4800, Hitachi Limited, Japan). To evaluate surface hydrophilicity of the composites, instrument of dynamic contact angle (DSA-100, Kruss, Germany) was used. Effect of the loading of carbon nanotubes on the T_g was analyzed by DSC (Perkin-Elmer, U.S.). The mechanical properties of the nanocomposite were characterized by single fiber electronic tensile strength tester (LLV-06 ED, Laizhou, China).

3. Results and Discussion

3.1 The Characterization of the Composites by DSC

Differential scanning calorimetry was performed to distinguish the effect of adding CNTs and surfactant to PS matrix on the T_g . Figure 1.a depicts the values of T_g obtained for the surfactant-treated CNTs/PS composites with different loadings of p-MWCNT, MWCNT-OH, and MWCNT-COOH. The T_g of pure PS and the composites with p-MWCNT loading from 1, 5 to 12.5 wt.% were 106, 81, 95, and 97 $^{\circ}\text{C}$, respectively. The increase of T_g with p-MWCNT loading suggests that the strong interfacial affinity between PS and p-MWCNT hinders the mobility of polymer chain segment resulting in the increase of T_g . Similar results were also found in the composites with MWCNT-OH or MWCNT-COOH. The T_g of the composites with MWCNT-OH was 66, 75, and 78 $^{\circ}\text{C}$, whereas T_g of the composites with MWCNT-COOH different loading was 60, 66, and 72 $^{\circ}\text{C}$. For the composites with functionalized MWCNTs, T_g values decline more than the composites with pristine MWCNTs. The highest declination of T_g was observed for the composites with MWCNT-COOH, which can be attributed to two possible effects: the length of CNTs and the type of the functional groups. As we known, the composites contained MWCNT-COOH also trend to lower thermal stability.

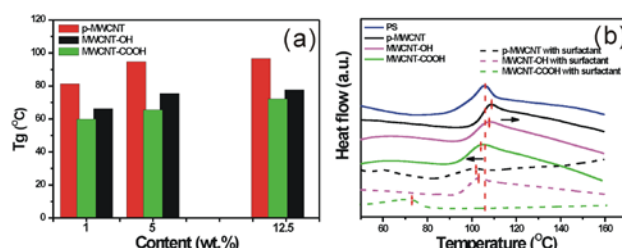


Figure 1. DSC analysis of PS composites with different MWCNTs. (a) surfactant-treated composites with CNT contents from 1, 5 to 12.5 wt.%; (b) a comparison of the composites with or without surfactant.

To distinguish the effect of adding surfactant to PS matrix on the T_g . Figure 1.b displays the T_g values obtained from PS/CNTs composites with or without the surfactant. The loading of p-MWCNT, MWCNT-OH, and MWCNT-COOH was all set as 5 wt.%. Comparing with T_g for pure PS, the non surfactant contained composites with p-MWCNT and MWCNT-OH exhibit an increase in the T_g . The

shift of T_g values to higher values may attribute to the interaction between polystyrene molecules and CNTs, which promotes the thermal stability. Whereas, the composite with MWCNT-COOH show a reduction in T_g , which arises from the degradation behavior of MWCNT-COOH. For the MWCNT composites with the surfactant, a decrease of T_g values was observed for all composites. As the composites contain surfactants for obtaining a better dispersion of CNTs in solution, the surfactant molecules attached on the side walls of nanotubes acts as a plasticizer within the PS matrix and reduces T_g of the composites.

3.2 Mechanical Performance of Composite Materials

Here, stress-strain curves for PS composites containing different types and contents of CNTs were tested to evaluate the mechanical properties. Comparing pure PS with composites containing 5 wt.% of p-MWCNT, MWCNT-OH, and MWCNT-COOH, the values of tensile strength are enhanced from 6.3 to 6.4MPa, 6.3 to 10.7MPa, 6.3 to 9.7MPa, respectively (Figure 2.a). Whereas the values of elongation at break are increased from 2.2 to 3.3%, 2.2 to 5.3%, and 2.2 to 4.0% (Figure 2.b). The highest tensile strength is especially found for the composite with 5wt.% loading of MWCNT-OH. The adding of p-MWCNT from 1 to 10 wt.% can not effectively improve the values of tensile strength due to CNT agglomerates. However, the fluctuation in the values of elongation at break may arise from such effects as: the addition of surfactants, the present of functional groups and the formation of agglomerates of CNTs. The present of surfactants and functional groups can improve the binding forces between CNTs and PS matrix and allows the ambient load being transferred to nanotubes when the composite is under external force. Therefore the elongation at break rises up with the adding of CNTs, which implies that CNTs are well dispersed in PS matrix. In contrary, when the loading of nanotubes exceeds a certain value, the larger agglomerates penetrate polystyrene and lower the interactions between polystyrene and CNTs, resulting in the elongation at break to decline. Our studies show that the composites with 5 wt.% CNTs tend to possess desirable mechanical properties.

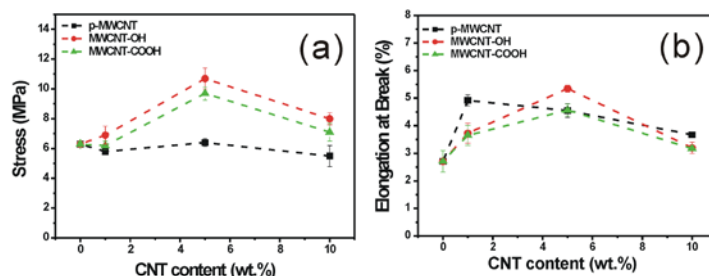


Figure2. Mechanical properties (a) and elongation at break (b) of composites with different CNTs.

3.3 Effect of Type and Content of MWCNTs on Composite Morphologies

The cross-section and surface morphologies of different surfactant-treated PS/MWCNT composites were depicted in Figure 3. The loading of p-MWCNT, MWCNT-OH, and MWCNT-COOH was varied from 1 to 10 wt.%. Microporous structures with micro-size from 6 μm to 1 μm appear in the cross-section of all CNTs/PS composites. The continuous fine structures can be assigned to a morphology stabilization effect, which seems to act bridging two different material phase. Homogeneously distributed of MWCNTs can be viewed from all composite surfaces (inset of Figure 3). The white spots in the inset of Figure 3.d-f indicate the presence of PS crystals. The phenomenon of agglomerates formation can be explained by crystal nucleation during the growth of PS crystals and the clusters of CNTs acts as nucleation agent and accelerates the growth of agglomerate. Such effect is consistent with previous report [7]. And the agglomerates of the longer CNTs easily occur even for the composites with much lower CNTs loading. It is envisaged that the polymer can better penetrate in the MWCNT agglomerates, especially in the MWCNT-OH. These results also explain why the composites with 5 wt.% possess better mechanical properties, especially for the composite without

porous structures (Figure 3.e).

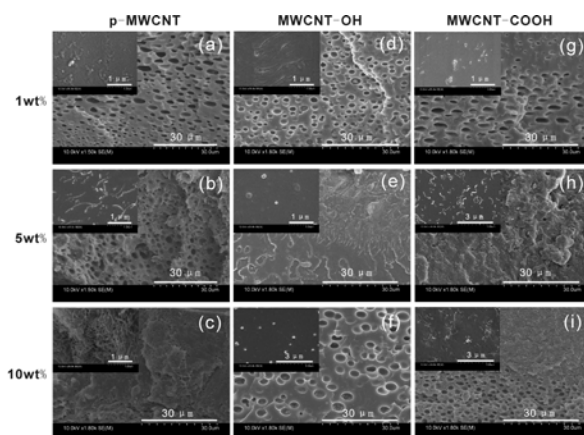


Figure3. SEM images of cross-section and surface (insets) morphologies of PS composites with different type of MWCNTs and CNT loading from 1, 5, to 10wt.%.

3.4 Surface Properties of the Nanocomposites

A better understanding of the effect of surface morphology on surface hydrophilicity was carried out by contact angle measurement to evaluate surface properties of PS composite membranes that containing different loading of p-MWCNT, MWCNT-OH, and MWCNT-COOH, as shown in Figure 4.a When the loading of CNTs is 1 wt.%, the contact angles of the composite membranes varies from 98° to 108° , which indicates that all the composite surfaces are hydrophobic regardless of the types of CNTs. With the increase of CNTs loading, the differences in contact angles of all composites diminish and almost are around $103 \pm 5^\circ$. As the loading of CNTs increases to 10 wt.%, the contact angles declines especially for the composites contained MWCNT-OH and MWCNT-COOH. Likely, the amount of hydrophilic functional group as $-OH$ or $-COOH$ is main factor for dominating the surface hydrophilicity. The fact that the water contact angles of the composites with functionalized MWCNT decreasing with the loading of MWCNT further demonstrates that the surface hydrophilicity of the composites are correlated to the amount of functional groups in MWCNT. The effect of surfactant on the surface hydrophilicity of composite membranes was studied by plotting the contact angles of MWCNT/PS nanocomposites as a function of different MWCNT, as shown in Figure 4.b. The surfactant-treated MWCNT nanocomposite surfaces remained similar hydrophobicity as pure PS surface. The non surfactant-treated MWCNT nanocomposites exhibited relatively higher hydrophilicity than those surfactant-treated MWCNT composites. We deduce that the surface homogeneity can be one of the major effects in dominating surface hydrophilicity of their composites.

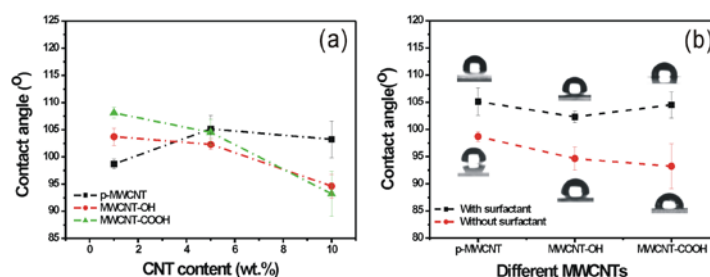


Figure4. Water contact angles of the PS composite membranes changed with fraction of three different CNTs (a) and addition of surfactant (b). The red, black and green lines represent the PS composites with p-MWCNT, MWCNT-OH, and MWCNT-COOH, respectively.

4. Conclusion

In this study, the composites were fabricated via a simple solution casting process using commercially available materials. The thermal properties, mechanical properties and the surface morphology of PS nanocomposites have been investigated with relation to several factors as the CNTs content, different functional groups, the surfactant and so on. The CNTs content was kept mainly below 12.5 wt% for obtaining the correlation between physical properties and surface morphology. It was found that the tensile strength of PS nanocomposites was promoted with increasing of CNTs content as the nanotubes loading was below 5 wt.%. The presence of surfactant and higher CNTs loading favors porous structure formation, especially for functionalized MWCNT composites. In addition, a minimum of T_g appears in MWCNT-COOH composites, indicating a prominent effect of instability of MWCNT-COOH on the thermal properties of MWCNT-COOH composites.

5. Acknowledgement

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6. References

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