Thermal Conductivity and Heat Capacity of a Nylon-6/Multi-wall Carbon Nanotube Composite Under Pressure

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Abstract. The thermal conductivity, κ , of nylon-6 increased 22% whereas the heat capacity per unit volume, ρc_p , decreased 10% by adding 2.1 wt% Multi-Wall Carbon Nanotubes MWCNTs. Simultaneously, the glass transition temperature, T_g , which was detected as a weak sigmoidal increase in ρc_p and a decrease in $d\kappa/dT$, increased 11 K. These results show that the MWCNTs-nylon-6 interaction restricts the segmental mobility of nylon-6 and decreases c_p of nylon-6.

Keywords: Thermal conductivity, heat capacity, nylon-6, multi-wall carbon nanotube, high pressure, glass transition.

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INTRODUCTION

Carbon nanotubes (CNTs) attract intensive attention because of their extraordinary thermal and mechanical properties, and high electrical conductivity. This new form of carbon material has great potential to be utilized in thermal management, high performance composites, electronics etc. [1]. The thermal conductivity κ of single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) has been studied experimentally. Fujii *et al.* [2] measured κ of individual SWCNT and found $\kappa > 2000 \text{ W m}^{-1} \text{ K}^{-1}$ for a CNT diameter of 9.8 nm, which further increased with decreasing diameter. Kim *et al.* [3] reported $\kappa > 3000 \text{ W m}^{-1} \text{ K}^{-1}$ for MWCNT at room temperature while that of SWCNTs and MWCNTs in bundles was ~ 250 and $\sim 20 \text{ W m}^{-1} \text{ K}^{-1}$ respectively [4, 5]. Thus, adding relatively small amount of CNTs may dramatically improve κ of poor thermal conductors such as polymers. Tonpheng *et al.* [6] reported an increase of κ by 120% for polyisoprene with 5wt% SWCNTs. The improvement was roughly proportional to the percentage of SWCNTs in the polymer composite, but the increase was lower than that predicted by simple mixture rules, which is likely due to high interfacial thermal resistance. In this work, we study κ , heat capacity and glass transition behavior for nylon-6 and its MWCNT composite and also explore the possibility of improved interfacial contact and percolation through high-pressure densification.

EXPERIMENTAL SECTION

MWCNTs (Nanocyl-3150) were purchased from Nanocyl, Belgium and purified before use. A typical purification procedure included oxidation in air, washing in 37% HCl acid (Sigma-Aldrich, ACS reagent) and, subsequently, rinsing by water, filtration and drying [7]. The syntheses of the nylon-6/MWCNTs composite was done by in-situ polymerization [8], using sonication to disperse MWCNTs (0.24 g or 2.1 wt%) in melted ϵ -caprolactam (10 g, Aldrich, 99%) at 80 °C, adding 6-aminocaproic acid (1 g, Sigma, $\geq 99\%$) as initiator afterwards and heating to 250 °C with simultaneous mechanical stirring under nitrogen atmosphere for 6 h. A pure nylon-6 control sample was synthesized using the same procedure.

The nylon-6/MWCNT and nylon-6 samples were hot pressed into plates (diameter: ~ 37 mm, thickness: ~ 3 mm) at 250 °C in an argon atmosphere, and inserted in a custom made Teflon[®] cell. The Teflon[®] cell, contained a type K thermocouple and a hot-wire probe (0.1 mm Ni-wire) for measurements of κ and ρc_p using the hot-wire method [9]. The cell was mounted in a piston cylinder apparatus and later loaded in a hydraulic press. The sample could be

heated up to ca. 530 K by an electric heater surrounding the cylinder and cooled down to ca. 100 K by liquid nitrogen. The estimated inaccuracies are $\pm 2\%$ in κ and $\pm 5\%$ in ρc_p .

Transmission electron microscope (TEM, JEM-1230) and tapping mode Atomic Force Microscopy (AFM, MultiMode, Veeco Metrology) were performed to exam the MWCNTs purity and the dispersion of MWCNTs in nylon-6. Differential scanning calorimetry (DSC, Pyris Diamond) was used to analyze the degree of crystallinity.

RESULTS AND DISCUSSION

As shown in Figure 1, height and amplitude images of the 2.1 wt% nylon-6/MWCNT composite suggest a fairly good dispersion of MWCNTs in the nylon-6 matrix. The long, tubular and twisted structures, which are the polymer wrapped MWCNTs, have a typical diameter of ~ 50 nm. The TEM image (insert) shows that highly purified MWCNTs, with no visible amounts of amorphous carbon or metallic catalyst, are obtained after purification.

FIGURE 1. AFM image of Nylon-6/MWCNTs composite: (a) height image, (b) amplitude image (scale bar is 1 μm). The insert (c) is a TEM image of the purified MWCNTs (scale bar is 200 nm)

A pressure scan of both nylon-6 and its composites was performed at 298 K from low pressure to 1.0 GPa, as indicated in Figure 2a. The thermal conductivity of both samples increases due to densification, which reduces the inter-particle distances and, thus, improves the heat transfer between polymer chains. However, there is no indication of a stronger increase for the composite, which shows that the densification is insufficient to form a percolation network of the MWCNTs and that the thermal contact between the MWCNTs and nylon-6 does not improve sufficiently to make an impact on $\kappa(p)$. The behavior of κ below 1 GPa is therefore mainly governed by the changes in the nylon-6 matrix.

Figure 2b shows $\kappa(T)$ from 290 to 440 K at 0.8 GPa for both nylon-6 and the 2.1 wt% nylon-6/MWCNT composite. The thermal conductivity of nylon-6 shows a distinct change in $d\kappa/dT$ from positive to negative near 368 K, which is a typical behavior at the glass transitions temperature T_g of polymers [10]. This result is also confirmed by the simultaneously measured data for ρc_p (figure 2c). These show the (stretched weak) sigmoidal increase, which is characteristic of a glass transition. Thus, T_g of nylon-6, which is difficult to observe in several other characteristics that normally show clear T_g features, gives a distinct change in the temperature dependence of κ . The corresponding results for the composite are similar but with a change in $d\kappa/dT$ at 379 K, i.e. the 2.1 wt% MWCNTs raised T_g about 11 K. The shift of T_g is due to restricted segmental mobility, which is apparently caused by the MWCNT-nylon-6 interaction or, in terms of the free volume theory, the MWCNTs reduces the free volume or voids in the polymer.

The κ of the composite is $0.549 \text{ W m}^{-1} \text{ K}^{-1}$, which is $\sim 22\%$ higher than that of nylon-6 ($0.452 \text{ W m}^{-1} \text{ K}^{-1}$) at 0.8 GPa, 298 K. As shown in Table 1, the degree of crystallinity of nylon-6 and the composite was the same, $\sim 20\%$ (melting enthalpy, ΔH , of 100% α crystalline nylon-6 is 241 J g^{-1}) [11], which shows that the enhanced κ of the composite was caused by the high κ of the MWCNTs and not by a change of crystallinity. Another interesting observation is the significant MWCNT induced decrease of ρc_p from $1.19 \text{ MJ m}^{-3} \text{ K}^{-1}$ for nylon-6 to $1.07 \text{ MJ m}^{-3} \text{ K}^{-1}$ for the composite at atmosphere pressure and 298 K (not shown in figure), i.e. a decrease of 10%. Since this is significantly larger than 0.2% calculated by the mixture rule [6, 12], it means that the MWCNTs decreases the heat capacity of nylon-6. Moreover, since the relative decrease is about the same above T_g as that below (figure 2c), the MWCNT-nylon-6 interaction apparently reduces the vibrational and configurational heat capacities of nylon-6 to about the same extent, and this effect should make the nylon-6 matrix slightly more rigid.

TABLE 1. Melting enthalpy (ΔH) and crystallinity (C_{DSC}) determined by DSC

Sample	ΔH (J/g)	C_{DSC}
Virgin Nylon-6	47.9	19.9%
2.1wt% MWCNTs in nylon-6	47.4	19.7%

FIGURE 2. (a) Thermal conductivity for: (●) 2.1 wt% nylon-6/MWCNT composite and (○) nylon-6 measured on increasing pressure at 298 K. The dashed line represents a range where the data for nylon-6 were affected by a transition in the surrounding Teflon. (b) Thermal conductivity and (c) heat capacity per unit volume of: (●) 2.1 wt% nylon-6/MWCNT composite and (○) nylon-6 at 0.8 GPa measured on heating. The dash lines in both panels represent linear functions fitted to the data below and above the distinct change of slope. The point of intersection represents T_g .

CONCLUSIONS

In summary, κ and ρc_p for nylon-6 and its 2.1 wt% MWCNT composite have been measured, *in-situ*, under high pressure by the transient hot-wire method. The high κ of the MWCNTs increased κ of the composite by 22%. This increase was almost independent of pressure, which shows that the densification was insufficient to cause thermal percolation through the MWCNTs. Simultaneously, the MWCNTs increased T_g (11 K) but decreased ρc_p (10%) of nylon-6, which reveal MWCNT induced effects on the bulk properties of the nylon-6 matrix. These effects may have a similar origin and seems to be associated with the MWCNT-nylon-6 interfacial interaction.

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REFERENCES

1. M. Moniruzzaman and K. I. Winey, *Macromolecules* **39** (16), 5194-5205 (2006).
2. M. Fujii, X. Zhang, H. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe and T. Shimizu, *Phys. Rev. Lett.* **95** (6), 065502 (2005).
3. P. Kim, L. Shi, A. Majumdar and P. L. McEuen, *Phys. Rev. Lett.* **87** (21), 215502 (2001).
4. W. Yi, L. Lu, Z. Dian-lin, Z. W. Pan and S. S. Xie, *Physical Review B* **59** (14), R9015 (1999).
5. D. J. Yang, Q. Zhang, G. Chen, S. F. Yoon, J. Ahn, S. G. Wang, Q. Zhou, Q. Wang and J. Q. Li, *Physical Review B* **66** (16), 165440 (2002).
6. B. Tonpheng, J. Yu and O. Andersson, *Macromolecules* **42** (23), 9295-9301 (2009).
7. J.-M. Moon, K. H. An, Y. H. Lee, Y. S. Park, D. J. Bae and G.-S. Park, *The Journal of Physical Chemistry B* **105** (24), 5677-5681 (2001).
8. J. Gao, M. E. Itkis, A. Yu, E. Bekyarova, B. Zhao and R. C. Haddon, *Journal of the American Chemical Society* **127** (11), 3847-3854 (2005).
9. H. Bjorn and G. R. Russell, *Journal of Applied Physics* **68** (7), 3285-3292 (1990).
10. D. W. Van Krevelen, *Properties of polymers: correlations with chemical structure*. (Elsevier publishing company, 1972).
11. V. K.-H. Illers and H. Haberkorn, *Die Makromolekulare Chemie* **142** (1), 31-67 (1971).
12. N. R. Pradhan, H. Duan, J. Liang and G. S. Iannacchione, *Nanotechnology* **20** (24), 7 (2009).