

Interfacial Interaction of Polyvinylidene Fluoride/Multiwalled Carbon Nanotubes Nanocomposites: A Rheological Study

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ABSTRACT: Polyvinylidene fluoride (PVDF)/multiwalled carbon nanotubes (MWCNTs) nanocomposites were prepared by solution blending method, and the melt viscoelastic behavior of the composites was studied. The results showed that the dispersion of MWCNTs in the matrix and the surface characteristic of MWCNTs had a profound influence on the melt rheological behaviors of the nanocomposites. Generally, the dynamic storage modulus (G') of the nanocomposites with well dispersed MWCNTs was greatly improved. However, PVDF/MWCNTs-g-OH nanocomposites exhibit more significant solid-like behavior than

PVDF/MWCNTs nanocomposites at an MWCNTs loading of 2 wt % or higher, even though the dispersion of MWCNTs-g-OH is poorer than that of virgin MWCNTs owing to the higher interfacial interactions from van der Waals force and hydrogen bonding. In this case, the influence of the interfacial interactions on the melt rheological properties was stronger than the dispersion state. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3041–3046, 2011

Key words: multiwalled carbon nanotubes (MWCNTs); nanocomposites; rheological properties; interfacial interaction

INTRODUCTION

Multiwalled carbon nanotubes (MWCNTs), with unique mechanical, electrical, magnetic, optical, and thermal properties, offer exciting opportunities for polymer-based nanocomposites.^{1–4} In the past decade, polymer/MWCNTs nanocomposites have attracted considerable attention owing to MWCNTs' unique properties resulting from the nanoscale microstructures.^{5–9}

Polymer/MWCNTs nanocomposites are expected to have good processability and high mechanical properties and functional performance because of the presence of MWCNTs. However, the properties of polymer/MWCNTs nanocomposites are strongly dependent on the dispersion and alignment of MWCNTs.^{10–12} So, much attention has been paid to improve the dispersion and alignment state of MWCNTs and great achievements have been made in these fields.^{13–16}

For the improved dispersion of fillers, including nanofillers such as MWCNTs in polymer matrix, the

interfacial interaction between the fillers and the interaction between the fillers and the matrix are significant factors. Lowering the interaction between the fillers and strengthening the interaction between the fillers and the matrix can effectively improve the dispersion of the fillers in polymer matrix by using methods such as surface treatment of fillers and addition of appropriate compatibilizers.^{17,18} For instance, Kim et al.¹⁹ found that the dispersion state of fillers in the epoxy matrix can be improved by surface modification of MWCNTs, and the nanocomposite containing modified MWCNTs exhibited higher storage, loss moduli, and shear viscosity than those with untreated MWCNTs. Similar results have also been reported by Lee et al.²⁰ Moreover, Moussaif and Greoninckx²¹ reported that polyvinylidene fluoride (PVDF) and layered silicate composites can be successfully compatibilized by blending with poly(methyl methacrylate) (PMMA), and the shear viscosity and storage moduli of the nanocomposites improved with the addition of PMMA, indicating that the addition of compatibilizers also can improve the dispersion state of nanocomposites. Therefore, the interfacial interactions in polymer-based composites such as polymer/MWCNTs nanocomposites are directly related with the final properties of the composites. Strengthening the interfacial interaction between the fillers and the matrix can also improve the tensile strength, bending strength,²² and glass transition temperature²³ of nanocomposites.

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Therefore, the study of interfacial interaction between fillers and matrix are very necessary.

Generally, the interfacial interaction of polymer-based composites can be characterized by dynamic-mechanic thermal analysis,²⁴ Raman scattering and X-ray diffraction²⁵ and so on. However, in this article, it is found that the interfacial interactions of PVDF/MWCNTs nanocomposites in the melt state can also be studied by means of dynamically rheological test for the sensitivity of the dynamic rheological properties to the chain relaxation and the dispersed state of the additives.

EXPERIMENTAL

Materials

PVDF (FR901, powder) used as the matrix were supplied by 3F Co., Shanghai, China (relative molecular masses $M_w = 285,547$ g/mol and $M_n = 148,126$ g/mol and Polydispersity Index (PDI) = 1.928). The MWCNTs (virgin MWCNTs and MWCNTs-g-OH with 3.70 wt % hydroxyl groups attached on the surface of MWCNTs) having the same outer diameter (8–15 nm) and length (~ 50 μ m) were produced via chemical vapor deposition and were obtained from Chengdu Organic Chemistry Co., Chengdu Branch of Chinese Academy of Science, Chengdu, China.

Preparation of sample nanocomposites

In this study, the nanocomposites were prepared by solution blending. Both MWCNTs and PVDF were dried in vacuum to remove moisture before usage. First, PVDF powder was dissolved in *N,N* dimethylformamide (DMF) solution at 60°C for 1 h to ensure complete dissolution of PVDF. At the same time, MWCNTs were dispersed in DMF with ultrasonic treatment and strong magnetic stirring for 30 min. Then the MWCNTs/DMF suspensions were mixed with PVDF/DMF solution and ultrasonic treatment and stirring of the solution for 1 h were performed to get full dispersion. Finally, the mixture was flocculated with deionized water and dried in vacuum for 48 h to remove the solvent. To facilitate description, the samples were labeled with PM (PVDF/MWCNTs nanocomposites) and PMO (PVDF/MWCNTs-g-OH nanocomposites). The two groups of nanocomposites contain 0 wt %, 0.3 wt %, 0.5 wt %, 0.7 wt %, 1 wt %, 2 wt %, and 5 wt % MWCNTs and MWCNTs-g-OH, respectively.

Characterization

Scanning electron microscope observation

The morphology of PVDF/MWCNTs nanocomposites was characterized with a JEOL JSM-5900LV scanning electron microscope (SEM) at an accelerat-

ing voltage of 20 kV. The samples were left in liquid nitrogen for 40 min and then impact fractured for SEM analysis. The freshly fractured surface was gold sputtered before SEM observation.

Rheological measurements

Rheological measurements were performed on a stress-controlled rheometer (AR2000 EX, TA Instruments) with a parallel-plate geometry (diameter of 25 mm) at 200°C. The linear viscoelastic range, determined by strain sweep test at 0.5 Hz, was found to decrease with the content of MWCNTs increasing. After these oscillatory strain sweeps, the samples were kept in the rheometer for 10 min to erase the strain history. Then frequency sweeps between 0.01 and 100 Hz were carried out at a strain of 1% which was within the linear viscoelastic range for these materials. The samples for rheological measurement were prepared by compression molding into disks with a thickness of 1.5 mm and diameter of 25 mm in a stainless steel die at 200°C and 10 MPa.

RESULTS AND DISCUSSION

Dispersion of MWCNTs

The morphologies of the two kinds of PVDF/MWCNTs nanocomposites with the same loading of MWCNTs (5 wt%) are shown in Figure 1. It can be found that virgin MWCNTs are well dispersed in the PVDF matrix, while MWCNTs-g-OH are slightly aggregated in some regions. This is because, for PVDF/MWCNTs-g-OH nanocomposites, the hydroxyl groups attached on the surface of MWCNTs formed hydrogen bonds,^{26,27} and the extra hydrogen bonding apart from van der Waals force made the dispersion of MWCNTs-g-OH more difficult than that of virgin MWCNTs. Therefore, under the same preparation conditions, MWCNTs-g-OH tends to form aggregates compared with virgin MWCNTs.

Rheological properties

The dynamic strain sweep was conducted to determine the linear viscoelastic region (LVR) of the two kinds of nanocomposites containing different contents of MWCNTs. Figure 2 shows the dependency of dynamic storage modulus (G') of the PVDF/MWCNTs nanocomposites on the applied strain (γ). For all the two groups of nanocomposites containing MWCNTs with different surface characteristics, it can be observed that G' increases with the increasing of MWCNTs loading, due to reinforcing effect of MWCNTs. Similar rheological behavior has been observed in polymer nanocomposites containing

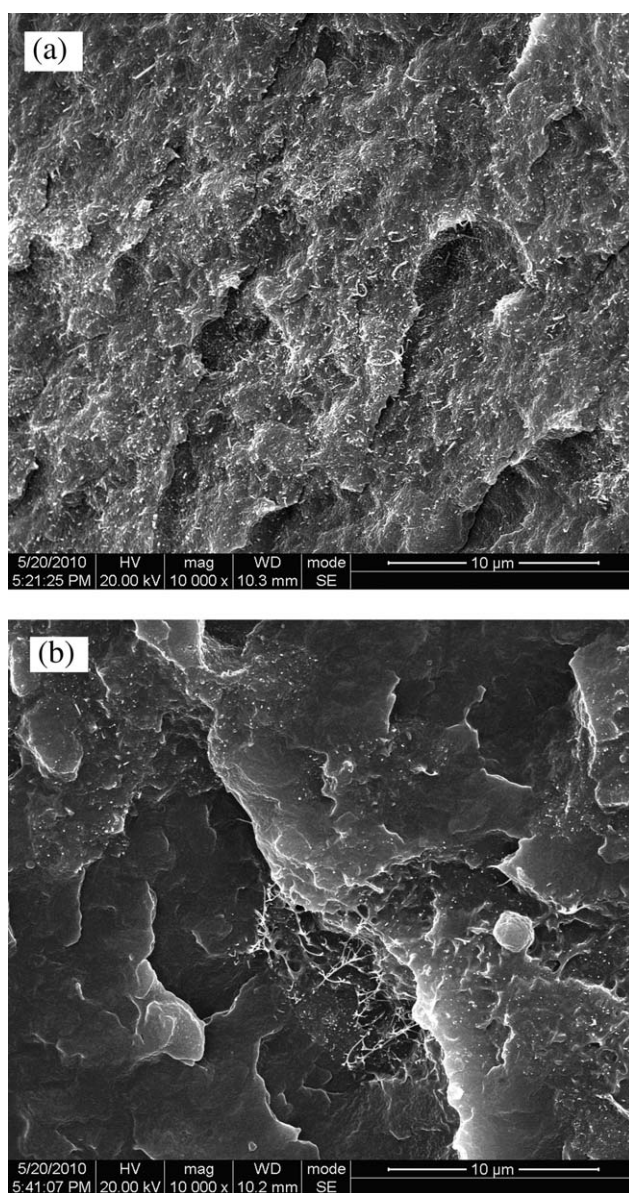


Figure 1 SEM graphs of PVDF/MWCNTs nanocomposites: (a) PM 5 wt%; (b) PMO 5 wt%.

clays or MWCNTs.^{28–31} At the same time, the presence of MWCNTs greatly reduces the LVR of the nanocomposites. The higher the MWCNTs content, the narrower the LVR. This phenomenon is due to that the movement of molecular chains is hindered by MWCNTs, which can weaken the restorability of the melt structure. Thus, the melt of the nanocomposites gets into the non-LVR (NLVR) in smaller strain.

The effect of loading of MWCNTs on G' for the two types of PVDF/MWCNTs nanocomposites is shown in Figure 3. With increasing MWCNTs loading, the dependence of G' on ω at low frequency region weakens gradually, as the relaxations of the polymer chains in PVDF/MWCNTs nanocomposites are effectively restrained by MWCNTs. This behav-

ior can be attributed to the formation of a network structure, which hinders the motion of polymer chains on the chain length scale.²⁹ When the loading of MWCNTs is 2 wt % or higher, a great enhancement of G' is observed in the low-frequency region. At high frequencies, the relaxations of the polymer chains on segment scale, such as a entanglement strand, are not significantly influenced by the existence of the network structure, so the effect of the MWCNTs on the rheological responses is relatively weak.

To show the effect of surface characteristics of MWCNTs, the dynamic storage moduli of the two groups of nanocomposites at 0.01 Hz are compared, as shown in Figure 4. It can be found that G' of PMO is higher than that of PM when MWCNTs loading is 2 wt % and especially 5 wt %. This phenomenon can be attributed to the presence of hydroxyl groups of MWCNTs-g-OH, that is to say,

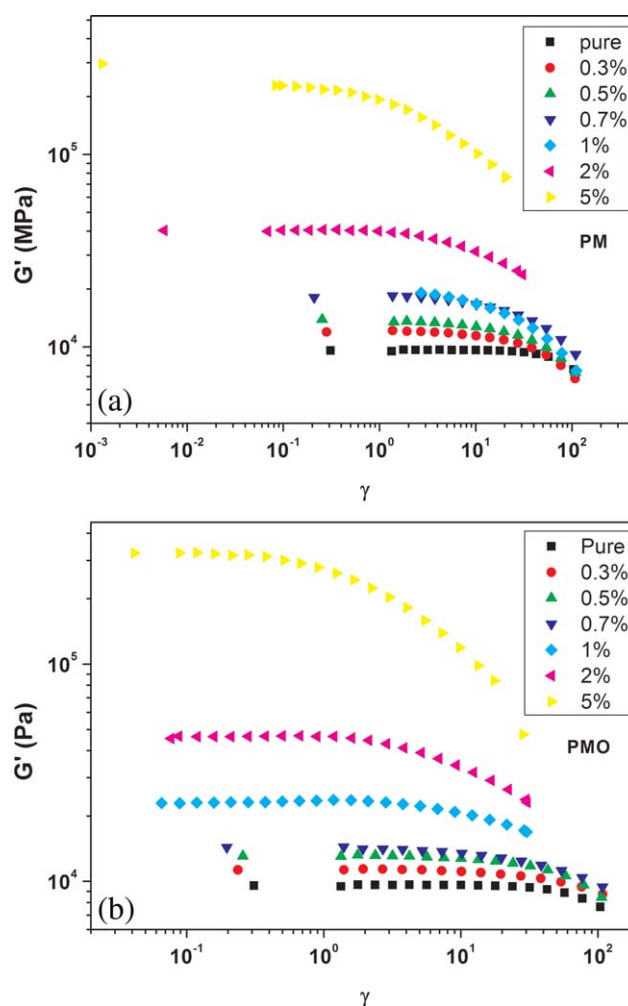


Figure 2 Dependence of dynamic storage modulus (G') on the applied strain (γ) for the two kinds of PVDF/MWCNTs nanocomposites with various MWCNTs loading: (a) PM, (b) PMO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

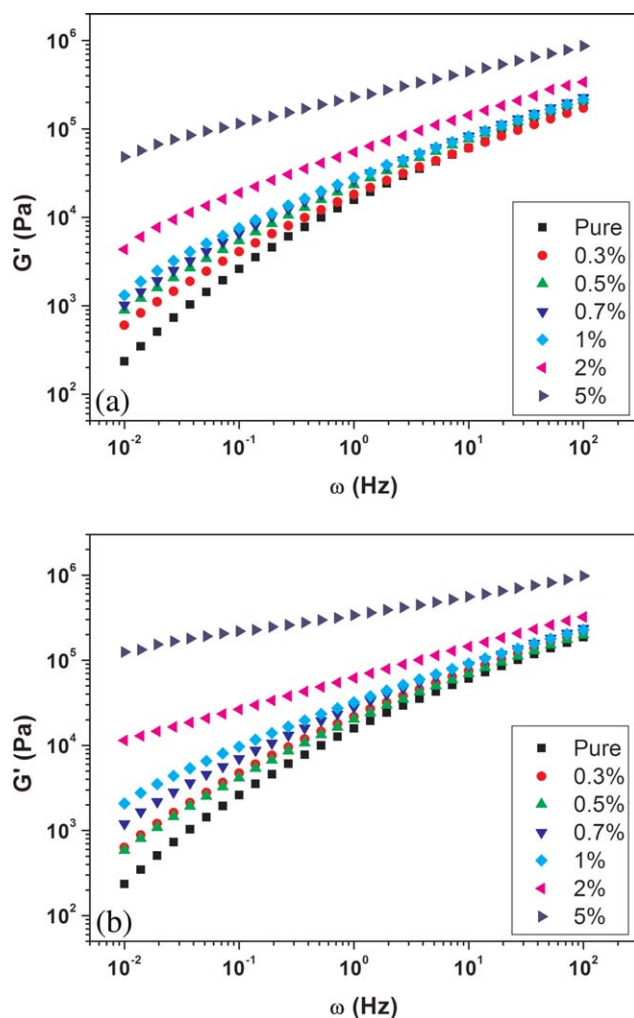


Figure 3 Dependence of G' on frequency (ω) for the two kinds of PVDF/MWCNTs nanocomposites with various MWCNTs loading: (a) PM, (b) PMO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

apart from the effect of van der Waals force between MWCNTs-g-OH and the matrix, the hydroxyl groups on the surface of MWCNTs and the fluorine atoms on the PVDF chains can form hydrogen bonds, resulting in stronger interfacial interactions between the MWCNTs and PVDF matrix, although hydroxyl groups attached on the surface of MWCNTs can form hydrogen bonds themselves which lead to aggregates of MWCNTs.

The dependence of complex viscosity on frequency for the two kinds of PVDF/MWCNTs nanocomposites is shown in Figure 5. We can find that with the frequency increasing, the complex viscosity decreased. The addition of the MWCNTs causes dramatic enhancement of the shear viscosity, especially at low shear rate. It can be found that $|\eta^*|$ of PMO (PVDF/MWCNTs-OH) is much higher than that of PM (PVDF/MWCNTs) and this behavior becomes more and more obvious as the content of nanotube

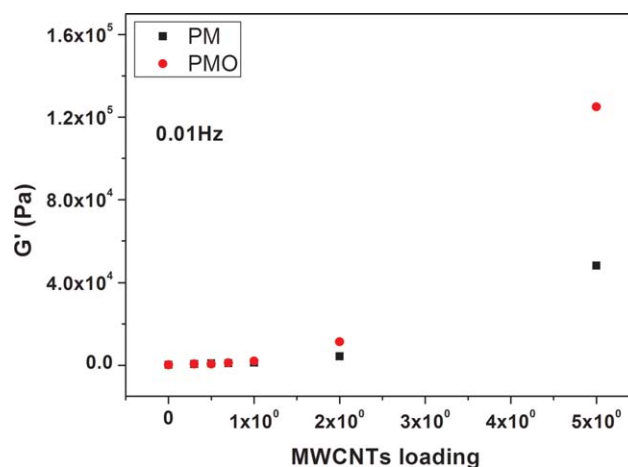


Figure 4 Dependence of G' at 0.01 Hz on the loadings of the two types of MWCNTs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

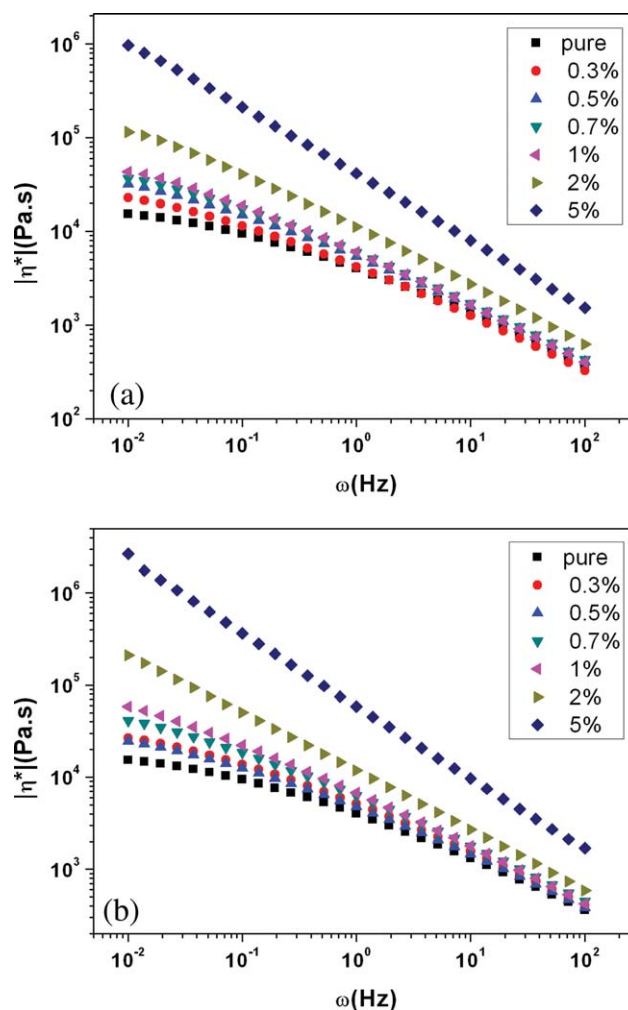


Figure 5 Dependence of complex viscosity on frequency for the two kinds of PVDF/MWCNTs nanocomposites: (a) PM, (b) PMO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

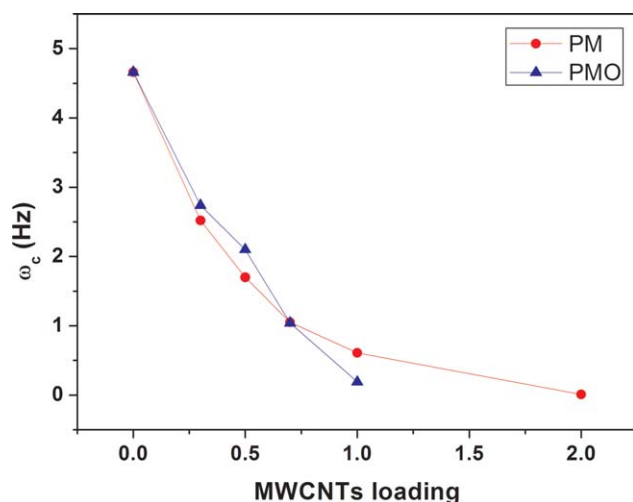


Figure 6 Dependence of crossover frequency (ω_c) on the loading of MWCNTs for PVDF/MWCNTs nanocomposites containing MWCNTs with different surface characteristics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases. It is believed that this difference in the contribution of the two kinds of MWCNTs to the rheological properties is mainly caused by the different surface characteristics of MWCNTs, or more exactly, the different interactions between PVDF and MWCNTs. For PMO, the hydroxyl groups on the surface of MWCNTs and the fluorine atoms on the PVDF chains can form hydrogen bonds, resulting in stronger interfacial interactions between the MWCNTs and PVDF matrix, although hydroxyl groups attached on the surface of MWCNTs can form hydrogen bonds themselves which lead to aggregates of MWCNTs. But for PM, virgin MWCNTs cannot form hydrogen bonds with PVDF chains and only the van der Waals force exists.

For the liquid-like behavior, G' is much lower than the loss modulus (G''), and vice versa for the solid-like system. The melt behavior of viscoelastic material is liquid-like ($G' < G''$) at low frequencies and solid-like behavior ($G' > G''$) at high frequencies. The crossover frequency (ω), defined as $\omega_{G'=G''}$, shifts toward low frequency with increasing filler loading, as fillers can restraint the movement of the polymer chains. A low value of ω_c indicates stronger interaction between the filler and the matrix. When the interaction between the filler and the matrix is strong enough, the crossover will disappear. Solid-like behavior can be observed in conventional filled polymer systems where strong interactions between the polymers and the fillers exist.²⁶

The dependence of ω_c on loading of MWCNTs for the two types of PVDF/MWCNTs nanocomposites is shown in Figure 6. It can be found that in the experimental ranges, ω_c for PMO disappears when

the loading of MWCNTs is higher than 1 wt %, indicating that the system is dominated by elastic (G' is greater than G'' for test frequency ranges; G' is greater than G'' for all frequency ranges). But for PM the transition occurs at a higher loading of MWCNTs, that is, 2 wt %. This is because the extra hydrogen bonds in PMO can supply stronger physical crosslinking effect, which greatly restrain the motion of polymer chains.

Figure 7 gives the relationship between the applied frequency and the tangent of loss angle ($\tan \delta$) for the two types of PVDF/MWCNTs nanocomposites with different MWCNTs loadings. $\tan \delta$ can be used to characterize the viscoelasticity of materials, and low value of $\tan \delta$ indicates that the material exhibits relatively more solid-like behavior or elasticity. As shown in Figure 7(a), at a MWCNTs

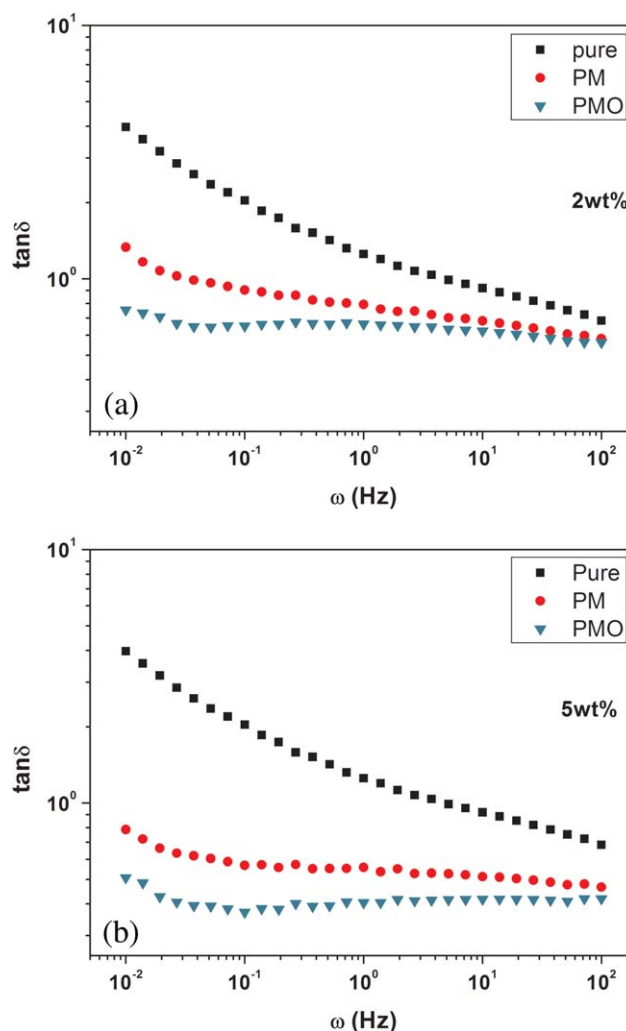


Figure 7 Dependence of tangent loss angle ($\tan \delta$) on frequency (ω) for PVDF/MWCNTs nanocomposites containing MWCNTs with different surface characteristics. MWCNTs loading: (a) 2 wt %, (b) 5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

loading of 2 wt %, $\tan \delta$ of PMO is almost independent of ω in the frequency range tested, but for PM, the dependence of $\tan \delta$ on ω is stronger than PMO. It is known that the storage modulus and loss modulus have the same dependence on frequency, i. e., $G' \propto \omega^n$ and $G'' \propto \omega^n$, it means that the system was into the gel state. So these results indicated that the gel point of PMO is lower than that of PM. The results suggested that the motion of polymer chains is getting more difficult with increasing MWCNTs loading, and the mobility of the polymer chains in PMO is more difficult than that in PM, because the interaction of PMO between the filler and matrix are stronger than that of PM.

CONCLUSIONS

The effect of MWCNTs loading and surface characteristics of MWCNTs on the rheological behaviors of PVDF/MWCNTs nanocomposites were examined and it was found that not only the MWCNTs loading but also the surface characteristics have a dramatic influence on the rheological properties of nanocomposites. The effect of surface characteristics is obviously shown by the different reinforcing effect of the MWCNTs, especially when the loading of MWCNTs is relatively high. When extra interfacial interaction between filler and filler and between filler and polymer matrix such as the case for PMO, the dynamic storage modulus would be greatly improved. At the same loading of MWCNTs, owing to the presence of extra interfacial interaction, the reinforcing effect of samples with relatively poor dispersion state is better than that of samples with good dispersion state, due to that the extra interfacial interaction can lead to obvious solid-like behavior and network structure.

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