

Preparation and Characterization of Poly(vinylidene fluoride) Nanocomposites Containing Multiwalled Carbon Nanotubes

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) nanocomposites with different loadings of multiwalled carbon nanotubes (MWNT) were prepared by melt-compounding technique. A homogeneous dispersion of MWNT throughout PVDF matrix was observed on the cryo-fractured surfaces by scanning electron microscopy. Thermogravimetric analysis results indicated that the thermal stability of neat PVDF was improved with the incorporation of MWNT. Dynamic mechanical analysis showed a significant improvement in the storage modulus over a temperature

range from -125 to 75°C with the addition of MWNT. The melt-rheological studies illustrated that incorporating MWNT into PVDF matrix resulted in higher complex viscosities ($|\eta^*|$), storage modulus (G'), loss modulus (G''), and lower loss factor ($\tan \delta$) than those of neat PVDF. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 644–650, 2009

Key words: poly(vinylidene fluoride); carbon nanotubes; nanocomposites

INTRODUCTION

During the past 15 years, carbon nanotubes (CNTs) have generated huge research activities in most areas of materials science and engineering because of their unprecedented physical and chemical properties.^{1–4} CNTs have displayed a combination of superlative mechanical, thermal, and electronic properties. This combination of properties makes them an ideal candidate as an advanced filler material for high strength and electronically conductive polymer nanocomposites. Compared with the conventional filled grades of polymer composites, CNT nanocomposites exhibit much higher stiffness, higher modulus, improved dimensional stability, a decreased coefficient of thermal expansion, and better electrical conductivity at relatively low concentrations of CNT filler.^{4–6}

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer with different crystalline forms and thus complicated microstructures.^{7,8} Because of its excellent mechanical and electrical properties, PVDF has many important commercial and technological applications, including its use as an electrode binder in lithium ion batteries, the membrane separator in polymer electrolyte membrane fuel cell, nonlinear optics, microwave transducers, biomedical applications, and its potential applications as piezoelectric and pyroelectric materials. These properties, combined with high elasticity and processability, made PVDF one of the most studied polymers in scientific research.

Specified to PVDF/CNT systems, their preparation and the structural and physical characterization have been reported recently.^{7–13} Owens et al.¹⁰ prepared single-walled carbon nanotube (SWNT)/PVDF composites by evaporating the suspensions of PVDF and SWNT in acetone and studied the interaction between PVDF and SWNTs by Raman spectroscopy and ¹⁹F-NMR. Goh et al. had investigated the microstructure, crystallization, and dynamic mechanical properties of PVDF/poly(methyl methacrylate) (PMMA)-grafted-MWNT nanocomposites and found that the miscibility between PVDF and PMMA could help improve the dispersion of PMMA-grafted MWNTs in the PVDF matrix and also the load transfer from PVDF matrix to the nanotubes.^{11,12} Chen et al.⁷ reported a novel way to fabricate

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PVDF/MWNT composites using an ultrahigh-shear processing approach, and this approach has been found to be effective in achieving homogeneous dispersion of unmodified MWNTs in a thermoplastic elastomer.¹⁴ However, there are few reports on the thermal stability and rheological behavior of CNT/PVDF nanocomposites. In this article, PVDF nanocomposites with different MWNT loadings are prepared by melt-compounding technique. The morphology, thermal stability, dynamic mechanical, and rheological properties of the nanocomposites are characterized and compared with those of neat PVDF resin.

EXPERIMENTAL

Sample preparation

Neat PVDF resin (Solef[®], Solvay, Brussels, Belgium) used in this study was commercially obtained from Solvay. The MWNTs were prepared on Co-Mo/MgO catalysts by catalytic chemical vapor deposition by using methane as the carbon source, which was described previously.³ The as-prepared MWNTs were purified by dissolving the catalyst in hydrochloric acid followed by refluxing in nitric acid for increasing more carboxylic and hydroxyl groups. Before melt compounding, all the samples were dried in a vacuum oven at 80°C for 12 h to remove the absorbed water. PVDF composites containing different MWNT contents (i.e., 0, 0.2, 0.5, 1, and 2 wt %) were prepared via melt-compounding method using a Brabender twin-screw extruder at 190°C for 10 min with a screw speed of 180 rpm.

Scanning electron microscopy

Scanning electron microscope (SEM, Tescan Brno, Czech Republic) was used to observe the morphology of the cryo-fractured surface (prepared by immersing into liquid nitrogen) and the dispersion of MWNTs in the PVDF/MWNT nanocomposites at an accelerating voltage of 30 kV. The sample surfaces were coated with a thin layer of Au before SEM observation.

Thermal analysis

Thermogravimetric analysis (TGA, Shimadzu TG-60H, Kyoto, Japan) was performed under nitrogen flow from 50°C to 600°C at a heating rate of 20°C/min. Dynamic mechanical properties of the samples were studied on compression-molded films of 30 × 10 × 0.5 mm³ in size using a dynamic mechanical analyzer (DMA) from TA Instruments (New Castle, DE) under tension film mode. The dynamic response tests were conducted from -140 to 120°C at a frequency of 1 Hz and heating rate of 3°C/min.

Rheological measurements

Sample disks (with thickness of 1.7 mm and diameter of 25 mm) for rheological measurements were prepared using a molding machine (LMM, ATLAS Electric Devices Co., USA) at 190°C. The rheological properties of neat PVDF and PVDF/MWNT composites were measured at 190, 200, and 210°C, covering the processing windows of the PVDF nanocomposites, with a strain-controlled ARES rheometer (TA Instruments). Disk specimens were placed between the preheated plates and allowed to perform steady preshearing for 4 min before each frequency sweep run. Small-amplitude oscillatory shear measurements were performed using parallel-plate geometry with the plate diameter of 25 mm and the plate gap setting of 1.0 mm, by applying a time-dependent strain, $\gamma(t) = \gamma_0 \sin(\omega t)$, and measuring resultant shear stress $\gamma(t) = \gamma_0[G' \sin(\omega t) + G'' \cos(\omega t)]$, where G' and G'' are storage and loss moduli, respectively. To maintain all the rheological experiments in the linear viscoelastic region, dynamic strain sweep tests were performed in advance for each sample, and consequently a strain of 1% was selected for all frequency sweep data in this work. The frequency ranges were varied between 0.1 and 100 rad/s. The rheological properties were reproducible after repeated temperature cycling and frequency sweep, indicating that there is almost no chain degradation during the measurements.

RESULTS AND DISCUSSION

Dispersion morphology of CNTs

Figure 1 shows the morphology of the cryo-fractured surface of PVDF nanocomposite containing 2 wt % MWNTs (as an example). A homogeneous dispersion of MWNTs throughout PVDF matrix can be seen and no evident aggregation is observed. The bright regions in the image were attributed to the MWNTs because of their high conductivity. In addition, an intimate adhesion of the MWNTs with the matrix is clearly observed, indicating good wettability between the nanotubes and the matrix.

Thermal properties

Figure 2(a) shows TGA thermograms of neat PVDF and its MWNT nanocomposites. The degradation temperature (onset of inflection) for neat PVDF was lower than those of the nanocomposites, indicating that the thermal stability of the matrix has been improved because of the addition of MWNTs. Besides that, the residual weight of the materials left increased steadily with the increase of MWNT loading. As shown in the TGA curves, the weight loss at 600°C for neat PVDF was about 85%, whereas the

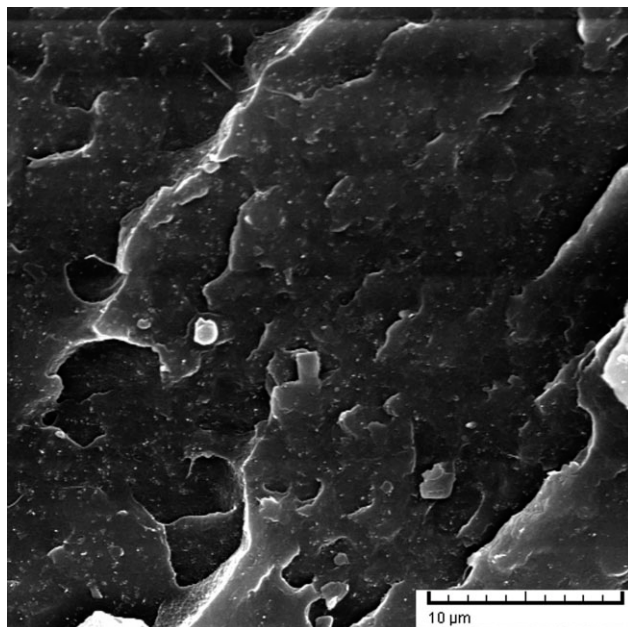


Figure 1 SEM image showing the fine dispersion of MWNTs (2 wt %) in PVDF matrix.

nanocomposites were only around 60–70%. This also indicates that the thermal stability of PVDF was significantly improved on incorporation of MWNTs. Figure 2(b) shows the variation of the decomposition temperature, T_d (5% weight loss temperature) as a function of the MWNT content. It can also be seen that the overall thermal stability of neat PVDF is significantly improved by the addition of MWNTs. As shown in Figure 2(b), the decomposition temperature of PVDF is enhanced by $>20^\circ\text{C}$ with addition of only 0.2 wt % MWNTs; whereas the T_d decreases somewhat as increasing the CNT content to 0.5 wt %; and then the thermal stability is steadily increased when further increasing the nanotube content. We believe that the thermal stability of PVDF/MWNT nanocomposites may be closely related to two main factors: the dispersion state and the loading level of CNTs. High loading level of nanotubes will be beneficial to the improvement of the decomposition temperature of PVDF matrix, probably due to the ease of compact char formation for the nanocomposites during the thermal degradation. However, high concentration of MWNTs used will definitely prevent fine dispersion of the nanotubes, and severe aggregation or bundles could often be formed because of van der Waals force among the nanotubes, thus deteriorating the thermal stability of the nanocomposites. Therefore, the changing tendency of the thermal stability observed here for PVDF/CNT nanocomposites may be the result of the competing effect between the dispersion state and the loading content of CNTs.

Dynamic mechanical properties

Figure 3(a,b) depict the storage modulus (G') and the loss factor $\tan \delta$ of neat PVDF and its MWNT nanocomposites over a temperature range of -125 to 75°C , respectively. It is apparent from Figure 3(a) that storage modulus decreases with the increase of temperature for all the samples though the decrease is not linear. And it can be seen that the addition of nanotubes has little effect on the glass transition temperature of PVDF, which is around -43°C as shown in Figure 3(b). The exact reason for this phenomenon is still unclear currently. It is probably due to the presence of carboxylic and hydroxy groups on the nanotubes which may play a role of plasticization effect. And another possible reason may be due to the microstructural changes of PVDF upon incorporation of MWNT which is now under investigation. Compared with neat PVDF, the G' of the PVDF/MWNT nanocomposites is enhanced due to the fine dispersion of high aspect ratio MWNTs.

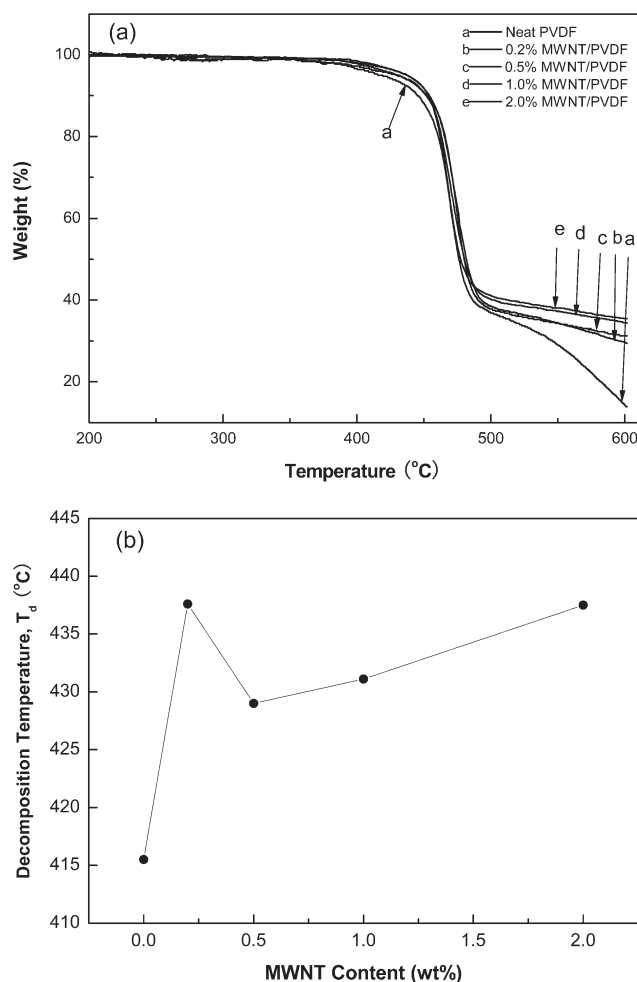


Figure 2 (a) TGA curves of neat PVDF and MWNT/PVDF nanocomposites under N_2 atmosphere and (b) variation of T_d with the MWNT loading.

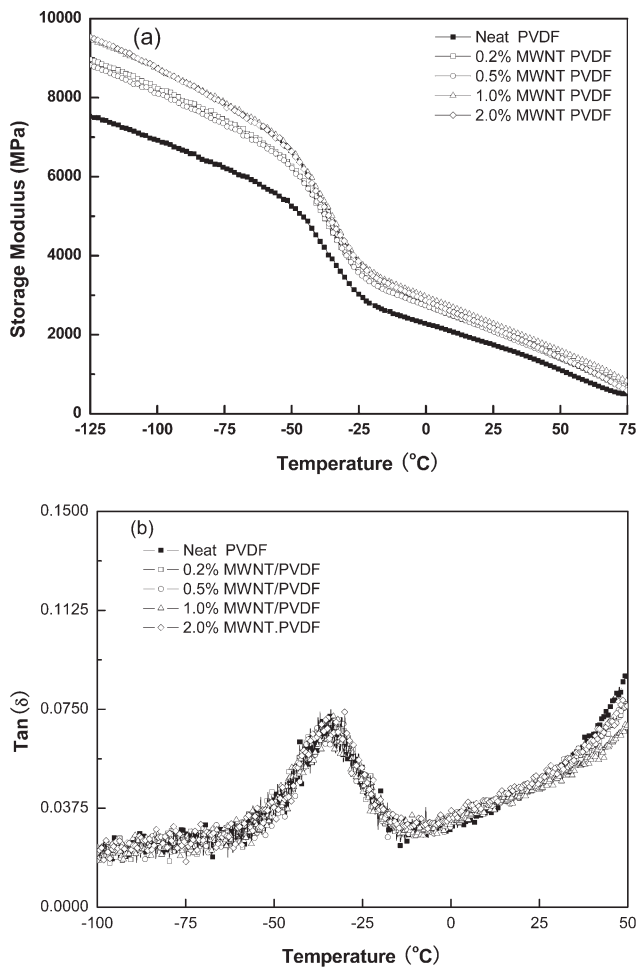


Figure 3 DMA curves of (a) storage modulus and (b) $\tan \delta$ versus temperature for neat PVDF and its nanocomposites as a function of MWNT concentration.

Melt-rheological behavior

To investigate the temperature effect on the rheological properties, the melt-rheological measurements for neat PVDF and its MWNT composite samples were carried out in the temperature range of 190–210°C. The complex viscosities ($|\eta^*|$) at 200°C for neat PVDF and its MWNT nanocomposites as a function of frequency are presented in Figure 4(a). The complex viscosities of neat PVDF and its composites decreased with the increase of frequency, indicating a non-Newtonian behavior and pseudo-plastic characteristics over the frequency range investigated. The shear thinning behavior observed may be attributed to the orientation of the chain segments during the applied shear force. It is interesting to note that the shear thinning behavior is most obvious for the nanocomposite containing 2 wt % MWNTs. This is probably due to the MWNTs at high loading level more easily tend to orient under shear force, thus disturbing the formation of the polymer chain entanglements and resulting in a more pronounced shear thinning behavior.

The frequency dependence of the $|\eta^*|$ of PVDF nanocomposite containing 2 wt % MWNTs measured at various temperatures is shown in Figure 4(b). It can be seen that the $|\eta^*|$ of the nanocomposite decreases with increasing temperature, indicating that the free volume of the nanocomposite increases with the increase of temperature and thus results in the decreased viscosity. And at lower shear force region, the temperature has more pronounced effect on $|\eta^*|$ than at higher frequency region, probably due to little effect of temperature on the segment movement of polymer chains at high shear force.

Figure 5 shows the complex viscosity $|\eta^*|$ versus MWNT content at different frequencies. It can be seen that the $|\eta^*|$ of the nanocomposites increased with the increase of MWNT loading. This is because the physical interactions between the matrix and the high aspect ratio MWNTs increase remarkably with the increase of MWNT loading, which results in the

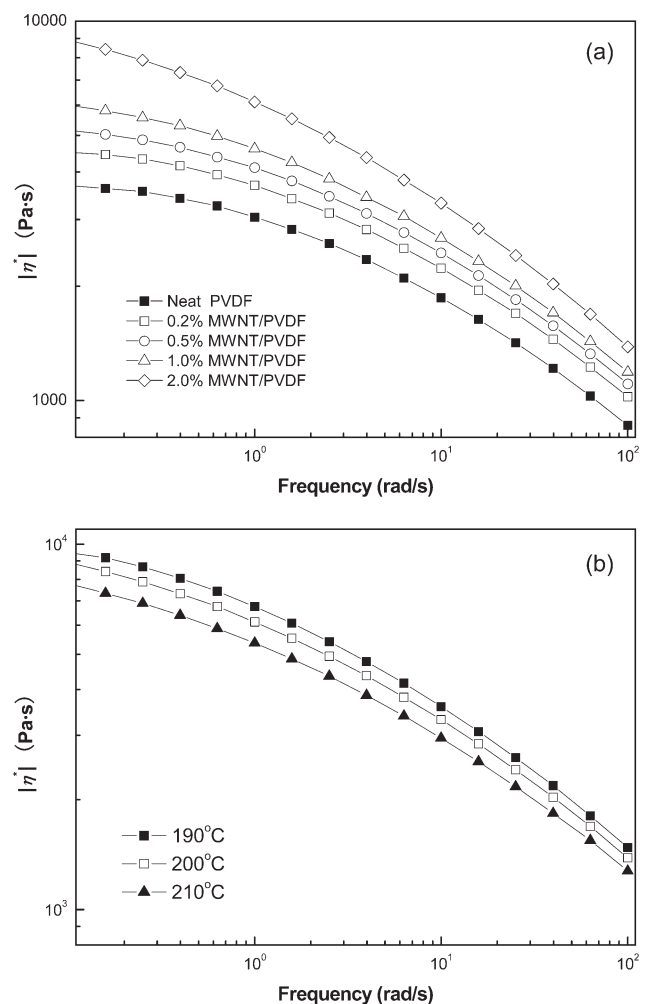


Figure 4 (a) The complex viscosity versus frequency with different MWNT loadings and (b) the frequency dependence of the complex viscosity at different temperatures for PVDF nanocomposite containing 2 wt % MWNTs.

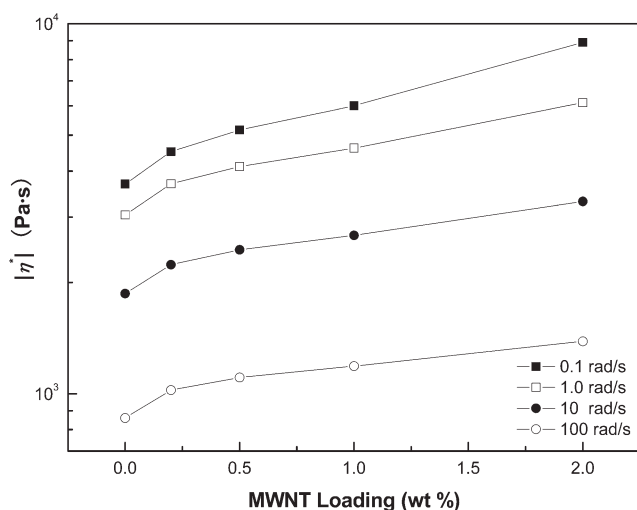


Figure 5 Variation of complex viscosities of neat PVDF and its MWNT nanocomposites at different frequencies.

increase of the complex viscosities of the systems. In addition, the extent of the increase of the $|\eta^*|$ with increasing MWNT content was more pronounced at low frequency compared with that at high frequency. The increase in the $|\eta^*|$ of the nanocomposites with the MWNTs was closely related to the large increase in the storage modulus.

The storage modulus (G') and loss modulus (G'') of PVDF/MWNT nanocomposites as a function of frequency at 200°C are shown in Figure 6(a,b), respectively. It is apparent that MWNT has an obvious effect on the rheological behavior of PVDF matrix. The storage modulus and loss modulus of the PVDF/MWNT composites were significantly improved relative to the PVDF matrix. The values of G' and G'' of neat PVDF and its nanocomposites increased with increasing frequency and MWNT content over the entire frequency range studied. And the modulus increment with frequency (the slopes of the curves) is more significant at low frequency. This rheological response is consistent with the relaxation behavior of the typical inorganic nanoparticles-filled polymer composite systems.¹⁵ For linearly homo-dispersed melts, polymer usually follows the relationship of $G' \sim \omega^2$ and $G'' \sim \omega$. The low frequency power law indexes of G' and G'' for neat PVDF are about 1.47 and 0.91, respectively, which are smaller than 2 and 1, probably due to the polydispersity of polymer chains. Thus, the flow curves for the PVDF/MWNT nanocomposites can be expressed by a power law relation of $G' \sim \omega^{1.45-1.07}$ and $G'' \sim \omega^{0.91-0.82}$. It can be seen that with the incorporation of MWNT into PVDF matrix, the dependence of G' and G'' on ω becomes comparatively weak at low frequency, and nonterminal solid-like rheological behavior were observed. The slopes of the terminal zone of G' and G'' are listed in Table I.

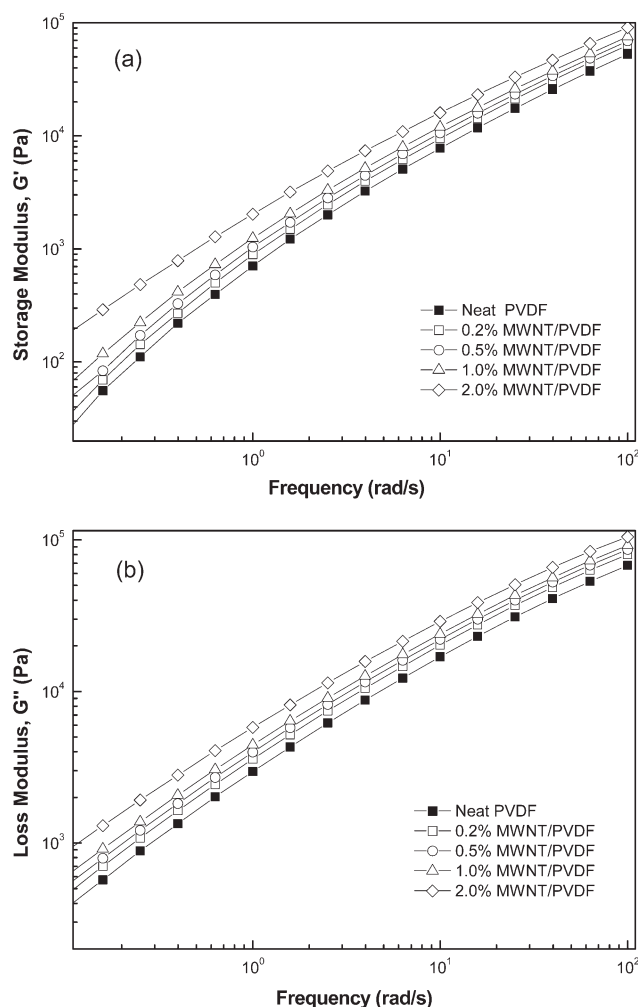


Figure 6 Variation of (a) storage modulus and (b) loss modulus of neat PVDF and its MWNT nanocomposites as a function of frequency.

It can be seen that the decrease in the slopes of G' and G'' for PVDF nanocomposites with the increase of MWNT content. Compared with the case of neat PVDF, the decrease in the slopes of G' and G'' for the composites can be explained by the microstructural changes of the polymer matrix due to incorporation of MWNT. The increase of the interfacial interactions between nanotube/nanotube and polymer/nanotube with increasing MWNT content leads

TABLE I
The Low Frequency Slopes of G' and G'' versus ω for PVDF/MWNT Composites with Different MWNT Loadings at 200°C

Materials	Slope of G'	Slope of G''
Neat PVDF	1.47	0.91
0.2% MWNT/PVDF	1.45	0.90
0.5% MWNT/PVDF	1.38	0.89
1.0% MWNT/PVDF	1.32	0.87
2.0% MWNT/PVDF	1.07	0.82

to the formation of the interconnected or network-like structures of MWNT in the polymer composites which restrains the long-range motion of polymer chains and thus results in the pseudo-solid-like behavior. Therefore, the PVDF composites undergo a transition from liquid-like to solid-like viscoelasticity with the increase of MWNT loading at low frequency region.

The variation of G' and G'' of PVDF nanocomposites with the MWNT content at different frequencies at 200°C is shown in Figure 7(a,b), respectively. It can be seen that at high frequency, the MWNT content has less effect on the moduli of the nanocomposites than at low frequency, as observed in the case of the complex viscosity (Fig. 5). This indicated that at high frequencies, the effect of the MWNTs on the rheological behavior is relatively weak, suggesting that the presence of MWNTs does not significantly influence the short-range motion or dynamics of PVDF chains but has a substantial influ-

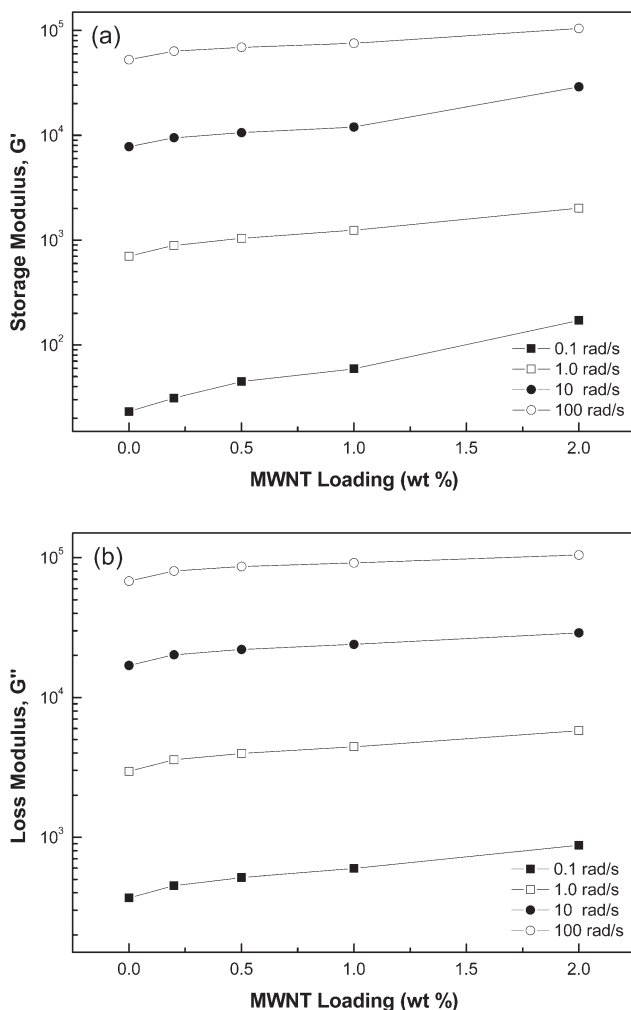


Figure 7 (a) Storage modulus and (b) loss modulus of neat PVDF and its MWNT nanocomposites as a function of MWNT content.

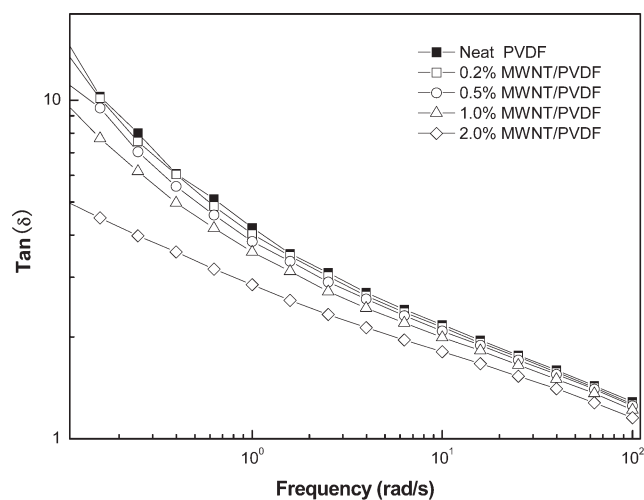


Figure 8 Variation of $\tan \delta$ with frequency for neat PVDF and its MWNT nanocomposites.

ence on large-scale polymer chain relaxations. The variation of loss factor, $\tan \delta$ (i.e., G''/G'), with the frequency at 200°C for neat PVDF and its nanocomposites is shown in Figure 8. Shear deformation leads to the partial orientation of the polymer chains, resulting in the decrease in $\tan \delta$ of the nanocomposites with the increase of frequency. It is noted that the $\tan \delta$ decreases with increasing MWNT loading, indicating that incorporating MWNTs into PVDF can help improve the elastic properties of the matrix.

CONCLUSIONS

PVDF nanocomposites containing different MWNT loadings were prepared by melt blending using twin-screw extruder. SEM observation showed fine dispersion of the MWNTs throughout PVDF matrix. TGA result illustrated that the addition of MWNTs into the matrix can significantly improve the thermal stability of PVDF. DMA indicated that the values of storage modulus G' of the nanocomposites were sharply increased compared with neat PVDF. The rheological investigation showed that the incorporation of MWNTs into PVDF matrix resulted in higher complex viscosities ($|\eta^*|$), storage modulus (G'), loss modulus (G''), and lower loss factor ($\tan \delta$) than those of neat PVDF. The G' , G'' , and $|\eta^*|$ of neat PVDF and its nanocomposites decreased with the increase of the frequency and the temperature.

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