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Increase the Mechanical Performance of Polyvinylidene Fluoride (PVDF)

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Keywords: Polyvinylidene fluoride, Carbon nanotube, Organo-modified layered silicate, Nano-composite, Mechanical Property, Creep resistance.

Abstract. Polyvinylidene fluoride (PVDF)/Carbon nanotubes (CNTs) and PVDF/Organo-modified layered silicates (OMLSs) nano-composites were prepared by phase inversion technique. Maleic anhydride grafted PVDF (PVDF-MAH), were used to fine tune the interface. Transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to characterize the nanocomposites. Elastic modulus and creep resistance of the PVDF nanocomposites were evaluated according to ASTM D-638. The results showed that both CNTs and OMLSs were good candidates to reinforce the PVDF and the addition of PVDF-MAH enhanced the interface between nanoparticles and PVDF, leading to further increase of mechanical property.

Introduction

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer with a variety of interesting properties. PVDF has been a widely studied polymer because of its potential as piezoelectric and pyroelectric materials. These properties, combined with high elasticity and processing ability, provide a variety of technological applications for this polymer [1]. Recent research results revealed this material can be used as a main component in film adhesive in the joining of thermoset composite materials [2, 3]. However, due to the nature of thermoplastic, creep resistance of the film adhesive is the major concern for its application. Therefore, it is urgent to modify the PVDF in order to increase its stiffness and creep resistance. The mixing of nanoparticles with polymer to form nanocomposite material is a good way to obtain high performance material. There are several ways to fabricate polymer nanocomposites [4, 5]: (1) solution mixing; (2) in-situ polymerization; and (3) melt processing. The solution method is the most common method for fabricating polymer nanocomposites. This is because good dispersion can be obtained by the selection of suitable solvent and treatment of the nanoparticles. At the same time, further interfacial modification can be easily achieved [6]. In our current research, a phase inversion technique was used to fabricate carbon nanotubes (CNTs)/PVDF and organo-modified layered silicate (OMLSa)/PVDF nanocomposites [6]. Long chain macromolecules, maleic anhydride grafted PVDF (PVDF-MAH), were used as coupling agent to fine tune the interface between the nanoparticles and polymer matrix. Transmission electron microscopy (TEM) was used to characterize the microstructure of the nanocomposites. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to investigate the melting and morphological behaviors. Mechanical properties of the nanocomposites were evaluated according to ASTM D-638.

Experimental

Materials: PVDF (Kynar 741, powder) and maleic anhydride grafted PVDF (ADX-161) named from here on as ADX were supplied by Arkema. Two nanoparticles, e.g. multiwall carbon nanotubes (CTNs) with diameter of 10-30 nm and organically modified montmorillonite nanoclays

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(OMLSs) were purchased from Tsinghua University, China and Southern Clay Products, Inc., respectively. Analytical grade N-methyl-2-pyrrolidone (NMP) and H_2O_2 were used as solvents and purchased from Aldrich.

Preparation of CNTs/PVDF and OMLSs/PVDF nanocomposites: N-methyl-2-pyrrolidone (NMP) was used as solvent in the phase inversion method. The evaporation temperature of NMP is about 200°C. Distilled water that has evaporation temperature of 100°C was used as the anti-solvent for NMP. The preparation procedure was reported in Ref [6]. The prepared nanocomposites were compression moulded in a hot press using matched metal die at temperature of 200°C and pressure of 5.0 MPa. The prepared nanocomposite sheets had a thickness of 0.5mm and were cut into test couples for subsequent characterization. Table 1 summarized the various formulations used in current study.

Table 1: Sample code of various formulations

Sample Code		Formulation
PVDF		PVDF (100% wt.)
OMLSs/PVDF	PO_5	PVDF(100%wt)+OMLSs(5%wt.)
	PO_5A_1	PVDF(100%wt)+OMLSs(5%wt.)+ADX(1%wt.)
	PO_5A_5	PVDF(100%wt)+OMLSs(5%wt.)+ADX(5%wt.)
CNTs/PVDF	PC_5	PVDF(100%wt) +CNTs(5%wt.)
	PC_5A_2	PVDF(100%wt)+CNTs(5%wt.)+ADX(2%wt.)
	PC_5A_5	PVDF(100%wt)+CNTs(5%wt.)+ADX(5%wt.)

Characterization: TEM samples of 50 to 100nm in thickness were cut with Leica EM UC6 ultramicrotome and investigated by Philips Tecnai F20 transmission electron microscope (TEM) at 200kV. DSC tests were conducted using TA Q20 differential scanning calorimeter. The DMA (tension deformation) was carried out using a TA Instrument Q800 DMA. The mechanical properties and creep resistance of nanocomposites were tested according to ASTM D-638 (type V). Dumbbells were punched out of the nanocomposites sheets. For static test, the testing speed was 5mm/min and at least five samples were tested for each formulated nanocomposite. The creep test was conducted at room temperature, at stress level of 20 MPa and at least three samples were tested for each formulation.

Results and Discussion

Morphology of nanocomposites: To obtain a true representation of the mirostructure, at least 10 positions were examined for each sample using TEM. Figure 1 shows the typical image of CNTs/PVDF and OMLSs/PVDF. Both samples contained 5% of nanoparticle. It can be seen that CNTs and OMLSs

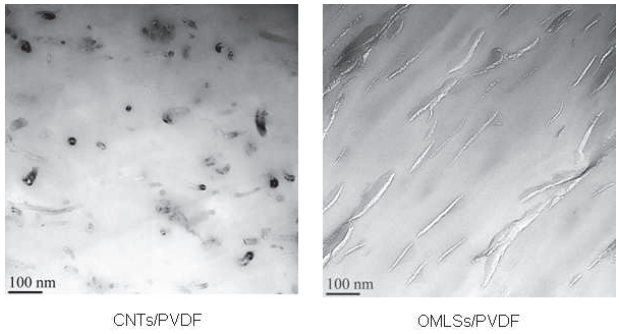

Fig. 1: TEM image of CNTs/PVDF and OMLSs/PVDF

were well separated from each other and dispersed quasi-homogenously among the matrix. Although NMP was used to prepare the nanocomposite, the solvent was easily removed into its anti-solvent (water). In addition, due to the large difference between the evaporation temperatures, the NMP can be easily recycled. Furthermore, this result also indicates that the phase inversion method has high potential to be used to prepare nanocomposites with very high content of nanoparticle. Nanocomposites with high content of nanoparticle can then be used as a master-batch material to mass-produce nanocomposite using a more conventional melt-blend process.

Crystallization behavior: In the DSC tests, samples of about 5 mg were heated to 200°C (1st heating) at a rate of 10°C/min under a nitrogen atmosphere and held at 200°C for 5 min to eliminate the thermal history. Afterward, the samples were cooled to 20°C at a rate of 20°C/min, held about 3 min and then heated again to 200°C (2nd heating) at a heating rate of 10°C /min. The results of DSC test are listed in Table 2. It can be seen that with the addition of 5%wt. of OMLSs and CNTs the value of enthalpy detected in PO_5 and PC_5 were lower than that of pure PVDF, indicating a decrease of crystallinity in the nanocomposites. Taking into account that the melting enthalpy of a 100% crystalline PVDF is 104.5 J/g [7], the degree of crystallity of nanocomposites is reduced by 3.0-5.4% (CNTs) and 4.2-4.8% (OMLSs), which is thought to be marginal and the solvent resistance of PVDF will not be affected.

Table 2: Results of DSC test

Sample Code	1st Heating		2nd Heating	
	ΔH_m (J/g)	Tm (°C)	ΔH_m (J/g)	Tm (°C)
PVDF	42.97	166.76	43.07	166.14
PC_5	40.53	165.96	40.19	166.42
PC_5A_2	37.73	166.41	37.63	166.62
PC_5A_5	38.90	171.63	38.86	166.38
PO_5	37.78	173.16	38.46	173.31
PO_5A_1	37.96	172.58	38.21	172.97
PO_5A_5	38.90	173.35	38.94	173.45

Dynamic mechanical behavior: Figure 2 shows the storage modulus of PVDF, and its CNTs (Figure 2a) and OMLSs (Figure 2b) namocomposites. All samples (tension deformation) were measured over a temperature range of -100°C to 150°C at a heating rate of 3°C /min and at a frequency of 1Hz. It is clear that the storage modulus of PVDF was increased by the addition of nanoparticles and further enhanced by the addition of ADX in both namoparticle/PVDF systems. The reinforcing effect was more profound at low temperature regions than high temperature regions. The increase of modulus across a wide range of temperature will enhance the creep resistance of PVDF.

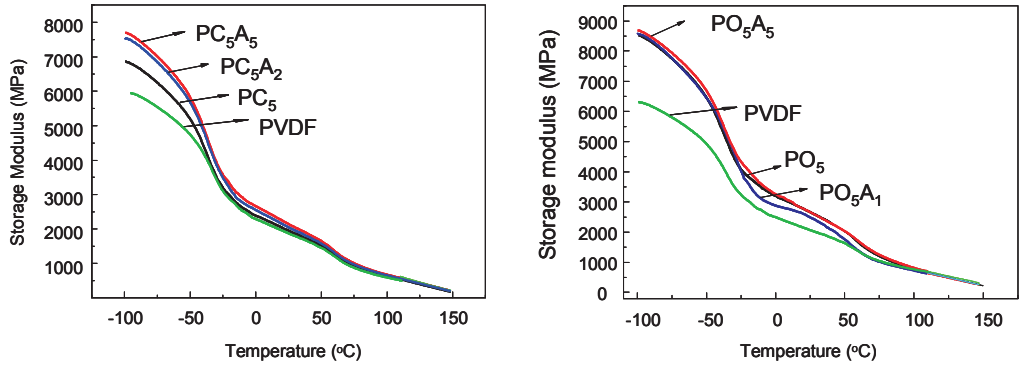

Fig 2: Storage modulus of PVDF and its nanocomposites

Mechanical performance: Figure 3 shows the Young's modulus of OMLSs/PVDF (Figure 3a) and CNTs/PVDF (Figure 3b). It can be observed from Figure 3a, that with the addition of 5%wt. of OMLSs the modulus was increased by 37% (from 1.98 to 2.72 GPa), and with an addition of 5 wt%

ADX, the modulus was further increased up to 55% compared with the pure PVDF (from 1.98 to 3.06 GPa). The improvement is attributed to two factors. The phase inversion method used in the preparation of OMLSa/PVDF guarantees good dispersion of nanoparticles. The OMLSs used in current study contains hydroxyl group which can react with the maleic anhydride groups that are grafted on ADX, leading to improved interactions at the interface [9].

The same trend of improvement in the modulus can also be observed with the CNTs/PVDF (Figure 3b), however, the enhancement is not as significant as that of OMLSs/PVDF. With the addition of 5%wt. functionalized CNTs, the modulus of PVDF was only increased by 15.6% (from 1.98GPa to 2.29GPa). This result indicates that even though good dispersion of CNTs among the PVDF (Figure 1) has been achieved, the interaction between CNTs and PVDF was relative weak. With the addition of ADX, the modulus of CNTs/PVDF was steadily increased. At the content of 5%wt. ADX, the modulus was increased by 31.8% (from 1.98 to 2.61). Because of the limited number of functional group in ADX (the PVDF-MAH has 0.1% polar group), the improvement of stiffness was marginal. However, the addition of functional group did show encouraging results and provide a useful clue for the future research direction.

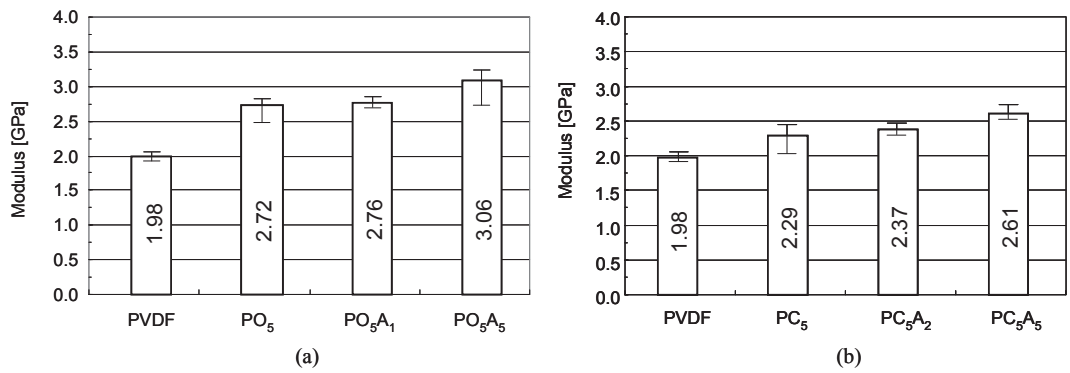

Fig 3: Modulus of CNTs/PVDF and OMLSs/PVDF

Creep resistance: The creep property was tested using tensile test at room temperature, where all samples were loaded to a stress level of 20 MPa and their strain were monitored using Advanced Video Extensometer [AVE] for two hours. The stress level of 20 MPa was within the elastic range of pure PVDF. The typical creep strain versus time curves for pure PVDF and its nanocomposites are shown in Figure 4. Normally, several regions can be found in the creep curve. The first one is the instantaneous increase in strain because of the elastic response, and then followed by a viscoelastic response, where time dependent molecular rearrangement occurred. It can be noted that in the first creep stage, the strain

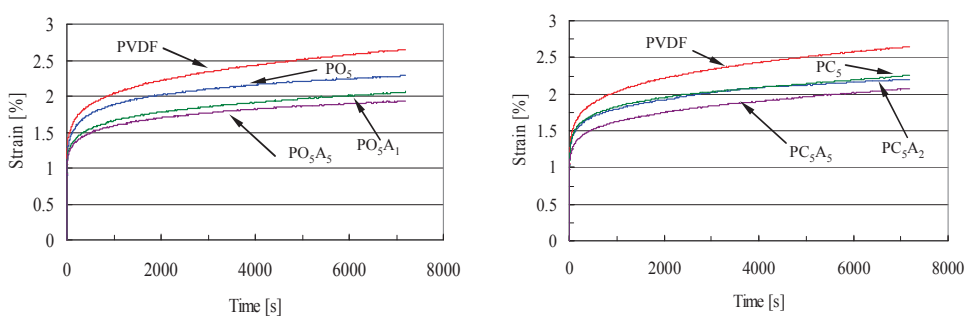

Fig. 4: Constant stress creep behavior of PVDF and its nanocomposites

increases rapidly with the strain rate decreasing monotonically, until the creep reaches the second stage, when the strain rate keeps constant. Obviously, nanocomposites have much lower creep strain and lower strain rate as indicated by the slop these curves. It should be pointed out that the strains grow up all the time and do not have asymptotic limit values within the two-hour testing range; this implies that during creep test some creep damages or plastic deformation occurs.

Burger model [10], as shown in equation (1), was used to simulate the creep behavior of PVDF and its nanocomposites. The experimental data were simulated by using the Non-Linear Curve Fit function in Matlab. The initial value of the undetermined parameters (E_1, E_2, η_1 and η_2) in Burger model is chosen by software named as 1STOPT. The simulation was performed by the program using a least square approximation procedure. The representative experimental curves of creep extension vs. creep time of the specimens are presented in Figure 5. It can be clearly seen that the modeling curves show a satisfactory agreement with the experimental curve.

$$\varepsilon(\sigma,t)=\frac{\sigma}{E_1}+\frac{\sigma}{E_2}\left(1-e^{-t/T}\right)+\frac{\sigma}{\eta_1}t,\quad T=\frac{\eta_2}{E_2} \tag{1}$$

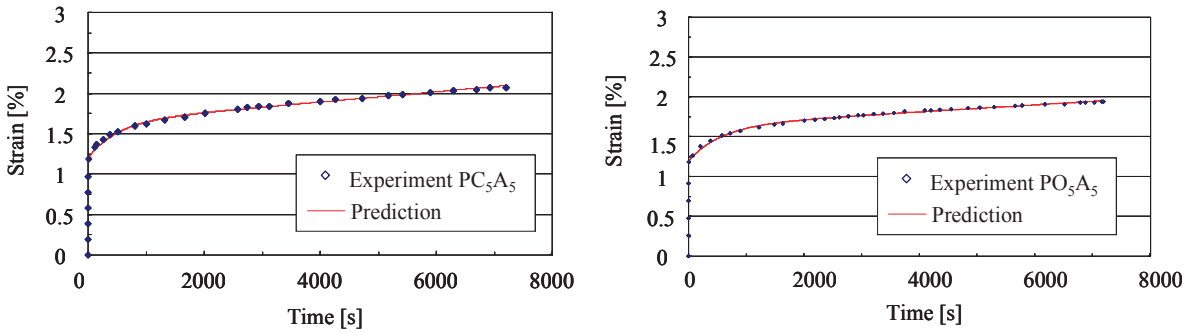

Fig. 5: Constant stress creep behavior of PC_5A_5 and PO_5A_5 namocomposites. Symbols are experimental data at stress of 20 MPa. Lines represent Burger model predictions at 20MPa.

Conclusions

Quasi-homogenous CNTs/PVDF and OMLSs/PVDF nanocomposites have been prepared using phase inversion method. DSC results showed that the addition of nanoparticles and interface modifier (ADX) caused slightly reduction of degree of crystallinity (3-5.5%). The Young's modulus of CNTs/PVDF and OMLSs/PVDF systems was 15% and 37% higher than that of pure PVDF. With the addition of ADX, an interface modifier, the Young's modulus was increased up to 31% and 55%. All nanocomposites had much better creep resistance than pure PVDF. These results showed that both CNTs and OMLSs were good candidate nanoparticles to reinforce the PVDF.

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