

Electronic Supplementary Information(ESI)

Assistant effect of poly(methyl methacrylate) grafted carbon nanotubes on beta polymorph of poly(vinylidene fluoride) during microinjection

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Materials

Poly (vinylidene fluoride) was provided by Alfa Aesar (Tianjin) Chemical Co., Ltd. The melt viscosity was 23500 poise at 230°C and 100s⁻¹.

Multiwalled carbon nanotubes with the purity of 99.9% were provided by Chengdu Institute of Organic Chemistry, China. The length was 50µm and the diameter was 8-12nm.

Poly(methyl methacrylate) was purchased from Sumitomo Chemical Singapore Pte Ltd.. Its weight average molecular weight was 5.5×10⁵g/mol.

Sample preparation

Solid-grafting of CNTs with PMMA: PMMA/CNTs mixtures(9/1) were fed into self-designed pan-mill type equipment. See previous papers for more information on

this equipment¹. The milled powders were extracted with boiling N,N-dimethylformamide(DMF) in Soxhlet extractor for 48h to remove free PMMA. The obtained CNTs was named as PMMA-g-CNTs.

Microinjection: The compounding of PVDF and 0.5wt% CNTs was conducted through DMF solution and the CNTs/PVDF nanocomposites were melt-processed on a Battenfeld MicroPower-5 molding machine (Wittmann Battenfeld GmbH, Austria). Figure 1 presented the photo of the microinjection machine and 3-D view of the injection unit configuration¹. The maximum injection speed and pressure generated by this machine could reached 700 mm/s and 3000 bar. In this study, the used injection speed was 400 mm/s and the melt temperature was 190 °C. The dimension sizes of the pouring gate channel were 2×0.2×0.5 mm. In this case, the shear rate was $1.28 \times 10^5 \text{s}^{-1}$. For comparison, the static samples were prepared under no stress filed, where the samples were melted at 190 °C in a hot stage for 5min followed by cooling.

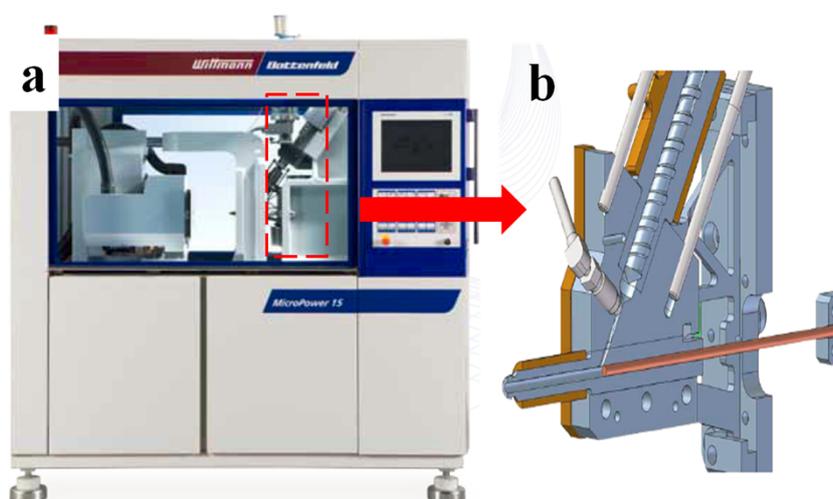


Figure 1 Photo of the microinjection machine and 3-D view of the injection unit configuration

Characterization

Scanning electron microscopy (SEM) of PMMA-g-CNTs was carried out using an Inspect F (FEI) SEM instrument at 0.5 Torr and 20 kV.

Thermal gravimetric analysis (TGA) of the samples were conducted under nitrogen atmosphere by using TA Instruments(TGA Q50) with a heating rate of 10 °C/min from 25 to 600°C.

Fourier transform infrared (FTIR) spectra of the samples were measured using a Nicolet 6700 spectrometer.

Rheological measurements were conducted on a AR2000EX rotational rheometer (TA Instruments, USA) at 190°C in a nitrogen atmosphere. The parallel plate geometry was 25 mm and the gap was 0.9 mm.

DSC analysis was performed by a Q20 differential scanning calorimetry apparatus (TA, America). The ~6 mg specimens were heated from 40 to 200°C at the 10°C/min heating rate under nitrogen atmosphere.

FTIR analysis of PMMA-g-CNTs

Figure 2 showed FTIR spectra of PMMA-g-CNTs composites after 48 h Soxhlet extraction with boiling N,N-dimethylformamide. Clearly, the characteristic peak of carbonyl group at 1742 cm^{-1} was observed, suggesting that PMMA was successfully grafted into CNTs.

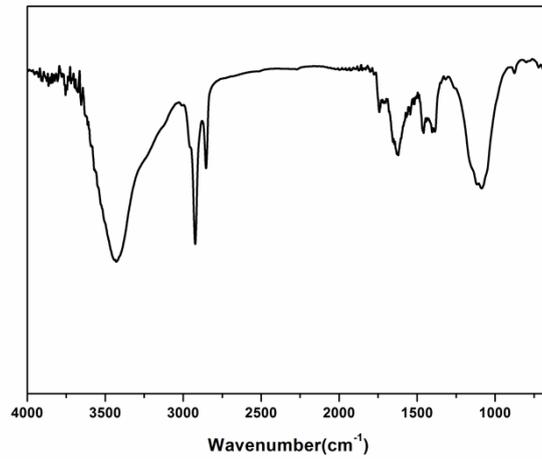
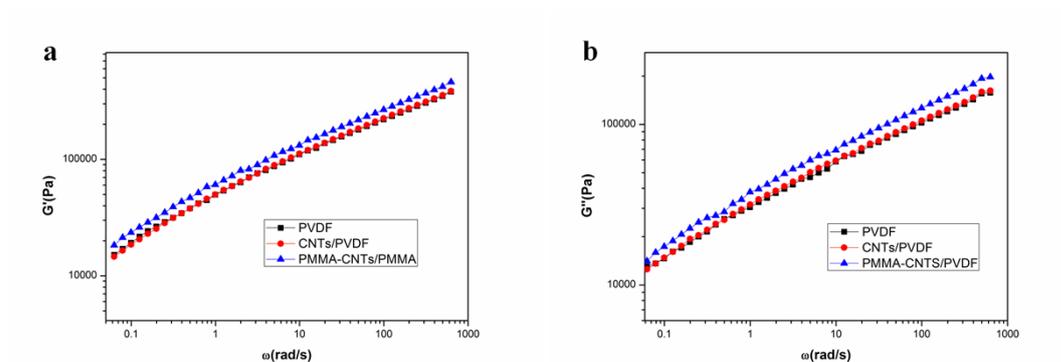


Figure 2 FTIR spectra of PMMA-g-CNTs composites after 48 h Soxhlet extraction with boiling N,N-dimethylformamide

Rheological Properties

Figure 3 presented the relationships of storage modulus (G'), loss modulus (G'') and viscosity (η^*) of pure PVDF, CNTs/PVDF composite and PMMA-CNTs/PVDF composite with frequency under 190°C. The similar curves in Figure 3 indicated that with the presence of pristine CNTs and the functionalized CNTs, the rheological properties of PVDF remained unchanged, that is, the two CNTs did not affect the processing behaviors of PVDF greatly. This could be ascribed to low content of CNTs in this study.



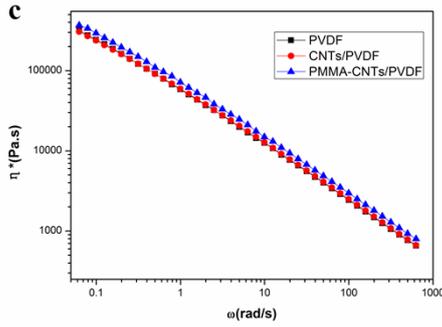


Figure 3. Dynamic rheological properties of pure PVDF, CNTs/PVDF composite and PMMA-CNTs/PVDF composite. (a) storage modulus (G'); (b) loss modulus (G''); (c) complex viscosity (η^*).

DSC analysis

DSC tests were adopted to demonstrate the effects of CNTs on the crystallization behaviors of PVDF. Figure 4 showed DSC curves of PVDF, CNTs/PVDF composite and PMMA-CNTs/PVDF composite prepared by static state and microinjection. Clearly, only a single melting peak appeared and the characteristic melting peak of γ -phase at 180°C was not detected, indicating no γ -phase existed for all samples. The crystallinities were calculated based on the melting enthalpy³:

$$X_c = \Delta H_f / \Delta H_{100} \times 100\%$$

where ΔH_f was the melting enthalpy of PVDF and ΔH_{100} was the melting enthalpy for PVDF with 100% crystallinity (104.6 J/g).

The results were listed in Table 1. All samples displayed similar crystallinity, indicating CNTs and flow hardly affected the crystallization behaviors of PVDF.

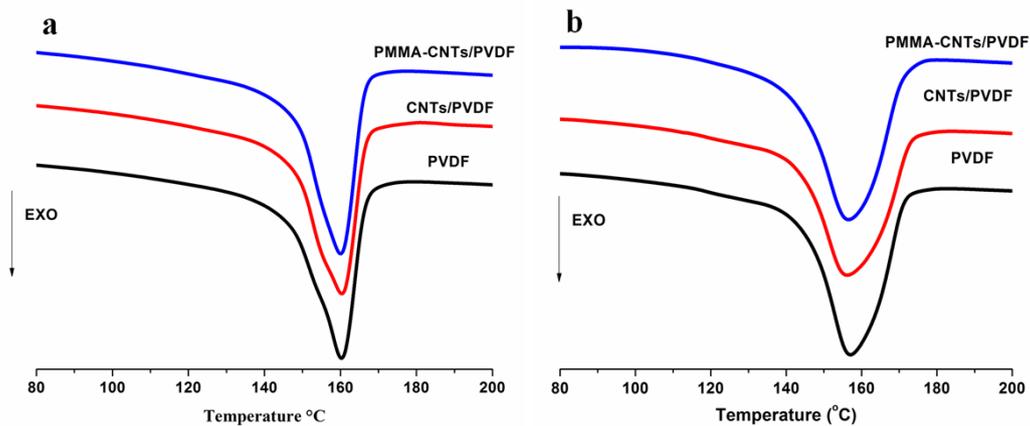


Figure 4 DSC heating curves of PVDF, CNTs/PVDF composite and PMMA-CNTs/PVDF composite prepared by static state (a) and microinjection(b)

Table 1 Crystallinity of PVDF, CNTs/PVDF composite and PMMA-CNTs/PVDF composite prepared by static state and microinjection

	PVDF	CNTs/PVDF	PMMA-CNTs/PVDF
Static samples	44.9	45.8	46.0
Microinjected samples	44.4	44.6	43.6

References

1. Wittmann Group, Technical report of MicroPower, http://www.battenfeld.se/pdf/battenfeld/battenfeld_MicroPower_V_GB.pdf, Sep. 2014,
2. H. Xia, Q. Wang, K. Li and G. H. Hu, *J Appl Polym Sci*, 2004, **93**, 378.
3. A. C. Lopes, C. M. Costa, C. J. Tavares, I. C. Neves and S. Lanceros-Mendez, *J Phys Chem C* 2011, **115**, 18076.