Supporting information

Effect of polystyrene long branch chain on melt behavior and foaming performance of poly(vinyl chloride)/graphene nanocomposites

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Synthesis of PVC-*g*-PS graft copolymers

The synthesis of PVC-*g*-PS was performed according to the reported method[1]. A typical polymerization process (for run 3 in Table S1) is as follows: PVC 6.25 g and DMF (150 mL) were placed in a 500 mL three-necked round-bottom flask equipped with a condenser pipe and a magnetic stir bar under an argon atmosphere. PVC was dissolved at 50 °C for 1 h. Then, St (50 mL) and a solution of CuBr/PMDETA in 5 mL of DMF (50 mg of CuBr and 0.20 mL of PMDETA, pretreated for 5 min at ambient temperature) were added to the flask and the mixture was maintained at 90 °C for 1 h under stirring. Thereafter, the reaction mixture was poured into a large amount of methanol and the resulting graft copolymer was filtered, washed with methanol, and dried under vacuum at 80 °C. In order to obtain pure PVC-*g*-PS graft copolymer, the obtained product was extracted with acetone in a Soxhlet extractor for 12 h. The results of PS from PVC macroinitiator are summarized in Table S1. The resultant products were described as PVC-*g*-PSx. Here the symbol x denotes the branch length (g/mol).

Characterization of PVC-*g*-PS graft copolymers

Graft copolymers of commercial PVC homopolymer as backbone with polystyrene as branch chains (PVC-*g*-PS) were synthesized by ATRP graft copolymerization initiated from PVC structural defects. In this way, the PVC-*g*-PS was prepared with high-conversion yields. The polymerization conditions and the results were summarized in Table S1. The resultant PVC-*g*-PS graft copolymers possessed the same backbones and the same branch density. In order to adjust the length of PS branch, the "Graft-from" method was carried out with controlling polymerization time at the same monomer concentration. The resultant samples were characterized by GPC. The traces show a monomodal molecular weight distribution and a significant shift of the peak value toward higher molecular weight with the increase of PS chain length (Fig. S1). This suggests that graft copolymerization occurred without detectable free homopolymer. However, the shape has little difference probably due to the polydispersity of the original PVC and the nonlinear structure of the graft copolymers. The molecular structural parameters of the obtained PVC-*g*-PSx are summarized in Table S1.
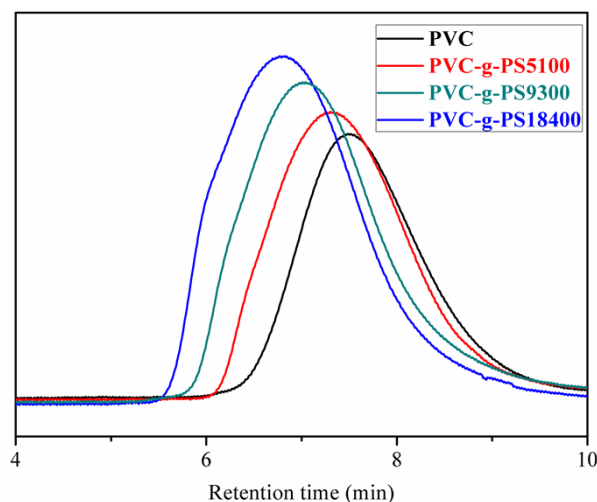

**Fig.S1.** GPC traces of PVC-*g*-PSx graft copolymers obtained with different length of PS branches

Table S1. Summary for Characterization Results by ^{1}H NMR, GPC and Caraculacu's Method.

Samples	St content[a] (mol%)	Branch length[b] (g/mol)	Branch density[c]	M_n[d] (g/mol)	M_w[e] (g/mol)	PDI[f]	T_g (^{o}C)
PVC	0	0	0	39,700	80,500	2.03	83.9
PVC-*g*-PS5100	15.7	5,100	0.32	46,200	97,900	2.12	85.8
PVC-*g*-PS9300	28.6	9,300	0.32	49,300	107,400	2.18	86.4
PVC-*g*-PS18400	56.6	18,400	0.32	56,500	127,100	2.25	88.2

[a]Calculated by ^{1}H NMR spectra; [b]calculated from Branch length=St content ×104/ Branch density; [c]Average number of branches per 100 chlorines in the PVC backbones, according to the method suggested by Caraculacu; [d, e]number molecular weight and weight molecular weight determined by GPC; [f]Polydispersity: M_w/M_n

The chemical structure of PVC-*g*-PSx was verified by FTIR and ^{1}H NMR. In the FTIR spectra (Fig. S2), the appearance of characteristic stretching vibrations of the benzene repeat units at 1600, 1580 and 1490 cm^{-1} confirmed the formation of PS branch chains on the backbone of PVC. The ^{1}H NMR spectrum of a representative PVC-*g*-PS graft copolymer (run 2 in Table S1) is presented in Figure S3. Besides the major chemical shifts corresponding to the PVC backbone, the aromatic and aliphatic proton signals of PS branches were observed at 6.4-7.4 and 1.4-2.2 ppm, respectively. From the ratio of the integrated peak areas of PVC to PS, the content of grafted PS in the resulting PVC-*g*-PS can be calculated, and the results are listed in Table S1. The grafting density of PS chains, which is determined by the labile chlorine content of the starting PVC, was calculated with the method suggested by Caraculacu *et al*[2]. The calculated value (0.32%) corresponded to 0.32 initiation sites per 100 repeat units of PVC. In addition, the samples present only one glass-transition temperature (T_g) by means of differential scanning calorimetry (DSC), which become higher with increasing the branch length of PS (Table S1). Because the obtained product was extracted, this revealed that PS chains are indeed grafted on the PVC backbones.
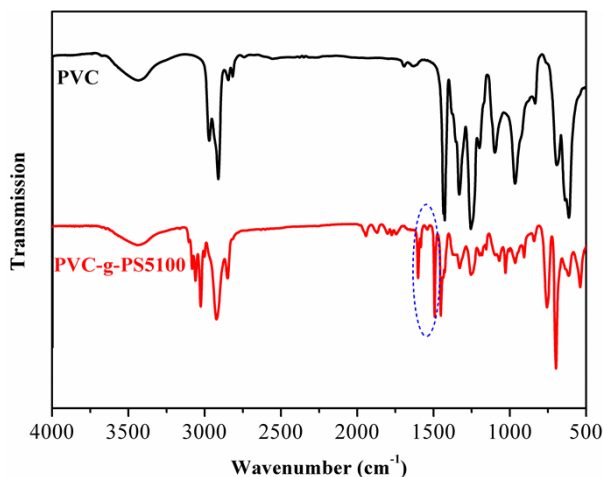
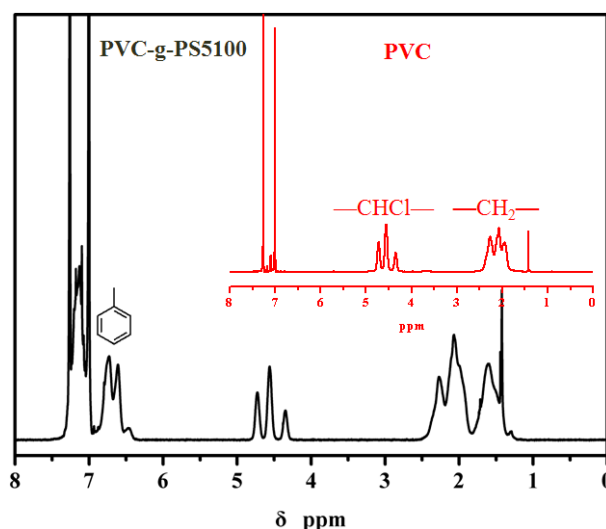**Fig. S2.** FT-IR spectra of PVC and PVC-*g*-PS5100.

Fig. S3. ^{1}H NMR spectra of a representative PVC-*g*-PS copolymer in o-dichlorobenzene-d$_4$

Fig. S4 shows the G'' versus ω for the PVC and PVC-*g*-PSx samples at 185 °C. Compared to PVC, the PVC-*g*-PSx samples exhibit higher G'' at low shear frequencies, and the terminal slope of G'' is less than that of PVC.
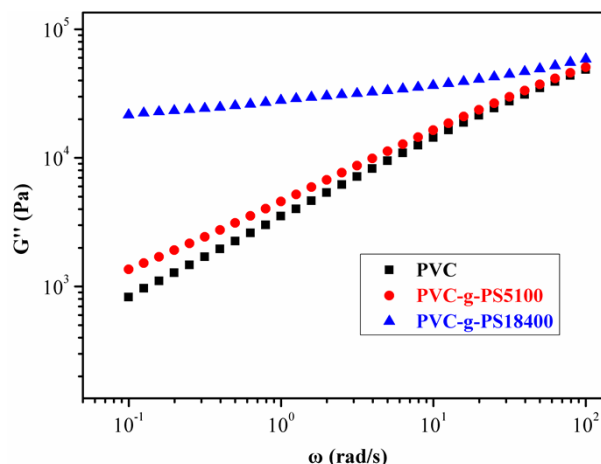
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Fig. S4. The comparison of loss modulus *vs* angular frequency for PVC-*g*-PS samples with different length of branches at 185 °C

Fig. S5 shows the plots of loss modulus (G'') versus angular frequency (ω), at 185 °C for PVC/FGS and PVC-*g*-PSx/FGS systems. The PVC-*g*-PSx/FGS samples exhibited much higher G'' at low shear frequencies, and the terminal slopes of G' were all less than that of PVC/FGS. The G' of PVC-*g*-PSx/FGS samples at low shear frequencies was enhanced when the branch length increased.
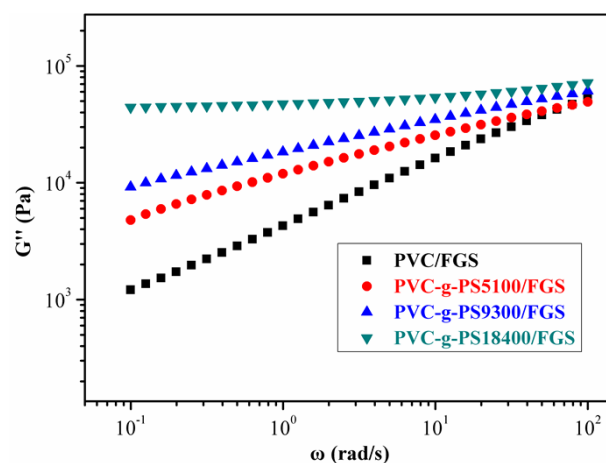
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Fig. S5. The comparison of loss modulus *vs* angular frequency for PVC-*g*-PS/FGS samples at 185 °C

3

Compared to PVC, PVC/FGS composite shows limited change in loss modulus (Fig. S6). However, there was a clear improvement in G'' when the PS branches was introduced on PVC backbone.
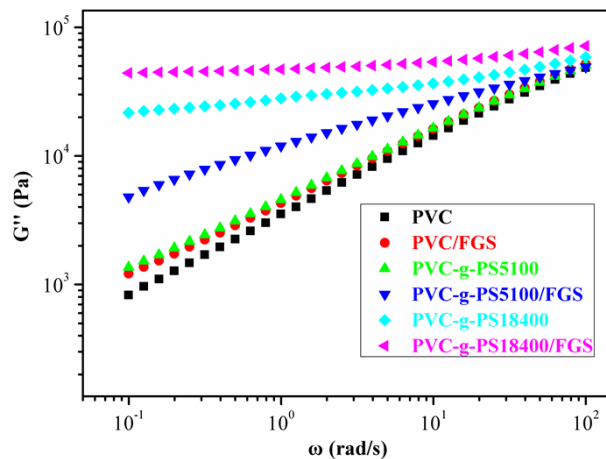

Fig. S6. The comparison of loss modulus *vs* angular frequency for the samples with and without FGS.

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References

1. V. Percec, F. Asgarzadeh, *J. Polym Sci., Part A: Polym. Chem.*, 2001, **39**, 1120-1135.
2. A. A. Caraculacu, E. C. Bezdadea, G. Istrate, *J. Polym Sci., Part A: Polym. Chem.*, 1970, **8**, 1239-1246.