

Supporting Information

Influence on thermal conductivity of polyamide-6 covalently-grafted graphene nanocomposites: varied grafting-structures by controllable macromolecular length

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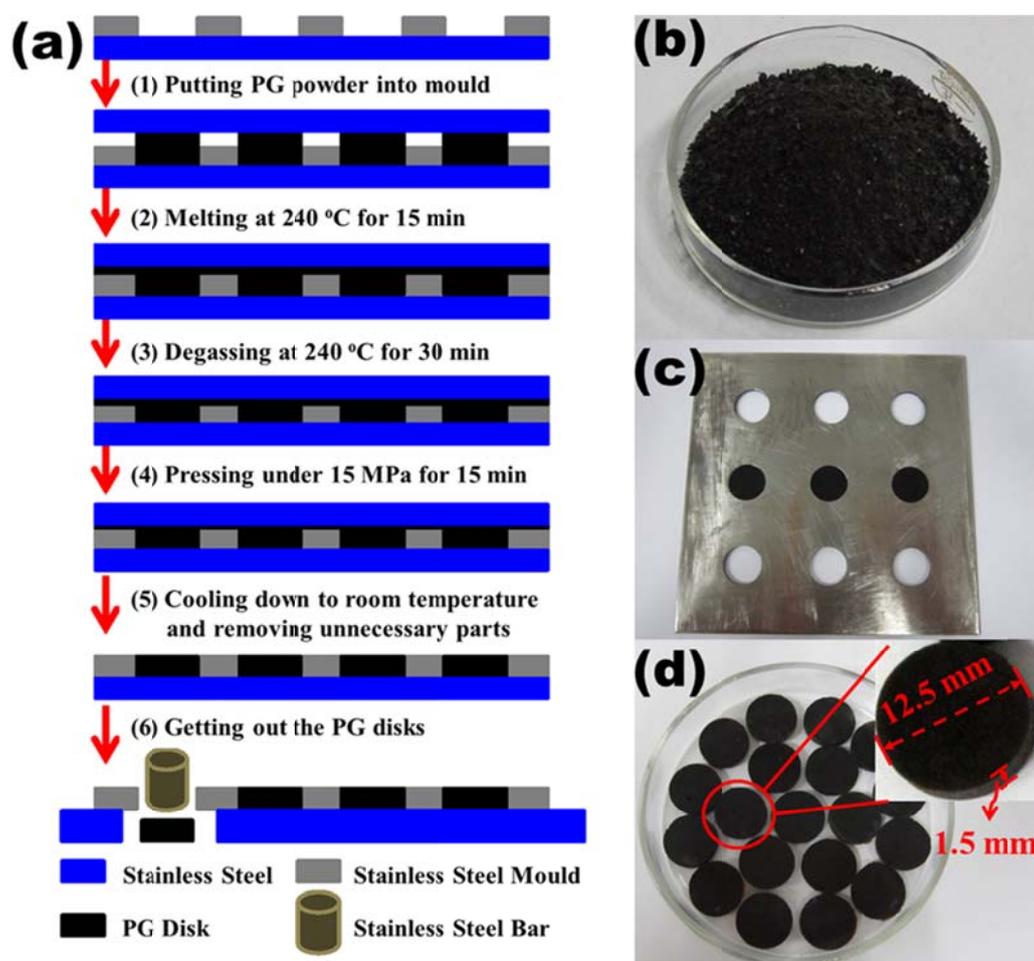


Fig. S1 a) The hot-pressing schematic diagram of fabricating PG nanocomposite disks, b) the PG nanocomposite powder, c) the stainless mould and d) the hot-pressed PG nanocomposite disks. The inset in d) shows the enlargement of the PG nanocomposite disk with the diameter of 12.5 mm and thickness of 1.5 mm.¹

The thermal conductive PG nanocomposite disks were fabricated through hot-pressing method in Fig. S1a: (1) putting the PG nanocomposite powder (Fig. S1b) into the mold (Fig. S1c), (2) melting at 240 °C for 15 min, (3) degassing at 240 °C for 30 min, (4) pressing under 15 MPa for 15 min, (5) cooling down to room temperature and removing unnecessary parts, and (6) getting out the PG nanocomposite disks (Fig. S1d). The PG nanocomposite disks hold the diameter of 12.5 mm and thickness of 1.5 mm to be suited to the measurement of thermal conductivity (λ) by the transient laser flash technique with the Netzsch LFA 447 Nanoflash later.

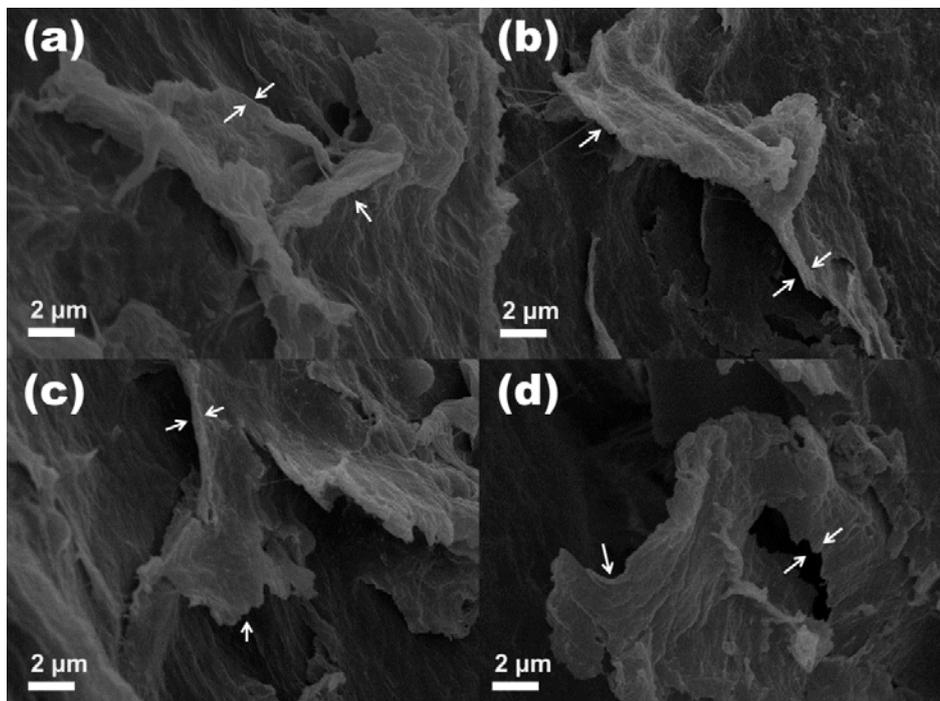


Fig. S2 SEM images of PG nanocomposites fracture surfaces: (a) PG-2, (b) PG-3, (c) PG-4 and (d) PG-6 nanocomposites (note the protruding flakes marked by arrows at the edges of PA6-grafted RGO sheets).

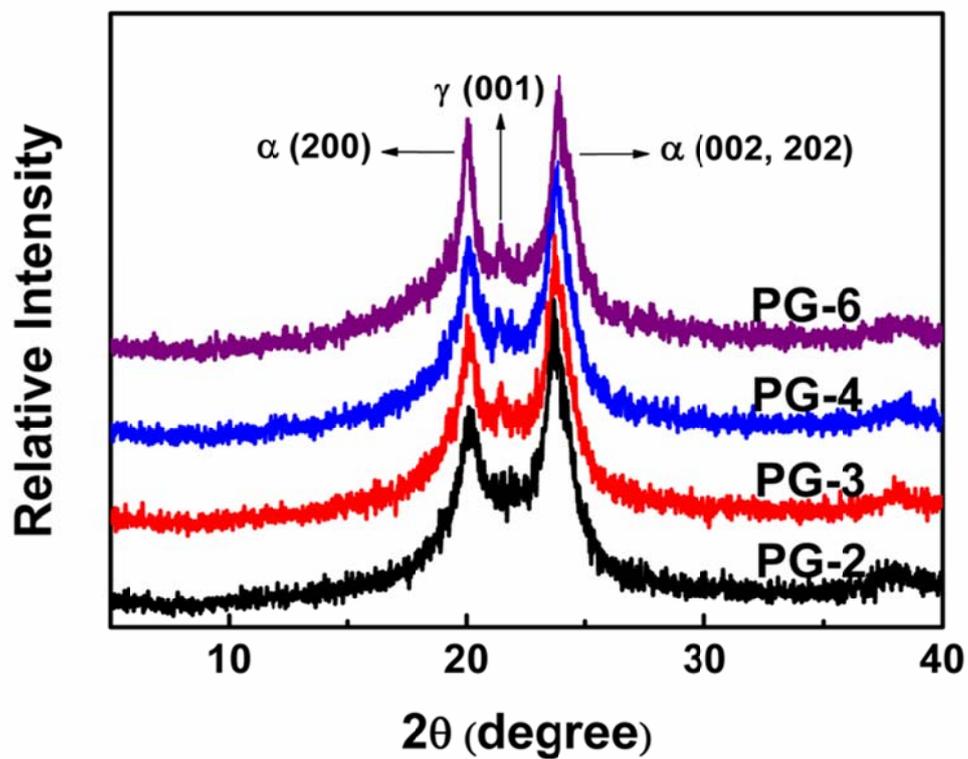


Fig. S3 XRD patterns of PG-2, PG-3, PG-4 and PG-6 nanocomposites.

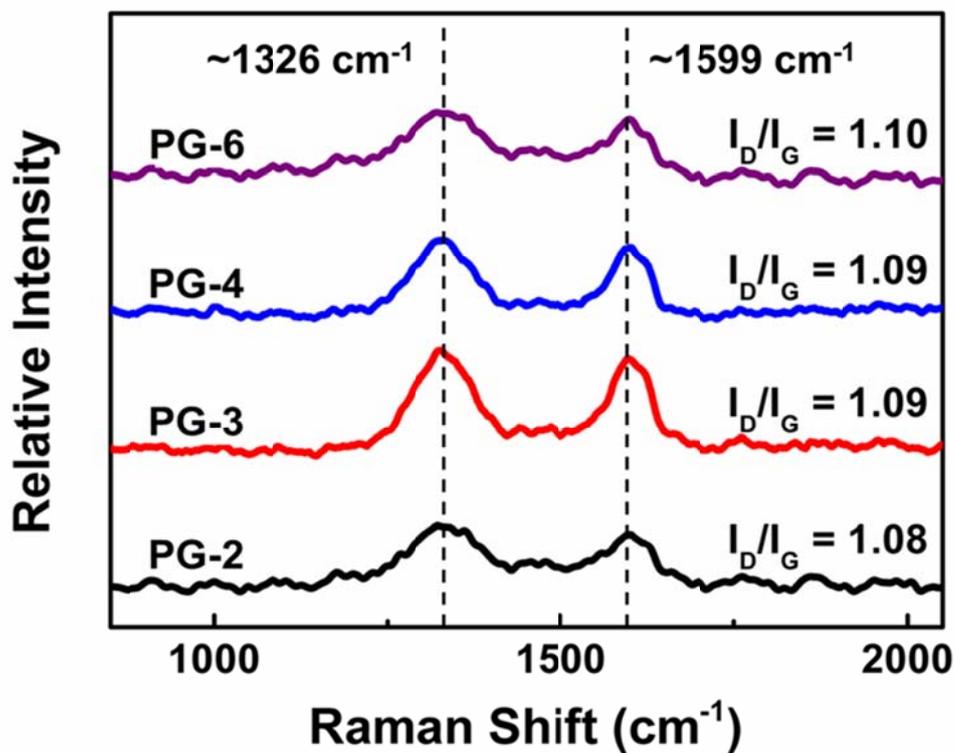


Fig. S4 Raman spectra of PG-2, PG-3, PG-4 and PG-6 nanocomposites.

Table S1 The structure and property of GO, RGO and PG nanocomposites

Samples	D peak (cm ⁻¹) ^a	G peak (cm ⁻¹) ^b	[I _D /I _G] ^c	Atomic percent (%) ^d			Atom ratio ^e	
				C	O	N	c(C/O)	c(N/C)
GO	1352	1594	0.81	65.3	33.2	0.8	1.967	0.012
RGO	1352	1591	0.95	86.9	11.0	2.1	7.900	0.009
PG-2	1321	1599	1.08	73.4	23.8	1.9	3.084	0.026
PG-3	1326	1596	1.09	73.6	21.8	4.4	3.376	0.060
PG-4	1333	1600	1.09	74.8	18.2	6.9	4.110	0.092
PG-5	1321	1599	1.09	73.4	18.2	8.4	4.033	0.114
PG-6	1323	1601	1.10	72.3	17.7	9.4	4.085	0.130

^{a, b, c} Obtained from Raman measurements. ^{d, e} Obtained from XPS measurements.

Table S2 The relevant data on PA6 chains length in PA6 and PG nanocomposites

Samples	η_{in} (dL·g ⁻¹) ^a	M_{η} (g·mol ⁻¹) ^b	[N] ^c	L_t (nm) ^d	T_p (nm) ^e
PA6	1.0170	28518	252	191.7	—
PG-2	0.3746	8437	74	56.3	1.8
PG-3	0.5381	13121	116	88.3	3.8
PG-4	0.6863	17653	156	118.7	5.4
PG-5	0.8032	21386	189	143.8	6.6
PG-6	0.8787	23863	211	160.5	7.4

^a Intrinsic viscosity of free PA6, obtained through Ubbelohde viscometer method at 25 °C in 85% formic acid solution². ^b Viscosity-average molecular weight, calculated from Mark-Houwink equation: $\eta_{in} = K[M_{\eta}]^{\alpha}$ (where $K = 2.26 \times 10^{-4}$ and $\alpha = 0.82$ at 25 °C).³ ^c Number of PA6 repeat unit, calculated from the equation: $N = (M_{\eta} - 18)/113$ (where 113 is the molecular weight of PA6 repeat unit, 18 is the molecular weight of -OH and -H). ^d Theoretical length of grafted PA6 chains, calculated from the equation: $L_t = NL_0$ (where L_0 is the length of PA6 repeat unit gained from the molecular dynamic simulation (Fig. S5)). ^e Practical thickness of grafted PA6 chains, obtained from the equation: $T_p = H_{PG} - H_{RGO}$ (where H_{PG} and H_{RGO} is the thickness of PA6 grafted RGO sheets (PG nanocomposites) and individual RGO sheets, respectively, collected from AFM measurements).

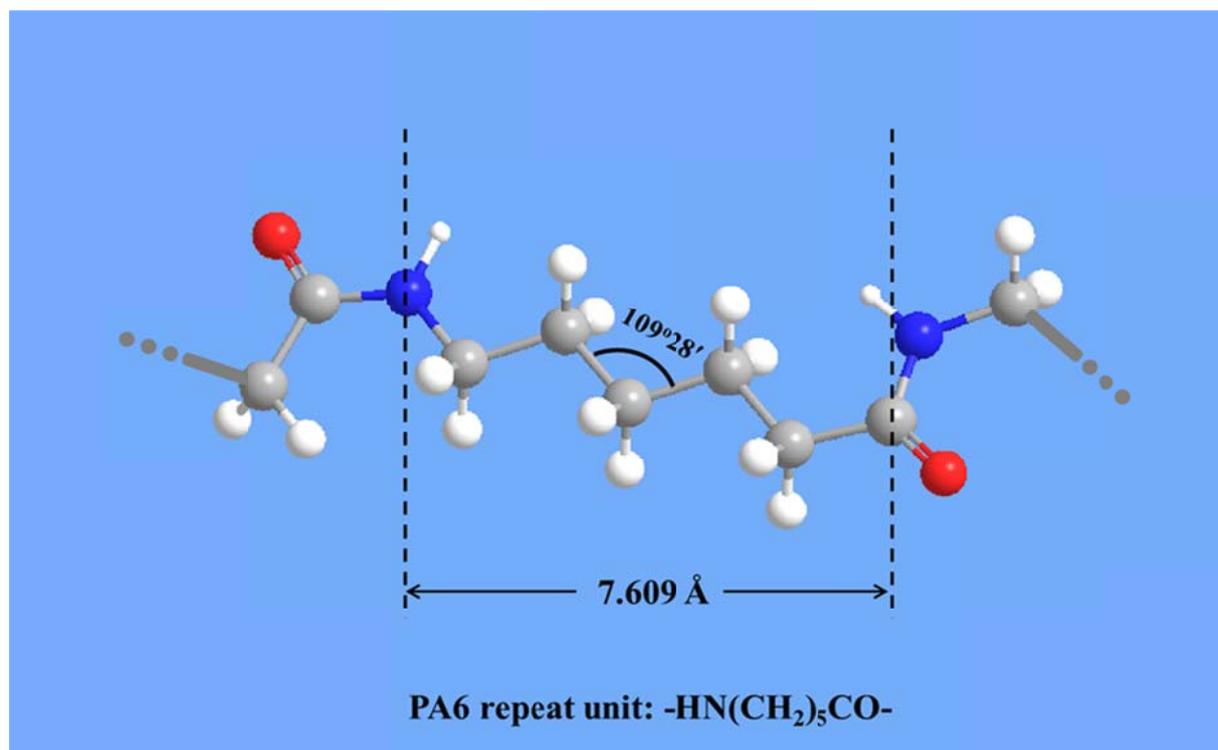


Fig. S5 The MD simulation of the length of a PA6 repeat unit. Where the gray, blue, red and white ball represents the carbon, nitrogen, oxygen and hydrogen atom, respectively.

Table S3 The thermal properties of PA6 and PG nanocomposites

Samples	Residue (wt%) ^a	T_m (°C) ^b	λ (W·m ⁻¹ ·K ⁻¹) ^c	$[\lambda/\lambda_0]$ ^d
PA6	0.79	220.7	0.253	1
PG-2	1.41	214.9	0.293	1.158
PG-3	2.69	215.3	0.282	1.115
PG-4	3.38	216.1	0.274	1.083
PG-5	3.95	216.3	0.266	1.051
PG-6	4.43	217.2	0.265	1.047

^a The residue carbon, obtained from the TGA measurements at 750 °C in N₂ atmospheres. ^b The melting temperature, collected from the DSC measurements in N₂ atmospheres. ^c The thermal conductivity, obtained from the Nanoflash measurements at 25 °C. ^d The normalized thermal conductivity, λ_0 is the λ of neat PA6.

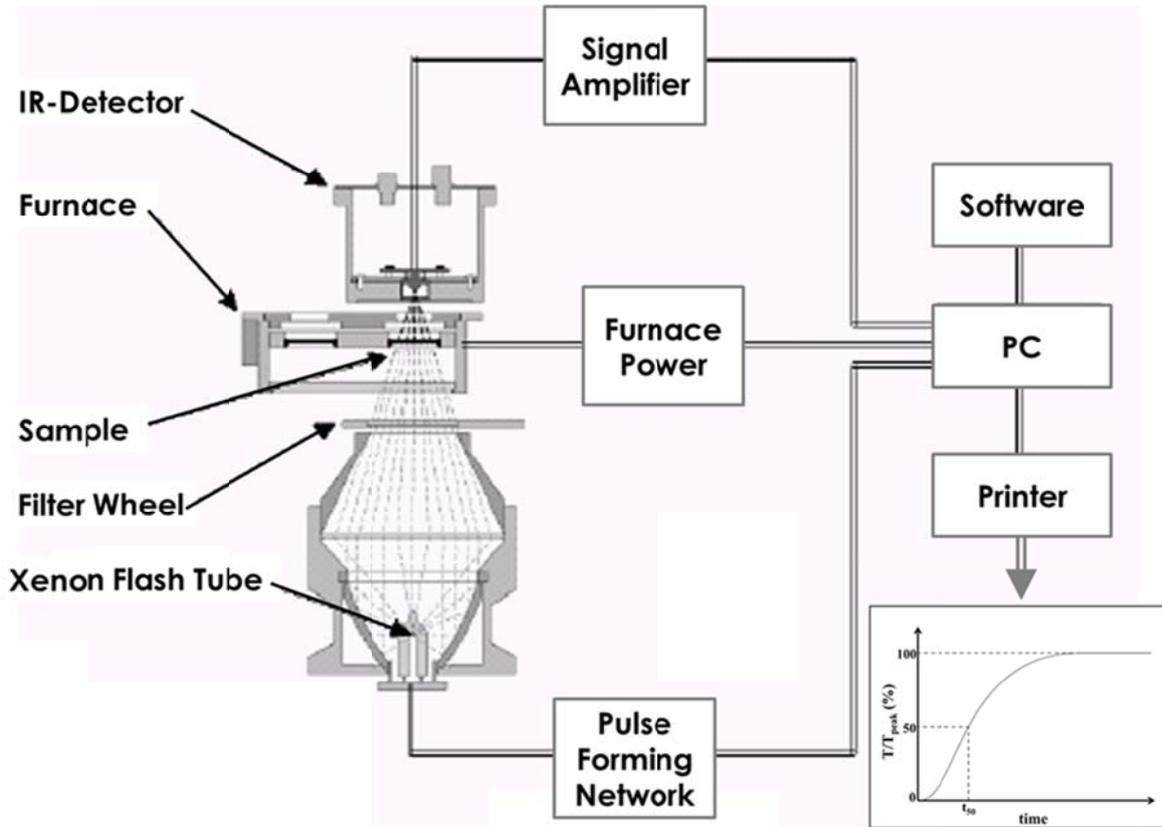


Fig. S6 Schematic diagram of PG nanocomposites λ by laser flash technique.

The thermal conductivity (λ) of PG nanocomposites were measured by the transient laser flash technique with the Netzsch LFA 447 Nanoflash at 25 °C in Fig. S6. The transient laser flash technique uses a xenon flash lamp to heat the sample from one side by producing shots with energy of 10 J/pulse. The temperature rise was determined at the back side with the nitrogen-cooled InSb IR detector. The output of the temperature detector was amplified and adjusted for the initial ambient conditions. The recorded temperature rise curve is the change in the sample temperature resulting from the firing of the flash lamp. The magnitude of the temperature rise and the amount of the light energy are not required for a diffusivity determination; only the shape of the curve is used in the analysis. From the analysis of the resulting relative temperature (T/T_{peak})-time curve, the thermal diffusivity (α) can be obtained.

For the specific heat (C_p) measurement, the magnitude of the temperature rise of an unknown sample was compared to that of the reference calibration sample. λ was calculated from the equation: $\lambda(T) = \alpha(T)C_p(T)\rho(T)$ (where ρ is the density of nanocomposite and can be obtained from the density measurement through a density balance) and recorded in Table S3d. The ρ of PG nanocomposites are similar with that of pure PA6 because of the relatively small additive amount of GO (1.5 wt%). To keep the good contact interface between the PG disks and the probe of Nanoflash, the surfaces of PG disks generally need to be polished with abrasive paper, though most of them are already flat after hot-pressing. Moreover, before the λ measurement, both sides of each PG disks need to be sprayed a layer of graphite to reduce the laser scattering by the initial surfaces of samples. In addition, the thermal conductivity of each temperature point needs to be measured for three times, and the average value is the final result. The laser flash technique has been generally known as the standard and the popular method for measuring thermal diffusivities of solid materials above room temperature.⁴

References

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