Supporting Information

Enhanced Thermal Conductive Property of Polyamide Composites by Low Mass Fraction of Covalently-Grafted Graphene Nanoribbons

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The detailed test procedure of thermal conductivity (λ) in the through-plane and in-plane directions

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. The thermal conductivity (λ) of the composites was measured by the transient laser flash technique with the Netzsch LFA 447 Nanoflash at 25 °C according to ASTM E1461 standard ("Compos. Sci. Technol. 2014; 90: 123", "Compos. Sci. Technol. 2014; 94: 147", "Compos. Sci. Technol. 2010; 70: 2176", "J. Mater. Sci. 2014; 49: 5256", "Carbon. 2012; 50 (14): 5052" and "Fiber. Polym. 2013; 14: 1317"). 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 was 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 were not required for a diffusivity determination; only the shape of the curve was 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 (Cp) measurement, the magnitude of the temperature rise of an unknown sample was compared to that of the reference calibration sample which we used pyrex in the direction of through-plane testing. λ was calculated from the equation: $\lambda(T) = \alpha(T)Cp(T)\rho(T)$ (where ρ is the density of the composites and can be obtained from the density measurement through a density balance). λ had been revised in the calculation process. The Cp of samples was a relative value which relative to the Cp of the reference calibration sample. To keep the good contact interface between the samples and the probe of Nanoflash, the surfaces of sample disks generally needed to be polished with abrasive

paper, though most of them were already flat after hot-pressing. Moreover, before the λ measurement, both sides of each disks needed 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 needed to be measured for at least three times, and the average value was the final result.

In this method, the samples with different shapes and sizes are necessary for testing the thermal conductive properties in in-plane and through-plane directions. For through-plane direction, the diameter and thickness were 12.7 and 1.0 mm, respectively. But for in plane direction, the diameter and thickness were 25 and 0.1 mm, respectively.

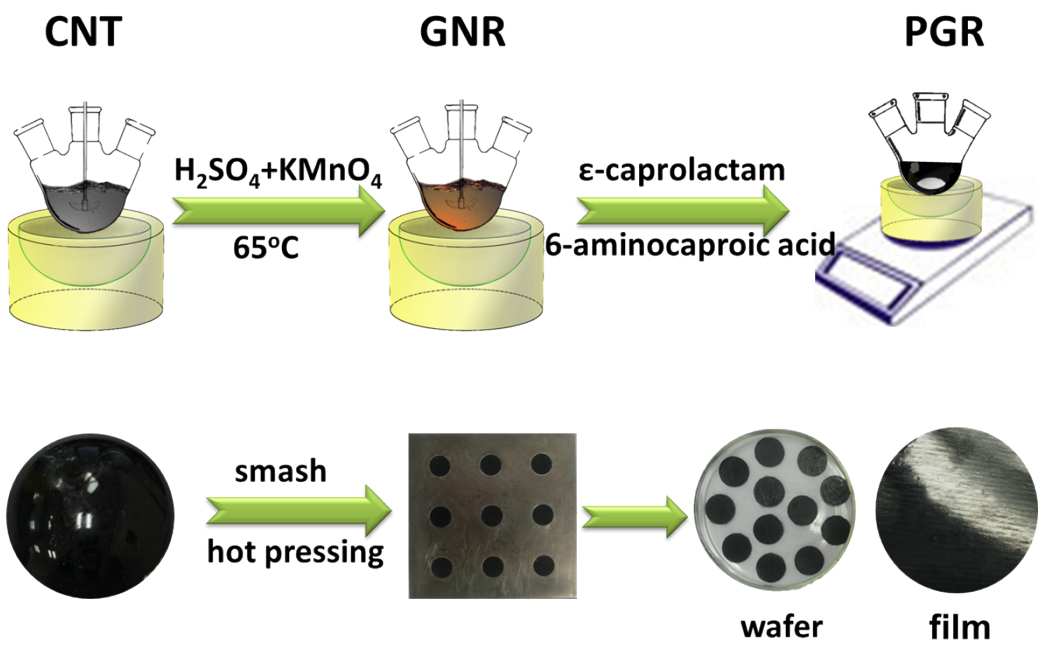

Fig. S1 Experimental diagram

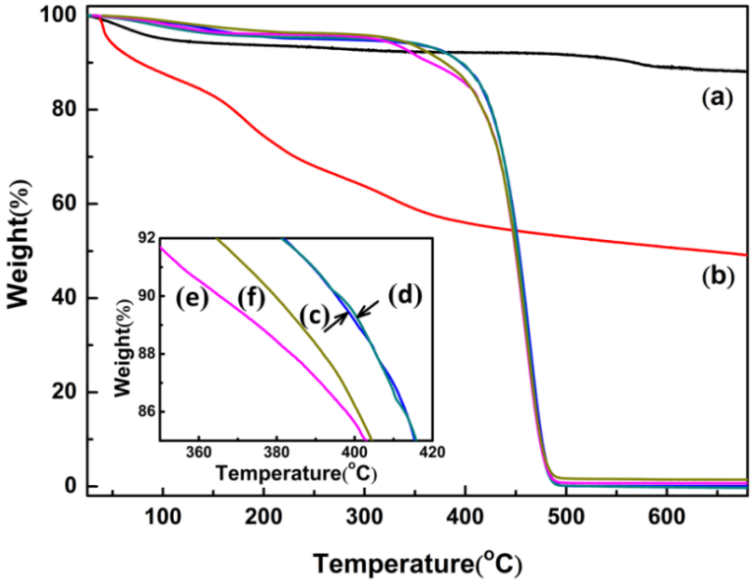

Fig. S2 TGA analysis of (a)CNT, (b)GNR, (c)PA6, (d)PGR-0.1, (e)PGR-0.5 and (f) PGR-1.0.

Thermogravimetric analysis and differential scanning calorimetry measurements were applied to study the thermal properties of the PGR composites. The TGA thermograms of pure PA6 and PGR composites were obtained under a nitrogen atmosphere. From Figure S2, there are more oxygen-containing functional groups on the surface and edges of GNR than CNT (weight loss of 50% and 10%, respectively). However there are little differences between TGA curves of PGR composites (PGR-0.1, PGR-0.5, PGR-1.0) and PA6, on account of the extremely low GNR wt.% including oxygen-containing groups have been grafted to the PA6 chains after thermal reduction progress at 250 °C.

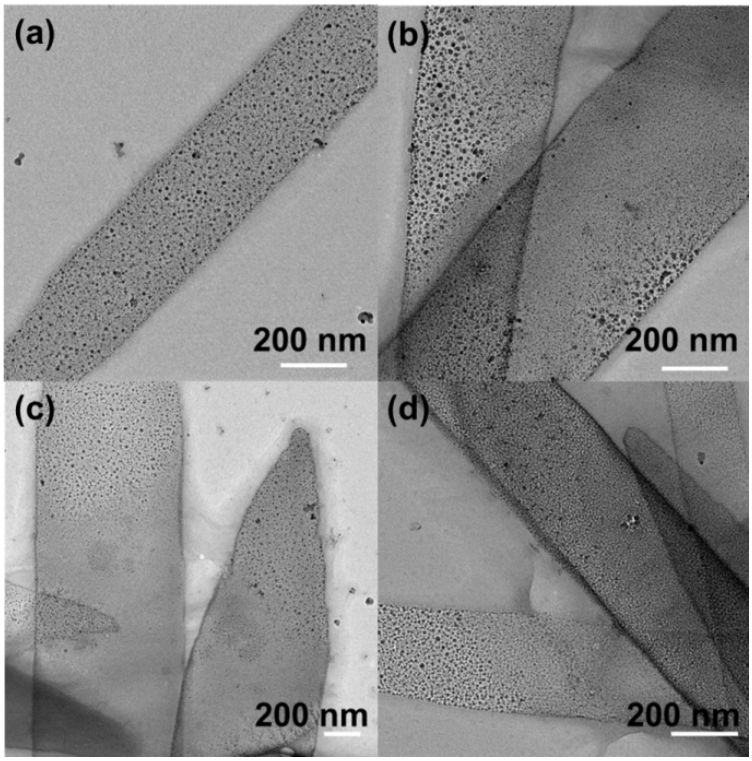

Fig. S3 TEM images of PGR-0.1.

PGR-0.1 samples were dissolved in formic acid with a concentration of 0.5 mg/mL and then sonicated for 5 min.

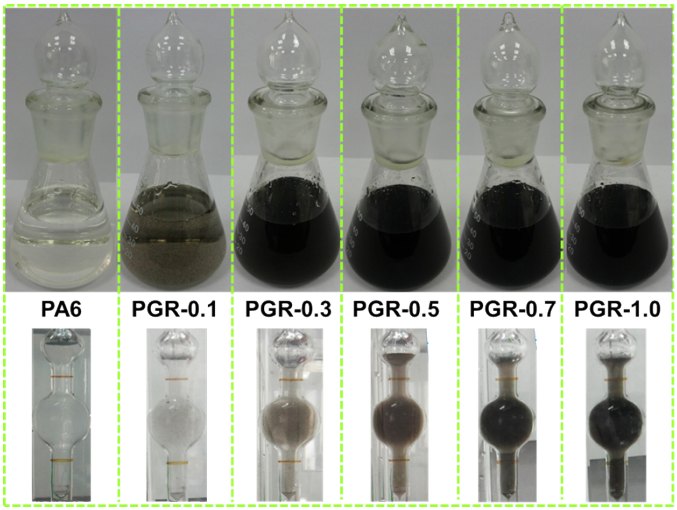

Fig. S4 Test for intrinsic viscosity and molecular weight for PA6 and PGR.

Sample	PA6	PGR-0.1	PGR-0.3	PGR-0.5	PGR-0.7	PGR-1.0
η_{in} (mL.g^{-1})	120.8	93.3	66.1	43.6	82.3	85.7

Table S1 The η_{in} of free PA6 in PGR composites.

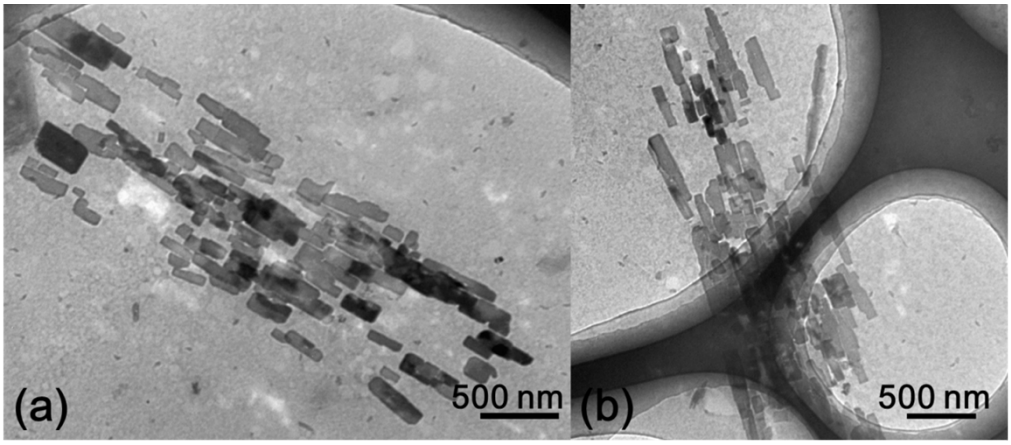

Fig. S5 TEM images of PGR-0.7.

PGR-0.7 samples were cutting into ultrathin sections, and loaded to a copper network.

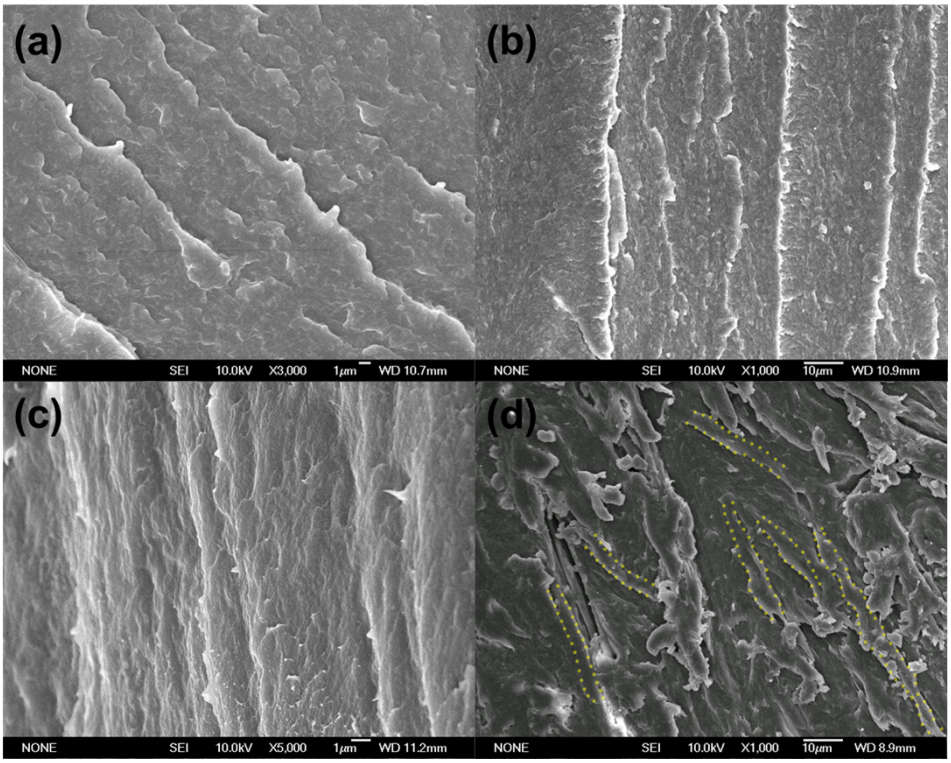

Fig. S6 SEM images of PGR-0.1 (a), PGR-0.5 (b), PGR-0.7 (c) and PGR-1.0 (d).

Samples were frozen in liquid nitrogen for 10 min and then clamped off with pliers to observe the fracture surface morphologies.

Table S2: Comprehensive comparison on the improvement in thermal conductivities of nanocomposites with different types of fillers

	Ref.	Matrix	Type of filler	TC of matrix λ_0 ($W \cdot m^{-1}K^{-1}$)	Thermal Conductivity			λ'/wt. %
					$\lambda_\perp$ ($W \cdot m^{-1}K^{-1}$)	Filler content	λ' (λ/λ_0)	
Thermal plastic polymer matrix	1	PA66	CF	0.3	0.44	20 wt.%	1.5	7.5
	2	PA66	CF	0.25	0.95	40 wt.%	3.8	9.5
					0.327	5 wt.%	1.3	26.2
	3	PA6	Graphite/CF	0.13	0.3	30 wt.% (no CF)	2.3	7.7
					2.05	60 wt.% (30wt.% CF)	15.8	26.3
	4	PA6	Copper plates	0.3	11.57	92.2 wt.%	38.6	41.9
	5	PA6	Glass fiber/CNT	0.041	0.058	2 wt.%	1.4	70
	6	PA66	Glass fiber/carbon black/graphite	0.25	0.7	30 wt.%	2.8	9.3
	7	PA66	Carbon black	0.3	1.142	30 wt.%	3.8	12.7
	8	PA6	Expandable Graphite	NA	1.965	15 wt.%	7	47
					32.33	70 wt.%	110	157
	9	PA66	Graphite	0.278	1.219	40 wt.%	4.4	10.9
			CF		1.034		3.7	9.3
	10	PA	OMMT	0.127	≈0.135	5 wt.%	1.1	21.3
	11	PA11	MWNT	NA	≈0.27	5 wt.%	NA	NA
	12	PA6	CF/Al_2O_3/Mg(OH)$_2$/graphite	0.27	2.1	50 wt.%	7.8	15.6
	13	PA6	LTEG	0.2939	21.05	60 wt.%	71.6	119.4
	14	PA6	CF	0.21	0.32	30 wt.%	1.5	5.1
	15	PA6	CF/BN	0.25	0.98	20 vol.%	3.9	19.6
	16	PA6	Fe_3O_4	0.22	0.93	47 vol.%	4.2	8.9
	17	PA11	CF	0.24	0.3	7.5 wt.%	1.3	16.7
	18	PA6	OMMT	0.28	0.45	20 wt.%	1.6	8
	19	PA6	MWCNT	0.33	0.42	2.1 wt.%	1.3	60.6
	20	PA6/PC(7/3)	Flake graphite	0.292	4.754	50 wt.%	16.3	32.6
	21	PA66/ polycarbonate	Carbon black	0.3	1.1	40 wt.%	3.7	9.2

	22	PAI	MWCNT	0.76	1.41	1.0 wt.%	1.9	190
	23	PS	MWCNT/C foam	0.12	0.32	20 wt.%	2.7	13.3
					0.17	1 wt.%	1.4	141.7
	24	PS	SWCNTs	0.133	0.62	30 wt.%	4.7	15.6
					0.36	5 wt.%	2.7	54.1
	25	PS	MWNT-g-SMA	0.18	0.89	35 vol.%	4.9	NA
					≈0.2	2.5 vol.%	1.1	NA
	26	PC	CNT	0.218	0.306	8 wt.%	1.4	17.6
					0.232	2 wt.%	1.1	53.2
	27	PC	GNP	0.215	0.489	15 wt.%	2.3	15.2
					0.251	2 wt.%	1.2	58.4
	28	PC	u-MWCNT	0.2	0.28	2.5 wt.%	1.4	56
	29	HDPE	Branch-structured nickel	0.468	1.99	30 vol.%	4.3	NA
	30	Bio-based polyester	Graphene oxide	0.19	0.542	1.45vol.%	2.9	NA
	31	PP	Graphite	~0.22	≈0.5	20 wt.%	2.3	11.4
					≈0.2	2 wt.%	0.9	45.5
	32	PP	Synthetic graphite	0.20	6.042	80 wt.%	30.2	37.8
			CNT		0.467	15 wt.%	2.3	15.6
	33	PP	CB/CNT/SG	0.206	0.36	15 wt.%	1.7	11.4
					0.5	15 wt.%	2.4	15.9
					9.47	80 wt.%	45.1	56.4
	34	PP	SG/CB/CNT	0.21	9.47	80 wt.%	45.1	56.4
					0.36	15 wt.%	1.7	11.4
					0.5	15 wt.%	2.4	15.9
	35	PP	GNP	~0.25	1.2	25 vol.%	4.8	19.2
	36	EVA	ZnO	0.25	≈0.78	27 vol.%	3.1	NA
	37	LCP	Graphite	0.4	28.3	70 wt.%	70.8	101.1
	38	LCP	Carbon black	1	2.06	15 wt.%	2.1	13.7
			Synthetic graphite		4.33	40 wt.%	4.3	10.8
			CF		2.49	60 wt.%	2.5	4.2
	39	LCP	Graphite	0.22	2.624	75 wt.%	11.9	15.9
	40	LCP	Carbon black	0.22	2.63	75 wt.%	12	15.9
	41	polysiloxane	BN nanosheets	0.086	0.127	5 wt.%	1.5	30
Our previous		PA6	Graphene oxide	0.196	0.416	10 wt.%	2.1	21.2

work[42]								
This work		**PA6**	**GNR**	**0.21**	**0.41**	**0.5 wt.%**	**1.952**	**390.5 ($\lambda_{\perp}$)**
				1.83	**4.85**		**2.654**	**530.8 ($\lambda_{//}$)**
Thermal set polymer matrix	43	epoxy	GNPs	0.195	5.864	20 wt.%	28	140
					0.303	2 wt.%	1.6	77.7
	44	epoxy	SiC-HBP	0.167	≈0.334	30 wt.%	2	6.7
	45	epoxy	Al_2O_3	0.236	0.4	20 wt.%	1.7	8.5
	46	epoxy	BN	0.258	0.265	5 wt.%	1.03	20.5
			BN-ODA		0.31	5 wt.%	1.2	24
			BN-HBP		0.329	5 wt.%	1.28	25.5
	47	epoxy	BN and Al_2O_3	0.188	0.808	26.5 vol.%	4.3	16.2
	48	epoxy	GNP	~0.212	0.72	2.7 vol.%	3.4	NA
					0.35	0.5 vol.%	1.7	NA
	49	epoxy	MWCNT	0.242	0.251	0.3 wt.%	1	345.7
	50	epoxy	MWCNT	~0.12	≈0.25	1.5 wt.%	2.1	138.9
					0.21	0.5 wt.%	1.8	350
	51	epoxy	Al_2O_3-CNTs	~0.17	0.4	0.75 wt.% (CNT: 0.15 wt.%)	2.4	320
	52	epoxy	GNP-SWCNT	-	1.75	10 wt.%	~8.0	80
	53	S160	Aligned CNT	0.56	1.21	0.3 vol.%	2.2	733.3
	54	FKM	Aligned CNT	0.21	23.3	13.2 wt.%	109.9	832.6

*LTEG, PC, CF, SMA, GNP, S160, and FKM represent: low temperature of expandable graphite, polycarbonate, carbon fiber, poly(styrene-co-maleic anhydride), graphite nanoplatelet, silicone elastomer (Sylard 160, Dow Corning) , and fluorinated rubber, respectively.

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