Research Article

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Polypropylene/graphene nanoplatelets nanocomposites with high conductivity via solid-state shear mixing

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Abstract: The research on facile, low-cost, and green process for the uniform dispersion of graphene nanoplatelets

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(GNPs) into polymer matrix has always been a considerable challenge in practical applications. The Van der Waals interaction between graphene layers can easily cause aggregation of the nanofillers. Here, we propose a new method to solve this problem by involving solid-state shear mixing to obtain a well-dispersed nanocomposite. The comprehensive properties of nanocomposite, including antistatic properties, mechanical properties, and thermal stability, can be significantly enhanced by this method. The surface resistivity of the nanocomposite can be up to $2.4 \times 10^7 \Omega \text{ sq}^{-1}$ under 1 wt% content of GNPs, which is significantly better than the value obtained by conventional melting compounding and meets the required standard of less than $3 \times 10^8 \Omega \text{ sq}^{-1}$ for actual application antistatic materials. The impact strength of the nanocomposite increased by 120.8% when compared with neat PP. At the same time, the heat distortion temperature and initial decomposition temperature of the nanocomposite with only 0.5 wt% content of GNPs are improved by 11.7°C and 110°C, respectively. In addition, GNPs is a heterogeneous nucleating agent that leads PP to emerge β crystal form. This study provides an effective and practical reference for the broad-scale industrial preparation of polymer-based graphene nanocomposites.

Keywords: graphene nanoplatelets, polypropylene, nanocomposites, solid-state shear mixing, high conductivity

1 Introduction

Graphene is a two-dimensional material with single-atom thickness connected by sp^2 -hybridized carbon atoms (1,2). Owing to the extremely high specific surface area, carrier mobility, thermal conductivity, and excellent mechanical strength, it is considered to be an ideal nanofiller for strengthening polymer and has also received considerable attention in the field of nanocomposites (3–11). However, same as other added nanofillers, the dispersion of graphene

nanoplatelets (GNPs) is the main problem in the preparation of composite materials (12–15), and this directly affects the performance of composites.

The dispersion of GNPs is primarily determined by the preparation method of the composites (15–18). The common methods mainly include *in situ* polymerization (17), solution compounding (16,18), and melt compounding (15). *In situ* polymerization is the best preparation method with homogeneous dispersion at present, but the polymerization reaction is easily affected by the reaction conditions and side reactions (17), so it is difficult to control. The solution compounding requires the use of large amounts of organic solvents during the processing, which is not suitable for environmental protection and industrial production. As for melt compounding, GNP is mainly dispersed in the PP melt by mechanical equipment, it is an economical, environment-friendly, efficient method and is most suitable for industrialized manufacture (13,14,19). However, due to the inevitable agglomeration phenomenon of GNP in the processing, it cannot achieve uniform dispersion. Therefore, avoiding GNP agglomeration, dispersing it in the polymer matrix effectively, and reducing the use of organic solvents remain a major challenge in achieving green industrial preparation.

When the matrix material is a non-polar polymer such as polyolefin, it is also necessary to consider the adverse effects of the poor interface compatibility between graphene and the matrix on the uniform dispersion of GNPs in the matrix (13,14,20). Polypropylene (PP) is one of the most common polyolefins, which has been widely used due to its low cost, easy processing and molding, and balanced mechanical properties (8,21–24). To promote the dispersion of GNPs in PP matrix, adding compatibilizer or functional modification of graphene in the preparation process are two commonly used methods. For example, using PP-g-MA (25) as a compatibilizer has been found to improve the compatibility between GNP and the PP matrix, to promote the dispersion of graphene in the PP matrix. In addition, surface functionalization of graphene or its derivatives is also an alternative method to improve its dispersion in the matrix. Graphene oxide (GO), a class of graphene derivative, is rich in functional groups, which can be used for modification. It has been reported to improve the interaction between GO and PP matrix by grafting isocyanates (18), silane coupling agents (14), and polymer chains (13) at the functional sites to prevent agglomeration and effectively promote dispersion. Nevertheless, the volatilization and post-treatment of a large number of organic solvents used in the graphene modification process are likely to cause safety and environmental problems, and the cost is also relatively high. Not only that, the conductivity and

mechanical properties of graphene after oxidation and reduction will be also lost to varying degrees (26). Therefore, it is significant to explore a green, simple, and low-cost method for preparing PP/GNP nanocomposites. It is reported that the mechanical shearing force provided by solid-state shear pulverization (SSSP) can overcome the above-mentioned problems and achieve uniform dispersion of nano-fillers such as lignocellulose nanofibers (27) and carbon nanotubes (28) in the PP matrix. Therefore, solid-state shear mixing may be a practical means for dispersing GNPs in the PP matrix.

In this work, a simple and environmental-friendly strategy of solid-state shear mixing was adopted to prepare PP/GNP nanocomposites with uniform dispersion. At the same time, the antistatic properties, mechanical properties, and thermal stability of the nanocomposites have also been improved to a certain extent. Besides, the relationship between the structure and performance of the nanocomposites and their related mechanisms were also discussed. This research will provide an effective and convenient way for large-scale industrial polymer-based graphene nanocomposites production.

2 Experimental

2.1 Materials

PP powder (PP-H, GD, 040) with melt flow rate (MFR) of 4 ± 2.0 g/10 min was purchased from Maoming Petrochemical Co., Ltd. (China). *N*-Methyl-2-pyrrolidone (NMP) was purchased from J & K Chemical Co., Ltd. (China). Graphene nanoplatelets with an oxygen content of 1 wt% were purchased from Qinquangdao Zhongke Hanqi Technology Co., Ltd. (China). All chemicals were used directly without purification.

2.2 Synthesis method of PP/GNP nanocomposites

Nanocomposites with different GNP contents were prepared. First, the PP powder, GNP, and a small amount of NMP were manually mixed together by stirring. The blend was further mixed with torque rheometer (Haake polylab OS) at 90°C with a torque of 15–20 N m for 1 h to achieve uniform dispersion of GNPs under the shearing force (Scheme 1). The sheared product was then dried in a vacuum oven at 50°C for 12 h to remove NMP thoroughly. A total of six samples were prepared and named as shown in Table 1.

To further disperse the GNPs in the PP matrix to facilitate storage and transportation, the above mixture was melt-mixed in a twin-screw extruder at 195°C and a screw

Scheme 1: Schematic illustration of preparation of PP/GNP nanocomposites.

speed of 90 rpm. Dumbbell-shaped test samples were injection molded with injection molding machine (Haake MiniJet Pro) at 205°C with a pressure of 70 MPa maintained for 15 s. The square plate samples (100 × 100 × 2 mm) were prepared by the hot press at 175°C and 15 MPa for 30 min.

2.3 Characterization

Section-cross morphology of the nanocomposites and surface morphology of GNPs were observed by scanning electron microscope SEM (S-4800, Hitachi) at 10 kV acceleration voltage. The samples were broken brittly in liquid nitrogen and subjected to gold sputtering treatment.

The dimensions of pure GNP and its products after solid shear mixing were analyzed by AFM (Multimode 8, Bruker) in which the samples (0.005 wt% suspensions of ethanol) were deposited on neat mica to dry.

The crystal structure was analyzed by X-ray diffractometer XRD (D8 focus, Bruker) with a Cu K α radiation source ($\lambda = 0.154$ nm), and the 2θ scan range was from 5° to 80° with the scanning speed of 0.1 s/step.

Differential scanning calorimetric (DSC) analysis was done by NETZSCH 200-F3 under N₂ atmosphere. Samples were heated from 30°C to 200°C and held at that temperature for 2 min to eliminate the thermal history. Then, the temperature of each sample was reduced to 30°C and kept constant for 2 min. The samples were later re-heated to 200°C while recording the cooling curve and the reheating curve. The mass of each sample was about 10 mg, and the heating and cooling rates were 10°C/min in all situations (16).

The electrical resistivity was measured by a megohmmeter (Model 800, ACL) at 25°C. Each sample was measured five times at different positions, and the measurement results were averaged.

Tensile test was carried out according to GB/T 1040-2006 with universal mechanics tester (5966, Instron) at a cross-head moving speed of 25 mm/min. Five specimens of each group were tested in parallel to obtain the mean value. The impact strength of samples (type V notch and 80 × 10 × 4 mm) was carried out according to ISO 179-1:2000 with a material testing machine (XJ-300). Five specimens of each group were tested in parallel to obtain the mean value.

Heat distortion temperature (HDT) was observed by heat distortion tester (HDV/V-3116, JJ-Test) according to GB/T1634.2-2004. Each sample was heated from 20°C at a rate of 2°C/min until the test specimen deflected 0.34 mm. The applied stress of the sample was 0.45 MPa, and the test was carried out in silicone oil. Three specimens of each group were tested in parallel to obtain the mean value.

Thermogravimetry of samples was examined by TGA (Q 50) under N₂ atmosphere. The 3–5 mg sample used was heated at 10°C/min from 30°C to 700°C (13).

3 Results and discussion

3.1 Morphology of PP/GNP nanocomposites

The dispersion of nanofillers in the matrix affects almost all properties of composites. The dispersion efficiency was evaluated by SEM analysis. As shown in Figure 1a, the surface of neat PP is relatively smooth. Original GNPs are stacked on each other in Figure 1b and i of the AFM image; it is found that its radial size and thickness are about 1–2 μ m and 35 nm, respectively. As shown in Figure 1c and d, flake-like GNP is well dispersed in the entire PP matrix without aggregation almost at lower content such

Table 1: Name and composition of samples

Sample name	PP (g)	GNP (g)	NMP (g)	Content of GNP (wt%)
PP	100	0.0	0.0	0.0
PP/G0.5	99.5	0.5	10.0	0.5
PP/G1.0	99.0	1.0	10.0	1.0
PP/G1.5	98.5	1.5	10.0	1.5
PP/G2.5	97.5	2.5	10.0	2.5
PP/G3.5	96.5	3.5	10.0	3.5

*Note: G is short for GNP.

as 0.5 and 1 wt%. Compared with Figure 1b, it is clear that the shear stress of the solid-state mixing during the preparation is beneficial for the dispersion of GNPs. However, GNPs cannot be sufficiently dispersed in the PP matrix by twin-screw compounding alone (Figure A1 in Appendix). From Figure 1j, it is found that the thickness of GNPs in the product (1.0 wt%) after solid-state shear mixing is about 35 nm, which is roughly the same as the thickness of the original GNPs. EDS was used to further analyze the dispersal of GNPs in the nanocomposites (Figure 1g and h) revealing the distribution of carbon and oxygen. Oxygen is evenly distributed on the entire sample surface, because the oxygen only comes from GNPs (oxygen content is about 1 wt%), which indicates that GNP is dispersed in the composite equally. However, due to the Van der Waals interaction between graphene layers, it is easy to cause agglomeration when GNP content is too high. As shown in Figure 1e, although GNP has good overall dispersibility under a content of 3.5 wt%, it partially agglomerated, weakening the dispersion effect.

Since PP is a semi-crystalline polymer, the crystalline behavior of PP including crystal type and crystallinity significantly affects the mechanical properties of the nanocomposites (29). The XRD patterns of PP and PP/GNP nanocomposites of different contents of GNP are shown in

Figure 2. For neat PP, the peaks at approximately 14.2° , 17.0° , 18.7° , 21.9° , and 25.6° corresponding to the (110), (040), (130), (041), and (060) crystal plane, respectively, of α crystal forms of PP (19,30). For nanocomposites, a new peak corresponding to the (300) plane of β crystal form is exhibited at about $2\theta = 16.2^\circ$ (19). This indicates that the addition of GNP changes the crystal form of PP, and GNP is a heterogeneous nucleating agent of β crystal form beneficial to enhancing higher impact strength and toughness of nanocomposites (30), and it will be described later.

According to the method proposed by Turner-Jones (19,31), the relative content of β crystal form K_β^* was calculated using Eq. 1:

$$K_\beta^* = \frac{I_{\beta(300)}}{I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)} + I_{\alpha(041)} + I_{\alpha(060)} + I_{\beta(300)}} \times 100\%, \quad (1)$$

where I is the intensity of the diffraction peaks of α (110), α (040), α (130), α (041), α (060), and β (300) crystal plane. As listed in Table 2, K_β^* of the samples increases with the improvement of GNP contents until the GNP content reaches 1.0 wt%. Owing to a small increase of GNP when it has low content can provide more nucleation sites so that induces more β crystal form. When the GNP content is too high, the nucleation is saturated, that

Figure 1: SEM images of neat PP (a), GNP (b), PP/G0.5 (c), PP/G1.0 (d), and PP/G3.5 (e). High magnification SEM images of PP/G1.0 (f). EDS mapping of C and O of PP/G1.0 (g and h). AFM images and height profile along the white line of GNP (i) and PP/G1.0 (j).

Figure 2: XRD patterns of neat PP and PP/GNP nanocomposites.

is, not enough PP polymer chains can be oriented and arranged along all of the graphene (30), so K_{β}^* basically remains unchanged.

3.2 Crystallization behavior of PP/GNP nanocomposites

DSC was used to explore the effect of the addition of GNP on the crystallization behavior of the PP matrix. Figure 3a and b is the melting curve and non-isothermal

crystallization curve, respectively. The DSC test parameters of neat PP and PP/GNP nanocomposites including melting enthalpy ΔH_m , crystallization enthalpy ΔH_c , melting point T_m , crystallization temperature T_c , and crystallinity X_c are summarized in Table 3. The crystallinity X_c was calculated using Eq. 2:

$$X_c = \frac{\Delta H_m}{\Delta H_0 F_{PP}}, \quad (2)$$

where ΔH_0 is the melting enthalpy of 100% crystalline PP and F_{PP} is the mass fraction of PP in nanocomposites (16).

It can be seen from melting thermogram (Figure 3a) that the addition of GNP has no obvious effect on T_m of the nanocomposites when compared with neat PP. From Figure 3b, it is obviously demonstrated that the T_c increases with the increase of GNP content, that is, the crystallization of PP starts at a higher temperature. This indicates that the crystallization of PP is facilitated by GNP. This is because the surface of GNP serves as sites for PP crystallization, and GNP acts as a heterogeneous nucleating agent. Although GNP has been shown to promote the crystallinity of PP and induce the formation of uncommon crystals such as β crystal form (Figure 2 and Table 2), it has little impact on the X_c of PP (Table 3). This indicates that the change in mechanical properties of nanocomposites is due to the transform of crystal form and the enhancement of nanofiller GNP, rather than by changing the crystallinity of the matrix.

Table 2: The relative content of β crystal form of samples

Samples	PP	PP/G0.5	PP/G1.0	PP/G1.5	PP/G2.5	PP/G3.5
K_{β}^* (%)	0	22.3	28.2	30.2	30.3	29.5

Figure 3: Melting (a) and crystallization (b) thermograms of neat PP and PP/GNP nanocomposites.

Table 3: DSC test parameters of neat PP and PP/GNP nanocomposites

Samples	ΔH_c (J/g)	ΔH_m (J/g)	T_m (°C)	T_c (°C)	X_c (%)
PP	-83.51	80.17	173.2	118.6	38.4
PP/G0.5	-80.32	81.36	175.1	128.0	39.1
PP/G1.0	-75.16	79.41	170.7	127.4	38.4
PP/G1.5	-83.80	81.05	175.5	128.9	38.6
PP/G2.5	-75.77	74.95	170.8	127.0	36.8
PP/G3.5	-79.52	78.30	175.2	128.6	38.8

3.3 Antistatic performance of PP/GNP nanocomposites

Surface resistivity is one of the commonly used indicators to characterize the antistatic performance of materials (32). The test results displayed in Figure 4 show that the increase in GNP content results in a downward trend of surface resistivity of the nanocomposites. This indicates that the nanofiller GNP can improve the conductive capacity of nanocomposites. The surface resistivity of the composite was $5.4 \times 10^{11} \Omega \text{ sq}^{-1}$ at 0.5 wt% GNP content. The surface resistivity of the nanocomposite can be up to $2.4 \times 10^7 \Omega \text{ sq}^{-1}$ under 1 wt% content of GNP, which meets the requirement that is less than $3.0 \times 10^8 \Omega \text{ sq}^{-1}$ for practical application of antistatic materials (32,33). However, as shown in Figure A2, the surface resistivity and volume resistivity of the composites prepared by twin-screw compounding under the same GNP content are relatively large (more than 10^{12}), which illustrates the necessity and superiority of the solid-state shear mixing preparation method. Besides, it can be concluded that the conductive percolation threshold is in the range of 1 wt%.

This is due to the formation of conductive paths by increasing GNP content in the nanocomposites (34). Through the EDS mapping of Figure 1g and h, it is observed clearly that the oxygen is uniformly dispersed in the PP matrix and touched each other, illustrating that the GNP forms a uniform and continuous conductive paths inside the matrix so that the surface resistivity of the nanocomposites drops sharply. The conductive percolation threshold of the composites prepared by twin-screw compounding is between 1.5 and 2.5 wt% (Figure A2). It is worth noting that the percolation threshold value of 1 wt% obtained by this preparation method can be matched with the value obtained by mixing solutions commonly used in laboratories (35,36). However, this instrument avoids the cost, post-treatment, and environmental pollution caused by a large amount of organic solvent. Hence, it displays a broader industrial application prospect. The conductivity obtained by different methods will be compared later (Table 6).

3.4 Mechanical properties of PP/GNP nanocomposites

Mechanical properties are critical to the practical application of antistatic materials (32). The impact strength of nanocomposites with different GNP contents is shown in Figure 5. The impact strength of the nanocomposites reaches a maximum value of 10.6 kJ m^{-2} at 1.0 wt% content of GNP. The impact strength of the nanocomposite increased by 120.8% when compared with neat PP (4.8 kJ m^{-2}), demonstrating the significant toughening ability of GNP. This is because it acts as a nucleating

Figure 4: Surface resistivity (a) and volume resistivity (b) of PP/GNP nanocomposites.

Figure 5: Impact strength of neat PP and PP/GNP nanocomposites.

agent for PP to produce β crystal form with higher impact strength and toughness as seen in the XRD patterns (Figure 2) (30). In addition, owing to the high aspect ratio and high mechanical strength of GNP and its uniform dispersion, it withstands part of the stress and hinders the spread and extension of cracks in the matrix. However, when the content of GNP is higher, it is impossible to avoid aggregation that generates stress concentration and weakens the enhancement effect under the applied stress (14). But until the content is increased to 3.5 wt%, the impact strength of the nanocomposites is still greater than that of neat PP. However, from Figure A3, the impact strength of the composites prepared by two-screw compounding decreases with the increase of GNP content, this is because of its poor dispersion effect, which can lead to defects in GNP. Hence, it shows the necessity and superiority of the preparation method of solid-state shear mixing.

The tensile performance test results of neat PP and its nanocomposites are listed in Table 4. The rigidity of nanocomposites is more strong than neat PP. Even with GNP content as low as 0.5 wt%, the yield strength and Young's modulus of the nanocomposite are 37.3 and

Table 4: Tensile mechanical properties of neat PP and PP/GNP nanocomposites

Samples	Yield strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PP	32.8 ± 0.9	945.3 ± 52.5	1004.5 ± 33.7
PP/G0.5	37.3 ± 0.4	1184.3 ± 11.0	534.8 ± 21.4
PP/G1.0	39.1 ± 0.1	1207.2 ± 16.4	554.0 ± 10.1
PP/G1.5	41.6 ± 0.4	1432.2 ± 41.3	145.1 ± 30.2
PP/G2.5	42.1 ± 0.7	1618.8 ± 52.7	153.5 ± 27.7
PP/G3.5	42.6 ± 0.3	1669.9 ± 24.2	29.9 ± 0.5

1,184 MPa, which is an improvement of 13.7% and 25.3%, respectively, when compared with neat PP. This is due to the high mechanical strength of nanofiller GNP, its uniform dispersion, and powerful interfacial interaction between GNP and PP matrix (13,14,32). Besides, the molecular arrangement of PP changes greatly during the stretching process, especially near the yield point. The move and orientation of polymer chains are hindered by GNP under applied stress (32). The barrier effect of GNP becomes stronger with the increases of GNP content so that the nanocomposites show stronger rigidity. In addition to the above factors, the large decrease of the elongation at break of nanocomposites is also related to the Van der Waals interaction between graphene layers, which is very easy to form aggregation at high levels of GNP content. Combined with the SEM images (Figure 1e), it is found that partial agglomerations are formed by GNP under high content of 3.5 wt%, which brings structural defects to the nanocomposite, resulting in stress concentration so that elongation at break reduces to 29.9% (29). Nevertheless, as shown in Table A2, the yield strength and Young's modulus of the PP/GNP composites prepared by two-screw compounding cannot be effectively enhanced. This is due to its poor dispersion effect, which is also proved by the SEM images (Figure A1).

3.5 Thermal stability of PP/GNP nanocomposites

The heat distortion temperature (HDT) represents the maximum temperature that a material can withstand under normal mechanical behavior (13). As shown in Figure 6, the HDT of nanocomposites improves with the

Figure 6: Heat distortion temperature of neat PP and PP/GNP nanocomposites.

Figure 7: TGA (a) and DTG (b) curves of neat PP and PP/GNP nanocomposites under N_2 atmosphere.

increase of GNP content. For the content as low as 0.5 wt%, the HDT of the nanocomposites is 95.9°C, which is a significant increase of 11.7°C when compared with 84.2°C of neat PP. This proves that a small amount of GNP can extend the temperature range of the nanocomposites, and it is a benefit to actual application value. This is due to many positive factors, such as the inherent high rigidity of GNP, its uniform dispersion, and the strong interfacial interaction between GNP and PP matrix (37).

Nanocomposites also need steady thermal stability to cope with different usage scenarios. Figure 7a and b is the TGA curve and the differential thermogravimetric (DTG) curve of samples. Through Figure 7a, it is clearly found that the thermal stability of nanocomposites is better than that of neat PP, and thermal stability of the nanocomposites increased with an increase of GNP load. The initial decomposition temperature T_{in} (the temperature when the sample mass loss is 5%), the maximum weight loss rate temperature T_{max} , the maximum weight loss rate MLR_{max} , and the decomposition temperature range ΔT_{dr}

are summarized in Table 5. For the content as low as 0.5 wt%, the T_{in} and T_{max} of the composite are 426°C and 458°C, which are 110°C and 36°C higher than that of neat PP. It proves that a small amount of GNP improves the thermal stability of nanocomposites. The improvement of the thermal stability is mainly caused by several positive factors of nanofiller GNP. It leads to a tortuous mass transfer barrier preventing the evaporation of volatile degradation products (11). In the meantime, its huge surface area can absorb free radicals generated by the thermal decomposition of PP (38). ΔT_{dr} is narrowed by increasing the GNP content. This may be due to the high thermal conductivity of GNP and the strong interfacial interaction between it and matrix (13).

Finally, we compared the preparation processing with other methods (Table 6). Compared with melt compounding, the electrical conductivity of nanocomposites prepared by solid shear mixing with the same GNP addition (1.0 wt%) is obviously superior (14,35,39,41). And the electrical conductivity acquired by this preparation method is comparable to that obtained by *in situ* polymerization and solution mixing, which are recognized by researchers as a good dispersive preparation method of graphene (17,40). But compared with both of them, our preparation method has the advantages of high production efficiency and environmental friendliness. In addition, the improved efficiency of this preparation method on impact strength, yield strength, and Young's modulus is higher than that of other methods, showing excellent comprehensive enhancement effect. These are all due to the admirable dispersion of GNP caused by the shear stress of solid-state mixing during the preparation process.

Table 5: TGA test parameters of neat PP and PP/GNP nanocomposites

Samples	T_{in} (°C)	T_{max} (°C)	MLR_{max} (%/°C)	ΔT_{dr} (°C)
PP	316	422	0.02	222
PP/G0.5	426	458	0.03	118
PP/G1.0	430	460	0.04	89
PP/G1.5	438	461	0.04	100
PP/G2.5	438	461	0.04	90
PP/G3.5	439	465	0.03	90

Table 6: Properties of PP/GNP nanocomposites by different processing

Processing	Contents of GNP (wt%)	The characteristics of processing	σ (S/m)	Modulus increase (%)	Yield strength increase (%)	Impact strength increase (%)	Ref.
Melt compounding	1	Poor dispersion effect	10^{-8}	13.3	9.3	N/A	(39)
<i>In situ</i> polymerization	0.96	Complex production equipment and low efficiency	10^{-8}	N/A	N/A	N/A	(17)
Solution compounding	1	Need a lot of organic solvents	10^{-7}	N/A	N/A	N/A	(40)
Melt compounding	1	Poor dispersion effect	10^{-20}	N/A	N/A	N/A	(35)
Melt compounding	1	Poor dispersion effect	10^{-13}	N/A	N/A	N/A	(41)
Melt compounding	1	Poor dispersion effect	10^{-13}	19.3	10.6	N/A	(42)
Melt compounding	1	Poor dispersion effect	N/A	N/A	12.5	33.3	(14)
Melt compounding	2.17	Poor dispersion effect	N/A	N/A	N/A	16.7	(29)
Melt compounding	1	Poor dispersion effect	N/A	22.8	7.2	N/A	(43)
solid-state shear pulverization	0.81	Complex production equipment	10^{-10}	62.6	48.1	-51.6	(44)
Our work	1	Uniform and high efficiency	10^{-8}	19.2	27.7	120.8	

4 Conclusion

An industrially applicable preparation method for PP/GNP nanocomposites has been developed. The characterization results showed that GNP was uniform dispersed in the PP/GNP nanocomposites. Additionally, the anti-static and mechanical properties of the nanocomposites were improved significantly. Just adding 1.0 wt% of GNP, it made the surface resistivity of the nanocomposite was $2.4 \times 10^7 \Omega \text{sq}^{-1}$, which met the required standard of less than $3.0 \times 10^8 \Omega \text{sq}^{-1}$ for actual application antistatic materials and much better than the value obtained by common conventional melting compounding. Besides, compared with solution compounding and *in situ* polymerization, our preparation method has the advantages of high production efficiency and environmental friendliness. This good dispersibility of GNP in the nanocomposite also induced PP to generate β crystal form with higher impact strength without changing its crystallinity. The impact strength of the nanocomposites increased by 120.8% compared with neat PP while the yield strength and Young's modulus also improved to varying degrees simultaneously. Finally, the addition of a small amount (0.5 wt%) of GNP greatly improved the thermal stability (HDT and T_{in}) of the nanocomposites by 11.7°C and 110°C, respectively. Therefore, this study has shown the methods to obtain high-performance PP/GNP nanocomposites with the multi-functional antistatic application for industrial production.

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Appendix

A1 Synthesis method

Nanocomposites with the same GNP content were prepared by two-screw compounding. First, the PP powder,

GNP were manually mixed together by stirring. The blend was further mixed with a twin-screw extruder at 195°C with a screw speed of 90 rpm. A total of six samples were prepared and named as listed in Table A1.

Figure A1: SEM images of T-PP/0.5 (a), T-PP/1.0 (b), T-PP/3.5 (c). It can be observed that large-scale GNPs are stacked together, and there are some holes in the cross-section, which indicates that the GNP dispersion effect is poor, and a satisfactory dispersion effect cannot be obtained through two-screw compounding. Compared with Figure 1, this further illustrates the necessity and superiority of solid-state shear mixing.

Figure A2: Surface resistivity (a) and volume resistivity (b) of composites prepared by two-screw compounding.

Figure A3: Impact strength of neat PP and composites prepared by two-screw compounding.

Table A1: Name and composition of samples

Sample name	PP (g)	GNP (g)	Content of GNP (wt%)
PP	100	0.0	0.0
T-PP/G0.5	99.5	0.5	0.5
T-PP/G1.0	99.0	1.0	1.0
T-PP/G1.5	98.5	1.5	1.5
T-PP/G2.5	97.5	2.5	2.5
T-PP/G3.5	96.5	3.5	3.5

*Note: T is short for two-screw compounding, G is short for GNP.

Table A2: Tensile mechanical properties of neat PP and composites prepared by two-screw compounding

Samples	Yield strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PP	32.8 ± 0.9	945.3 ± 52.5	1004.5 ± 33.7
T-PP/G0.5	34.2 ± 1.6	1129.0 ± 57.9	554.5 ± 139.2
T-PP/G1.0	34.1 ± 0.6	1136.9 ± 38.4	370.4 ± 118.0
T-PP/G1.5	32.6 ± 0.7	1110.0 ± 40.9	58.9 ± 5.7
T-PP/G2.5	34.3 ± 0.9	1196.3 ± 59.2	78.9 ± 78.5
T-PP/G3.5	33.5 ± 0.7	1175.1 ± 34.5	39.8 ± 17.9

Table A3: The molecular weight and molecular weight distribution of samples

Samples	M_n (g/mol)	M_w (g/mol)	PD
Neat PP	60000	246000	4.1
Neat PP after solid-state shear mixing	57000	275000	4.8
PP/G1.0	58000	265000	4.6

Note: M_n is short for number average molecular weight, M_w is short for weight average molecular weight, PD = M_w/M_n , which is short for polydispersity coefficient.