

CHARACTERIZING BIAXIALLY STRETCHED POLYPROPYLENE/GRAPHENE NANOPATELET COMPOSITES

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ABSTRACT

During moulding processes such as thermoforming and blow moulding, heated polymer materials are subjected to rapid biaxial deformation as they are drawn into the shape of a mould. It is therefore essential to accurately measure and model this behaviour for new materials subjected to these processes. In this work, the processing and characterization of polypropylene (PP) nanocomposites containing graphite nanoplatelets (GNPs) is reported. PP/GNP nanocomposites were prepared by melt-mixing using an industrial-scale, co-rotating, intermeshing, twin-screw extruder. A bespoke screw configuration designed in-house was used to enhance nanoparticle dispersion in a polymer matrix. The effects of nanofiller content and biaxial stretching on the bulk properties of PP/GNP nanocomposites have been investigated in details.

1 INTRODUCTION

Due to its outstanding properties, graphene has become the topic of much research activity in recent years. Because of the two-dimensional structure of graphene, it is unlikely to exhibit the same toxicity as one-dimensional carbon-nanotubes (CNTs). A further advantage is in cost, with graphene between 10-30 times less expensive than carbon nanotubes. In addition to its excellent mechanical properties, graphene has the advantage of being electrically and thermally conductive. As such, there are a range of potential applications for this material, particularly if it can be successfully incorporated into polymers by conventional processing routes.

Research on the production of polymer-graphene composites is still in its early stages, with only a small range of polymers (polyethylene, polyethylene naphthalate, polycarbonate, thermoplastic polyurethane, and natural rubber) having been melt processed with graphene fillers [1-3]. The processing route used to manufacture polymer-graphene composites is likely to have a large influence on the dispersion and orientation of graphene, and consequently on the properties of the resulting composite materials. Thorough characterization of structural parameters including dispersion and orientation is critical in order to correctly attribute property enhancements to specific processing conditions.

In the present work, polypropylene (PP) was selected as the polymer matrix material for its good balance of physical and mechanical properties, easy processing and recyclability, and low cost, which makes PP a versatile class of polymer material [4]. In addition, PP has a low density and high crystallinity in comparison with other engineering thermoplastics (enabling potential weight reductions), very good heat resistance, good optical properties and is an excellent moisture barrier. Consequently, PP is used in many industrial applications for packaging, laboratory equipment, automotive components and many others [5].

The focus of this work is to manufacture PP/GNP composites via melt-mixing using an industrial, co-rotating, intermeshing, twin-screw extruder and to examine the influence of GNP content and extruder screw speed on the bulk properties of the nanocomposites. The effect of biaxial deformation of extruded polymer/GNP composites on the structure and properties of the composites was also investigated.

2 METHODS

2.1 Materials

Moplen HP500N grade Polypropylene (PP) was supplied by Basell. Graphene Nanoplatelets (GNPs) are ultrathin particles of graphite that can also be thought of as short stacks of graphene sheets. Grade M xGnP® GNPs are made through a proprietary manufacturing process, and were supplied by XG Sciences. The technical specifications for the xGnP® grade M GNPs are detailed in Table 1.

GRADE	Product	# layers	Thickness (nm)	Diameter (μm)	Surf. Area (m^2/g)
M	M-5	18-24	6-8	5	120-150

Table 1: XG Sciences xGnP® grade M GNP technical specifications.

2.2 Pre-Melt-Mixing Processes

In order to obtain better nanoparticle dispersion into the polymer matrix, the as-purchased polymer pellets were cryogenically ground to a micro-scale powder using a Wedco SE-12 UR pilot plant grinding mill at 7000 rpm and a gap size set to 400 μm . Liquid nitrogen was used for temperature regulation in order to prevent shear heating, which could degrade the material. PP and GNPs, were pre-mixed at 5 wt% and 10 wt% GNPs using a Thermo Scientific Prism Pilot 3 High Speed Mixer at 2000rpm for 2 min.

2.3 Melt-Mixing of PP/GNPs

Melt-mixing process was performed using a co-rotating intermeshing twin-screw extruder (Collin GmbH), having a screw diameter of 25 mm and a barrel length of 750 mm ($L/D=30$). The bespoke screw configuration was designed in-house [6] to enhance the nanoparticle dispersion into a polymer matrix. In brief, this configuration consists of forward conveying and forward kneading block elements with the addition of a toothed mixing element into the mixing zone and a reverse conveying element after the mixing zone. On exiting the capillary die, the extrudate was drawn through a cooled water bath at a constant haul off rate and pressure. The extrudate was dried by passing through an air ring and then pelletized using a Collin Pelletiser.

2.4 Compression Moulding

The extruded pellets were dried in an oven at 80°C for 4 hours before compression moulding. Materials were compression moulded at 200°C and 150 bars for 3 mins in a Rondol platen press. Square samples of 12 x 12 mm and 1.0 mm thickness were prepared for die cutting of tensile test specimens.

2.5 Biaxial Stretching of PP/M5 Composites

In order to carry out biaxial deformation experiments, the softening region of the materials was determined from DSC analysis to estimate the softening and melting behaviour of the polymer. The PP showed a narrow softening temperature in the range 145°C to 155°C. The addition of GNPs modified the PP thermal properties; 147°C was determined as the optimum temperature for stretching the nanocomposite specimens. Only samples of unfilled PP and nanocomposite PP with 5 wt% GNPs were successfully biaxial stretched. It was not possible to find a softening temperature suitable for stretching the PP with 10wt% GNPs. This can be explained by the high thermal conductivity of PP/GNP composites with > 5 wt% GNP content, which led to rapid dissipation of thermal energy, accelerated crystallisation, and facilitated rapid cooling before it was possible to stretch the polymer [7].

Biaxial stretching at strain rates of 1, 2, 4, 8, 16 and 32 s⁻¹ were trialled on unfilled PP to assess the limits to which these materials could be deformed. However, addition of GNPs to PP limited the applied strain rate achievable to lower values. The best results were obtained at a strain rate of 2 s⁻¹, and so this strain rate was used to explore the effect of GNP addition on the deformation behaviour of unfilled PP and of PP/GNP composites with 5 wt% M-5 xGnPs. Biaxial stretching was conducted to a final stretch ratio (SR) of 1.5 and 2 and the true stress and nominal strain data were recorded for all tests.

2.6 Mechanical Analysis

Tensile tests were carried out at room temperature following BS EN ISO 527-1: 1996 and using an Instron 5564 Universal Tester with a clip-on extensometer and a 2 kN load cell. Dumbbell-shaped samples (type 1BA) were cut after compression moulding or after biaxial stretching using a stamping press. For modulus measurement, nominal strain was determined using data from the extensometer, which was attached to the narrow portion of the dumb-bell samples, and at a crosshead speed of 1 mm/min. The elastic modulus was determined from the slope of the regression of the stress-strain data between 0.05-0.25 % strain. For strength and elongation, the nominal strain was derived from the grip displacement at a crosshead speed of 50 mm/min.

2.7 Thermal Analysis

Differential scanning calorimetry (DSC) was performed to study the melting and crystallisation behaviour of PP and PP/GNP composites using a Perkin-Elmer DSC model 6 under an inert nitrogen atmosphere and a heating and cooling rate of 10 K/min. in a range from 30°C to 275°C. In all cases the samples were held at 275 °C for 3 min., cooled to 30°C and reheated to 275°C to ensure complete melting of the crystalline fraction of PP and to remove thermal history. The apparent crystalline content of the PP composites was determined using a value of 148J/g for the heat of fusion for a theoretically 100% crystalline PP.

2.8 Electrical conductivity

Volume resistivity measurements were performed in accordance with ASTM D-257 on compression moulded and stretched specimens using a Keithley electrometer (Model 6517A) equipped with an 8009 test fixture with circular samples of diameter 60 mm was used. The sample was placed between two circular electrodes and the volume resistivity measured by applying a DC voltage across opposite sides of the sample and measuring the resultant current through the sample.

3 RESULTS AND DISCUSSIONS

3.1 Thermal properties

PP/GNP composites were characterized before and after biaxial deformation using DSC, and the resulting thermal properties are given in Table 2. The results indicate a strain induced increase in crystallization, and a γ - β phase transition due to biaxial stretching.

Biaxial stretching of unfilled PP resulted in an increase in crystallization temperature (T_c) of 8–12°C, depending on the SR. Significant increases in the percentage crystallinity (X_c) resulted from biaxial stretching, from ~40% for unstretched to ~63% at a SR of 1.5 and ~70% at a of SR2 for unfilled PP. No significant differences in T_g and T_m were observed when unfilled PP was biaxially deformed.

For the PP/GNP composites with 5 wt% GNPs, T_c increased by about 13–17°C depending on SR. After biaxial stretching, the increase in X_c for PP/GNP composites was smaller compared to unfilled PP, and the X_c was similar for both unfilled PP and PP/GNP composites when stretched to the same SR. Similar trends have been reported with polymer/MWCNTs in previous research [8].

	UNSTRETCHED			BIAXIAL STRETCHED			BIAXIAL STRETCHED		
	T_m	X_c	T_c	SR1.5			SR2		
				T_m	X_c	T_c	T_m	X_c	T_c
	(°C)	(%)	(°C)	(°C)	(%)	(°C)	(°C)	(%)	(°C)
PP Unfilled	168.6	40.4	108.2	169.5	63.0	116.0	171.8	70.7	120.3
PP/5wt% M-5	169.2	61.5	122.9	169.9	65.9	135.7	172.2	71.0	139.4

Table 2: Effect of biaxial deformation and GNP addition on the thermal parameters of PP and PP/GNP composites

3.2 Mechanical properties

The tensile mechanical properties of the PP/GNP composites before and after biaxial deformation were measured in the extrusion direction and results are presented in Table 3. Both Young's modulus and yield stress increased with the addition of 5 wt% GNP, and after biaxial deformation. The increase in Young's modulus due to stretching was significant for unfilled PP, but smaller increases were measured for PP/GNP composites. In contrast, biaxial stretching resulted in large increases in yield stress for both unfilled PP and PP/GNP composites. Similar trends have been reported for polymer/MWCNTs composites [8].

			Elastic Modulus (MPa)	Impr* (%)	Yield Stress (MPa)	Impr* (%)
PP unfilled	Unstretched	Mean	1110.43		26.16	
		SD	89.6		1.84	
	Biaxial Stretched SR1.5	Mean	1810.26	63.02	40.64	55.35
		SD	93.8		2.1	
	Biaxial Stretched SR2	Mean	2159.61	94.48	41.13	57.22
		SD	101.6		1.9	
PP/GNP (5 wt%)	Unstretched	Mean	2567.76		29.38	
		SD	78.7		1.1	
	Biaxial Stretched SR1.5	Mean	2789.61	8.64	57.18	74.20
		SD	59.8		1.4	
	Biaxial Stretched SR2	Mean	2873.25	11.90	53.96	83.66
		SD	89.0		2.3	

*Percent improvement with respect to corresponding unstretched material

Table 3: Effect of biaxial deformation on the tensile mechanical properties of PP unfilled and PP/GNP composites

3.3 Electrical properties

Table 4 shows the change in volume resistivity of PP/GNP composites after biaxial deformation to stretch ratios of 1.5 and 2. In both cases, volume resistivity increased (conductivity decreased) with increasing stretch ratio. This can be attributed to the disruption of GNP network pathways and increasing distance between GNPs.

When PP/GNP composites samples stretched to SR1.5 were annealed at 150°C (below the T_m of PP), the volume resistivity decreased (conductivity increased) and returned to approximately the same value measured prior to stretching. Annealing after deformation permits some polymer chain relaxation and as a consequence increased GNP-GNP contacts to a similar level obtained prior to deformation recovering the electrical network.

		Vol. Resistivity (Ω .cm)
PP unfilled	Unstretched	1.30E+14
	Biax Stretch SR1.5	2.73E+14
	Biax Stretch SR2	1.30E+14
PP/GNP (5 wt%)	Unstretched	2.15E+12
	Biax Stretch SR1.5	5.89E+12
	Biax Stretch SR2	8.92E+12

Table 4: Effect of biaxial deformation on electrical properties of unfilled PP and PP/GNP composites.

4 CONCLUSIONS

The effects of graphene nanoplatelet (GNP) addition and biaxial stretching on melt processed polypropylene (PP) and PP/GNP composites were investigated. The results show that the addition of 5

wt% GNPs resulted in increased the yield stress and ultimate stress to failure by approx. 20% compared with unfilled PP. The improved mechanical properties of the composites were maintained after stretching. The increase in yield stress in the composites can be attributed to the greater restriction on molecular mobility and increased entanglement of molecules due to the presence of GNPs.

Thermal analysis of the stretched samples revealed a strain induced increase in crystallization. The electrical conductivity of composites decreased after biaxial stretching and with increasing SR, which is consistent with the disruption of GNP network pathways and increasing distance between GNPs. However, the conductivity of stretched composites remained higher than pure PP, and annealing of the stretched specimens resulted in nearly full recovery of the conductivity prior to stretching.

The materials and processing techniques developed and utilized in this study have a wide range of potential applications including low cost, light weight, electromagnetic insulating shielded computer housings and cables, anti-static packaging, lightweight, high strength automotive and aerospace components, high barrier packaging as well as smart clothing/personal sensor systems.

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REFERENCES

- [1] J.R. Potts, D.R. Dreyer, C.W. Bielawski and R.S. Ruoff, Graphene-Based Polymer Nanocomposites. *Polymer*, **52**, 2011, pp. 5-25 (<http://doi.org/10.1016/j.polymer.2010.11.042>)
- [2] B. Li, W.H.Zhong., Review on polymer/graphite nanoplatelet nanocomposites. *Journal of Materials Science*, **46**, 2011, pp. 5595-5614 (doi:10.1007/s10853-011-5572-y)
- [3] H. Kim, A.A. Abdala and C. Macosk., Graphene/polymer nanocomposites. *Macromolecules*, **43**, 2010, pp. 6515-6530 (DOI: 10.1021/ma100572e)
- [4] <http://www.dow.com/polyolefins/about/pptechctr/primer/typical.htm>.
- [5] L. Valentini, J. Biagiotti, J.M. Kenny, M.A. Lopez-Manchado , Physical and mechanical behavior of single-walled carbon nanotube/polypropylene/ ethylene-propylene-diene rubber nanocomposites. *Journal of Applied Polymer Science*, **89**, 2003, pp. 2657 (DOI: 10.1002/app.12319)
- [6] B. Mayoral, T. McNally, G. Garrett, Effect of screw configuration profiles on the Dispersion of MWCNTs in a Poly (propylene) Matrix. *Macromolecular Materials and Engineering*, **299**, 2014, pp. 748-756 (DOI: 10.1002/mame.201300172)
- [7] Tan C.W, H.-J.E.M.A., Menary G.H, Martin P.J, Armstrong C.G. ANTEC Massachussets **3**, 2005, pp. 1186-1191.
- [8] Mayoral, B., P. R. Hornsby, T. McNally, T. Schiller, K. Jack, D. J. Martin, Quasi-Solid State Uniaxial & Biaxial Deformation of PET/MWCNT Composites: Structural Evolution, Electrical and Mechanical Properties. *RSC Advances*, **3**, 2013, pp. 5162-5183 (DOI:10.1039/C3RA22597F)