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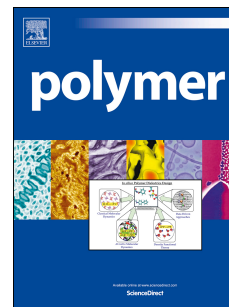
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Plasticisation and compatibilisation of poly(propylene) with poly(lauryl acrylate) surface modified MWCNTs

Jaipal Gupta,[†] Chaoying Wan,[†] David M. Haddleton,[‡] and Tony McNally^{†}*

[†]International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK.

[‡]Department of Chemistry, University of Warwick, Library Road, Coventry, CV4 7AL, UK.

Keywords; poly(propylene), multi-walled carbon nanotubes, nanocomposites, poly(lauryl acrylate), non-covalent functionalisation, percolation threshold, plasticisation, interface, electrical conductivity,

Abstract

Poly(lauryl acrylate) P[LA] synthesised using Cu(0)-mediated polymerisation was used to non-covalently functionalise multi-walled carbon nanotubes (MWCNTs) achieved via combined CH- π interactions and physical wrapping. The inclusion of P[LA] competed with the attractive van der Waals forces between MWCNTs altering interfacial interactions between neighbouring CNTs and, assisted their dispersion and distribution in a poly(propylene) (PP) matrix, confirmed from SEM/HR-TEM imaging and oscillatory rheology measurements. A rheological percolation threshold measured for composites of unmodified MWCNTs and PP at ~0.5 wt% was shifted to lower MWCNT concentrations (~0.25 wt%) for P[LA] functionalised MWCNTs. Addition of P[LA] also reduced the nucleating effect of MWCNTs for PP as a coating of P[LA] on the nanotube surfaces hindered trans-crystallisation of the PP. Evidence from static and dynamic mechanical measurements confirmed the P[LA] plasticised PP as both an increase in ductility and a decrease in the glass transition temperature (T_g) of PP of up to 25 °C was obtained. Addition of unmodified MWCNTs to PP resulted in an increase in the DC electrical conductivity of PP of 15 orders of magnitude, from 10^{-14} S/m to 10^1 S/m for a MWCNT loading of 5 wt%. Non-covalent functionalisation of MWCNTs utilising P[LA] only degraded electrical conductivity by about 2 orders of magnitude across the composition range.

1. Introduction

The addition of 0D, 1D or 2D functional fillers to polymers is receiving interest due to the many unique properties of these materials.^[1] Since the successful characterisation of carbon nanotubes (CNTs) by Iijima,^[2] the use of carbon based materials such as, CNTs and graphene/GO have attracted a particular interest due to their multi-functional properties including low density, large aspect ratio, excellent electrical, thermal and mechanical properties.^[3, 4] CNTs have shown to be able to carry very high current densities up to $\sim 10^8$ to 10^9 A cm^{-1} .^[5] Additionally, CNTs have shown to possess exceptionally high elastic modulus (~ 1 TPa), high tensile strength (11–63 MPa), large elastic strain and strain fracture capability.^[6, 7] It is this unique combination of properties which make CNTs excellent candidates for use as nanoscale fillers in the fabrication of advanced polymer composites.^[1, 8] CNT based composites having exceptional electrical properties can be used in many applications such as in electromagnetic interference shielding.^[9]

However, strong attractive interactions between CNTs cause them to agglomerate and form bundles or ‘ropes’ during processing of the composites due to van der Waals interactions between tubes. Their agglomeration during processing reduces the effective surface area between CNT and polymer matrix and hinders the formation of an interconnected CNT network structure in 3D. Enhanced electrical, thermal and mechanical properties of the composites can only be realised if a fully dispersed interconnected CNT network structure is formed and when translation of CNT properties to the polymer matrix is achieved.^[10] As synthesised MWCNTs exist as entangled agglomerates with sizes typically in order of several hundred microns, direct melt-mixing of MWCNTs with polymers does not always result in homogenous dispersions due to poor compatibility between the MWCNTs and the polymer matrix.^[9] CNT surface

functionalisation is essential to overcome van der Waals interactions between neighbouring CNTs and subsequently improve dispersion and prevent re-agglomeration.^[11] Many papers have focused on preparation and properties of composites of PP and MWCNTs through simple melt compounding or solution mixing of PP and unmodified MWCNTs.^[1, 5, 9, 12-20] Although the properties of the PP could be improved through these methods, the MWCNT content could be reduced to achieve similar efficiencies by improving the level of dispersion with functionalised MWCNTs.

Modification of the polymer matrix-nanotube interface can be approached using either covalent or non-covalent methods.^[21] Covalent functionalisation involves either direct attachment of functional groups to the graphitic surface or by linking functional groups with CNT-bound carboxylic acids which are inherent defects on the CNT surface.^[22] Chemical treatments can be used to introduce oxygen containing functional groups (i.e. carboxyl, hydroxyl and epoxy) which can be used to either 'graft from' or 'graft to' polymers from the surface of CNTs.^[23] Covalent functionalisation has been used to improve compatibility between the polymer matrix and CNTs such as, by attaching alkyl chains to the surface using alkyl radicals generated by the thermal decomposition of lauryl peroxide which achieved better CNT dispersion and enhanced polymer plasticity.^[24] However, the covalent approach causes damage to the MWCNTs disrupting the translational symmetry by destroying the sp^2 hybridisation of the CNT and therefore, reduces their ability to reinforce the polymer and importantly weakens the intrinsic electronic transport properties of the CNT.

The non-covalent approach of using polymers synthesised with specific properties and well defined structures provides a route to functionalise CNTs via chain wrapping, assisted by CH- π interactions, to produce well dispersed CNTs in the polymer matrix without the damage caused

to MWCNTs through covalent functionalisation.^[25] Aromatic compounds which employ π - π stacking^[25] and hydrophobic polymers have shown to be able to adsorb on to the surface of CNTs and therefore, can be used to improve compatibilisation between CNTs and polymers.^[26]

Isotactic polypropylene (PP) is a thermoplastic having a wide range of applications, arising from good chemical, impact and, heat resistance as well as being semi-crystalline and translucent. In order to enhance the use of PP in an even wider range of industrial sectors, its tensile strength and cold temperature performance need to be significantly enhanced. The ultimate tensile strength of PP is in the region of 30-40 MPa and the tensile modulus is typically 1.5 – 2 GPa.^[24, 27, 28] There is also an ever increasing demand for such commodity polymers to have combined improved electrical and thermal conductivity.^[16] Machado *et al.* showed the mechanical properties of composites of PP and SWCNTs (up to 0.75wt%) were enhanced, the Young's modulus from 855 MPa to 1187 MPa and tensile strength from 24.5 MPa to 31 MPa. However, once the filler content was increased above 0.75 wt%, the stiffness and strength were significantly reduced.^[29] Zhou *et al.* reported the tensile strength of PP increased from 36 MPa to 38 MPa for up to a 0.5 wt% MWCNT loading however, increased loading caused a reduction in tensile strength. Even at a 0.25wt% MWCNT loading, the elongation at break decreased from 150% to 6%.^[10] The tensile properties of composites of PP and MWCNTs were also determined by Dondero and Gorga. Their results also confirmed an increase in yield strength, tensile stress and modulus after blending MWCNTs with PP. Elongation at break was also shown to decrease after the introduction of MWCNTs.^[30] The tensile properties of composites of PP and MWCNTs prepared by dynamic packing injection moulding were measured by Xiao *et al.* The tensile strength and impact toughness increased for up to 0.6 wt% MWCNT loading.^[31] Clearly, dispersion of MWCNTs at even modest loadings in PP is a challenge without significantly

degrading static mechanical properties. There is also a contribution from the effect of MWCNT inclusion on the crystallisation behaviour of PP.

Use of differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) can be used to investigate the changes in crystallisation behaviour of PP upon addition of MWCNTs.^[32, 33] MWCNTs have shown to act as α -nucleating agents. CNT-induced polymer crystallisation can create nano-hybrid shish-kebab structures, induce the formation of different crystal polymorphs and alter significantly crystallisation kinetics.^[34-36] Therefore, it is important to characterise changes in crystal structure and morphology when incorporating CNTs into polymer melts.^[22] Additionally, reports have suggested modification of MWCNTs can lead to the formation of the β -polymorph of PP which leads to weaker mechanical properties and such behaviour can be studied using WAXD,^[37] and scattering techniques (WAXS/SAXS). CNTs almost exclusively disperse in the amorphous phase of the polymer matrix and the extent of this phase controls the CNT loading at which percolation is attained. MWCNTs have a strong nucleating effect on polymers cooled from the melt which can cause an increase in crystallinity. It has also been suggested that MWCNTs may partially reside within the inter-lamellae spacing of polymers.^[38, 39]

The rheological properties of PP/CNT composites can be characterised in the melt-state as an indirect method for measuring the extent of dispersion of CNTs in the PP matrix and, assist with the understanding of interfacial adhesion between CNTs and polymer matrices. Prashantha *et al.* produced composites by diluting a PP-MWCNT masterbatch using twin-screw extrusion. A rheological percolation was achieved at 2 wt% MWCNT loading by demonstrating pseudo-solid like behaviour.^[16]

Electrical percolation threshold concentrations lower than 0.1 wt% CNTs have been reported by many research groups. Efficient compatibilisation between MWCNTs and the polymer will result in highly electrically conducting composites at loadings low enough to prevent any significant alteration of polymer properties, such as processability, ductility, toughness and tensile strength. Al-Saleh achieved electrical percolation of composites of PP and MWCNTs as low as 0.5 vol% with conductivities in the range of 10 Ω .cm for a 5 wt% nanotube loading.^[13]

Our previous work has shown that poly(lauryl acrylate) P[LA] synthesised using reversible deactivation radical polymerisation (RDRP) techniques is thermally stable that it can be melt mixed at the relevant processing conditions for PP. By way of example, P[LA] was selected based upon its known good compatibility with PP, and because its hydrophobic chains are known to be able to co-crystallise with PP. P[LA] has shown to adsorb onto the surface of MWCNTs via a combination of hydrophobic interactions and possible CH- π interactions.^[26] Koval'chuk *et al.* demonstrated covalent functionalisation of MWCNTs using lauryl alkyl chains and subsequent composite preparation via *in-situ* polymerisation of propylene, provided improved dispersion, enhanced stiffness and improved plasticity. However, interfacial adhesion between the non-polar polyolefin and CNTs remained unresolved. Moreover, covalent functionalization of 1D and 2D graphitic materials alters the ratio of sp^2 and sp^3 hybridised carbon atoms which in turn degrades electron conduction. Our work attempts to solve the problem by taking a novel non-covalent approach.^[24]

In this current work, we report the preparation via melt-blending, and the characterisation of composites of PP with MWCNTs functionalised with P[LA] synthesised using Cu(0)-mediated polymerisation.^[40] Due to the non-polar chemical structure of PP chains, the use of P[LA] wrapping on the CNT surface is expected to provide efficient interfacial adhesion and improve

CNT dispersion.^[41] PP was blended with various concentrations of MWCNTs and P[LA] to prepare a range of composites. The mechanical and rheological properties and, crystallisation behaviour of these composites were investigated so as to assess the role of P[LA] in plasticising and compatibilising PP and MWCNTs.

2. Experimental Section

2.1 Materials

Non-functionalised, commercially available multi-walled carbon nanotubes (MWCNTs) produced by a catalytic carbon vapour deposition (CCVD) process with an average diameter of 9.5 nm and average length of 1.5 μm (grade NC7000, purity: >90%) were purchased from Nanocyl S.A., Belgium and used as received. The density of these MWCNTs was reported to be 1.85 g cm^{-3} ,^[38] and the oxygen to carbon ratio 0.0045:1,^[42] respectively. Isotactic poly(propylene) (PP), grade H734-52RNA ($M_{w, \text{GPC}} = 216,000$, $\mathcal{D} = 19.7$ (see Supplementary Fig. S1) had a melting temperature range of 165 – 180 $^{\circ}\text{C}$, density = 0.9 g cm^{-3} and a melt flow rate (MFR) of 52 g/10 min. at 230 $^{\circ}\text{C}$ (2.16 kg -ISO 1133D) was supplied by Braskem Europe GmbH. GPC (Fig. S1) showed minimal degradation of PP after the cryo-milling process. Methanol, chloroform, ethyl 2-bromoisobutyrate, copper(II) bromide and isopropanol (IPA) were purchased from Sigma Aldrich and used as received. Lauryl acrylate (LA) was also purchased from Sigma Aldrich and passed through a column of basic alumina prior to use in order to remove inhibitors. Cu(0)-wire (gauge 0.25 mm) was purchased from Comax Engineering Wires and treated by immersion in conc. HCl prior to use. *Tris*-(2-(dimethylamino)ethyl)amine

(Me₆TREN) was synthesised following a previously published procedure,^[43] degassed and stored in a fridge under nitrogen prior to use.

2.2 Typical Cu(0)-mediated polymerisation procedure

P[LA] was synthesised using the procedure described by Anastasaki *et al.*^[44] Ethyl 2-bromoisobutyrate (EBiB, 2.31 mL, 15.8 mmol, 1.00 mol equiv.), lauryl acrylate (LA, 180 mL, 662 mmol, 42.0 mol equiv.), CuBr₂ (176 mg, 0.79 mmol, 0.05 mol equiv.), IPA (180 mL) and a magnetic stir bar wrapped with pre-activated copper wire (15 cm) were charged to a polymerisation reactor vessel with a rubber septum and the mixture was degassed via bubbling with argon for 15 min. Me₆TREN (0.758 mL, 2.84 mmol, 0.18 mol equiv.) was added via a degassed syringe and the polymerisation was allowed to proceed for 24h at ambient temperature. Samples of the reaction mixture were carefully removed at the end of the polymerisation for ¹H NMR, and GPC analysis. The samples for ¹H NMR spectroscopy were diluted in CDCl₃, while the GPC samples were diluted with chloroform and then passed through a column of basic alumina to remove the copper salts. The poly(lauryl acrylate) was precipitated in a mixture of cold methanol and water (4:1 v/v).

2.3 Composite preparation

The PP pellets were first ground to a powder, using a SPEX[®] SamplePrep Freezer Mill (Stanmore, UK). The pellets (25 g batch) were pre-cooled for 12 min. using liquid nitrogen followed by two 5 min. grinding cycles at 15 Hz. Between each cycle, the sample was cooled for a 2 min. interval. The cryo-milled PP powder was dried in a vacuum oven at 30 °C for 12h prior to processing. Composites were prepared by firstly dry blending P[LA] with MWCNTs at a ratio of 1:4 MWCNTs:P[LA]. Subsequently, the P[LA] modified MWCNTs were further dry-blended with a given amount of PP ensuring the loading of MWCNTs in the composite was as follows;

0.01, 0.1, 0.3, 0.5, 1, 3 and 5 wt %. The pre-blend (consisting of all three components) was then fed into a Haake™ Mini-Lab II micro-compounder fitted with two conical co-rotating screws that facilitates recirculation of the mixture within a chamber volume of 5 cm³. The composite material was processed for 5 min. at 80 rpm and 165 °C (conditions previously optimised for unfilled PP in a control experiment). After 5 min., the composite materials were extruded through a 3.90 x 1.20 mm rectangular die directly into the hot melt chamber of a micro-injection moulding machine. The samples were injection moulded using a piston injection moulding system (Thermo-Scientific Haake™ MiniJet Pro) to produce standard dumbbell-shaped test specimens conforming to ASTM D638 V and disk samples (d = 25, h = 1.5 mm) for rheology measurements. The injection temperature was set to 185 °C and the mould temperature to 60 °C with an injection pressure of 350 bar. (Neat cryo-milled PP powder was also extruded and injection moulded using the same parameters for the purpose of comparison). For the P[LA] coated MWCNTs blended with PP, the MWCNTs were dry blended with the P[LA] in a ratio of 4:1 P[LA]: MWCNTs. Table 1 lists the blending ratios and nomenclature used for all samples in this study. In summary, three sets of composites were prepared; PP/MWCNTs; PP/P[LA] and PP/P[LA]/MWCNTs, so the effect of P[LA] functionalised MWCNTs on the properties of the composite materials could be isolated and assessed.

Table 1. Blending ratios (wt%) composites of PP, P[LA] and MWCNTs and corresponding composite nomenclature.

PP	MWCNTs	P[LA]	Nomenclature
100			PP
99.99	0.01		A ₁
99.9	0.1		A ₂
99.7	0.3		A ₃
99.5	0.5		A ₄
99	1		A ₅
97	3		A ₆
95	5		A ₇
99.96		0.04	B ₁
99.6		0.4	B ₂
98.8		1.2	B ₃
98		2	B ₄
96		4	B ₅
88		12	B ₆
80		20	B ₇
99.95	0.01	0.04	C ₁
99.5	0.1	0.4	C ₂
98.5	0.3	1.2	C ₃
97.5	0.5	2	C ₄
95	1	4	C ₅
85	3	12	C ₆
75	5	20	C ₇

2.4 Characterisation of composites of PP, P[LA] and MWCNTs

Tensile tests were performed to measure Young's modulus (MPa), yield strength (MPa), fracture strength (MPa) and elongation at break (%) using a Shimadzu Autograph AGS-X fitted with a 10 kN load cell, equipped with a twin TRViewX non-contact digital video extensometer (500 and 120 mm field of view) using the Trapezium X Version 1.4 software package. The standard dumbbell-shaped test specimens (ASTM D638 V) with a gauge length of 7.62 mm were deformed using a constant crosshead speed of 10 mm/min and data acquisition rate of 100 points/s. Five replicates of each sample were run to obtain average and standard deviation values. To obtain the elastic modulus, a linear regression technique was utilized to define the slope of the stress-strain curve in the initial region before yield.

Thermograms were obtained using a Mettler-Toledo differential scanning calorimeter (DSC) (DSC1, model 700) and evaluated using a STARe Version 12.10 software package. The non-isothermal scans were performed under nitrogen using the following procedure: samples of 10 ± 1 mg were heated to 200 °C and held for 2 min. to eliminate thermal history, then cooled from 200 °C to 80 °C at -10 K/min., then heated from 80 °C to 200 °C at 10 K/min., then cooled from 200 °C to 80 °C at -10 K/min. The thermograms were used to determine the onset melting temperature, crystallisation temperature (T_c), peak melting temperature (T_m), enthalpy of melting (ΔH_m) and crystallisation (ΔH_c). The degree of crystallinity was calculated by dividing the (ΔH_m) or (ΔH_c) for the sample by the enthalpy of melting for a theoretically 100% crystalline PP ($\Delta H_f^\circ = -207.1$ J/g)^[28], and compensating for blend composition.

Wide-angle X-ray diffraction (WAXD) was used to characterise the crystalline structure of the composites. WAXD patterns were collected using a PANalytical Empyrean X-ray diffractometer equipped with a Co($K_{\alpha 1} = 1.789$ Å) source. A tube voltage of 45 kV and current of 40 Amps was

employed. The measurement was carried out in reflectance mode using a stage spinner (disk shaped sample mounted using minimal plasticine) with a speed of 1 rps. The patterns were collected in the 2θ range $5^\circ - 60^\circ$. Crystallinity values from XRD were obtained using the High Score Plus software program (version 4.6a) by comparing the area of the crystalline peaks to the amorphous halo using the software's inbuilt calculation tool.

The oscillatory rheological properties of the three sets of composites (A, B and C) were measured using a Thermo Scientific Haake MARS III rheometer equipped with parallel-plate geometry (plate diameter = 25 mm, gap set to 1650 μm). Oscillatory stress sweeps were first undertaken over a stress range of 0.1 to 100 Pa at a fixed temperature and frequency of 180 $^\circ\text{C}$ and 1 Hz, respectively. The test indicated the region in which the deformation was small enough for the storage modulus (G') to be independent of deformation. Under such conditions the viscoelastic properties of the material became apparent. The samples, all 1.65 mm thick, were then subjected to oscillation frequency sweeps in the range 0.1 to 100 Hz and melted at the same temperature and a controlled stress frequency sweep at 100 Pa.

Volume resistivity was measured using a two-point probe method on injection moulded test bars (length 18 mm, width 9.4 mm, thickness 3.25 mm) prepared by coating each end with silver conducting paint and attaching copper tape over the conducting paint to minimise contact resistance. An electrometer (Keithley, Ohio, USA, model 6517B) was used to measure volume resistivity using an applied voltage of 1V. The surfaces of all samples were cleaned with ethanol prior to measurement. According to ASTM D4496 and D257, the measured volume resistance, R_v , was converted to volume resistivity, ρ_v , using the formula;

$$\rho_v = R_v * A / t \quad (1)$$

where, A is the effective area of the measured electrode and t is the specimen thickness.

The density of PP and P[LA] was measured using a Mettler Toledo NewClassic Balance (Model ME204) with attached density kit using water as the displacement fluid.

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl_3 . Chemical shifts are given in ppm downfield from the internal standard of tetramethylsilane.

Size exclusion chromatography (SEC) measurements of P[LA] were conducted using an Agilent 1260 GPC-MDS fitted with differential refractive index (DRI), light scattering (LS), and viscometry (VS) detectors equipped with 2 x PLgel 5 mm mixed D-columns (300 x 7.5 mm), 1 x PLgel 5 mm guard column (50 x 7.5 mm) and auto-sampler. Low molar mass linear poly(methyl methacrylate) standards in the range 200 to $1.0 \times 10^6 \text{ g mol}^{-1}$ were used to calibrate the system. All samples were passed through a $0.45 \mu\text{m}$ PTFE filter prior to analysis. The eluent was chloroform with 2% trimethylamine at a flow rate of 1.0 mL min^{-1} . SEC data was analysed using Cirrus v3.3. SEC of PP was conducted using an Agilent PL220 instrument equipped with differential refractive index (DRI), viscometry (VS) and dual angle light scatter (LS 90 + 15) detectors. The system was equipped with 2 x PLgel Mixed D columns (300 x 7.5 mm) and a PLgel 5 μm guard column. The mobile phase was TCB with 250 PPM BHT (butylated hydroxytoluene) additive. Samples were run at 1 ml/min at $160 \text{ }^\circ\text{C}$. Polystyrene standards (Agilent EasyVials) were used to create a third order calibration. Analyte samples were filtered through a stainless steel frit with $10 \mu\text{m}$ pore size before injection. Respectively, experimental molar mass ($M_{n,\text{GPC}}$) and dispersity (\mathcal{D}) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

3. Results and Discussion

In the first instance, a high degree of MWCNT dispersion throughout the PP matrix and conclusive evidence for a well-defined rheological percolation threshold at 0.5 wt% was observed. An improved degree of dispersion and a reduction of the rheological percolation threshold to 0.3wt% was observed upon addition of P[LA] functionalised MWCNTs to the PP matrix. A combination of techniques addressing structural, thermal, dynamic and static mechanical and rheological properties were used to rigorously understand this P[LA] induced plasticisation of PP and compatibilisation behaviour between PP and MWCNTs which in turn provide a framework to describe the electrical properties of the composites obtained.

Melt mixing achieved a highly dispersed and interconnected network of MWCNTs in the PP matrix as shown in the representative SEM micrograph, Fig. 1a). Agglomerate size and distribution was reduced upon addition of P[LA] functionalised MWCNTs, see SEM, Fig. 1b). The addition of P[LA] as a compatibiliser further improved the dispersion of MWCNTs in an already relatively well dispersed system. Fig. 1a) shows there are regions where the MWCNTs have not completely dispersed within the PP. However, from Fig. 1b) the addition of P[LA] has enabled the CNTs to disperse more homogenously by reducing the attractive van der Waals forces between MWCNTs but promoting CH- π interactions and physical wrapping between P[LA] and MWCNTs. This results in a well dispersed but interconnected MWCNT system and reduced MWCNT agglomeration. The HR-TEM images in Figures 1 c) and d) confirm a coating of P[LA] on the surface of the CNTs, the contrast between the MWCNT and the P[LA] and PP obvious.

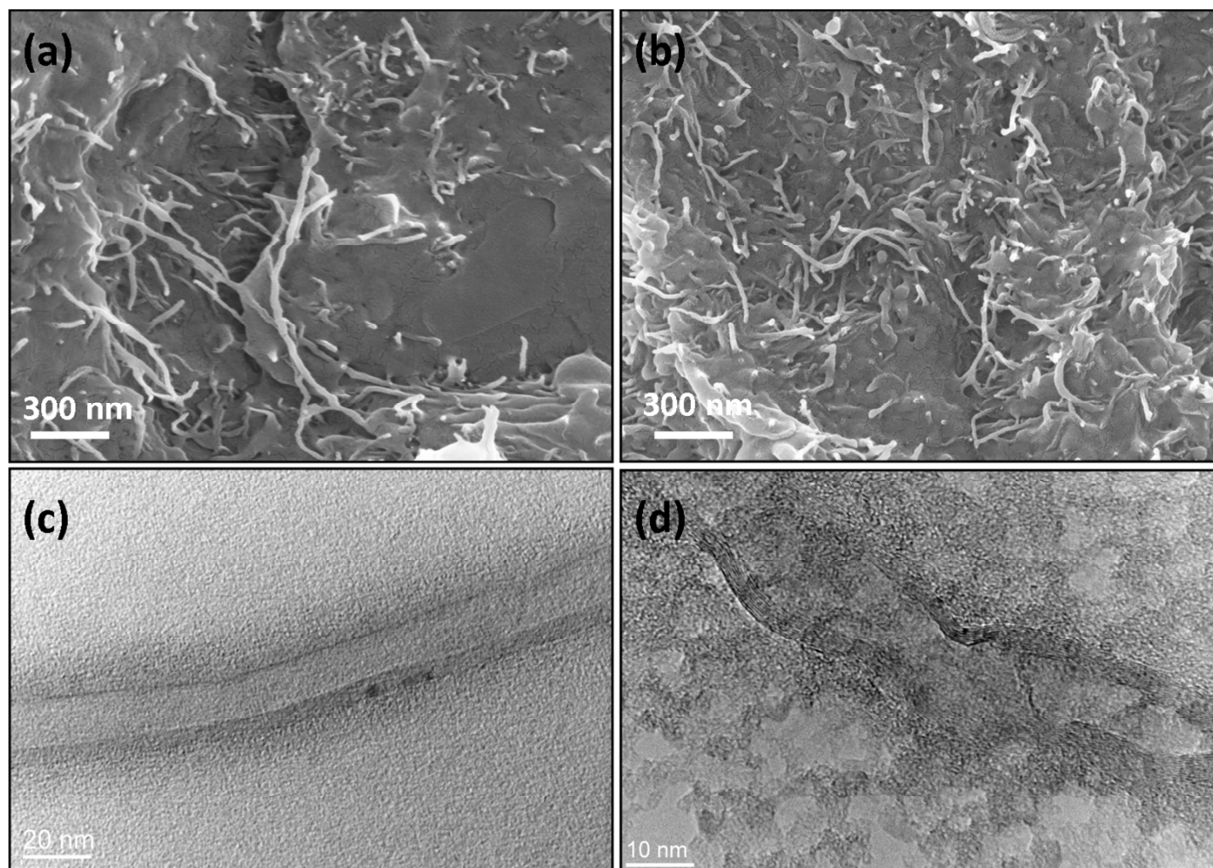


Figure 1. SEM images of cryo-fractured surfaces showing the extent of MWCNT dispersion for composites of PP with (a) 1 wt% MWCNTs (A_5) x 100K and (b) 1 wt% MWCNTs modified with 4 wt% P[LA] (C_5) x 100k and HRTEM images of MWCNTs functionalised with P[LA] at (c) x 200k and (d) x 300k magnification.

The strong nucleating effect of CNTs on polymers cooled from the melt can alter the crystalline content and crystallisation kinetics of semi-crystalline PP. On the assumption that the majority of MWCNTs are dispersed in the PP amorphous phase, it is important to consider the effect of MWCNT loading on the crystallisation behaviour of PP. It is worth noting recent studies have shown CNTs can reside within the inter-lamella spacing of certain polymers.^[39] The crystalline content (X_c) and relevant thermal properties of composites of PP with MWCNTs

loading up to 5 wt%, PP with P[LA] modified MWCNTs at loadings up to 5 wt% and PP with P[LA] loading up to 20 wt%, were determined from a combination of DSC (Fig. 2) and WAXD (Fig. 3), the relevant thermal properties are listed in table 2. For composites of PP with MWCNTs, an increase in both melt temperature (T_m) of ~ 4 °C and crystallisation temperature (T_c) also of ~ 4 °C was obtained on addition of up to 5 wt% MWCNTs. The increase in T_m and T_c is evidence for the nucleating effect typically exhibited by MWCNTs on semi-crystalline polymers cooling from the melt. However, a change in X_c with increasing MWCNT content was not observed from DSC. In fact, X_c remained unchanged even after the addition of 5 wt% unfunctionalised MWCNTs. In contrast, a modest decrease in X_c for PP with increasing MWCNT content was obtained from, ~ 37 % to ~ 28 % when measured by WAXD again on addition of 5 wt% MWCNTs. The contrasting values for X_c can be explained by fundamental differences in the two techniques. Full width at half-height values for both the melting ~ 4 °C and cooling ~ 1 °C peaks for composites of PP and 5 wt% unfunctionalised MWCNTs showed peak broadening compared to unfilled PP, evidence for heterogeneous nucleation of PP by the MWCNTs.

For composites of PP with P[LA] modified MWCNTs, T_m and T_c of PP remained unchanged at 163 °C and 124 °C respectively, even after the addition of 5 wt% P[LA] modified MWCNTs. The lack of any observable change in T_m and T_c show the P[LA] influences the CNTs ability to nucleate PP. WAXD data showed a decrease in X_c with increasing P[LA] modified MWCNT content, from ~ 37 % to ~ 28 %. Presumably, the coating of P[LA] on the CNT surface hinders nucleation and trans-crystallisation of PP. The strong nucleating effect of MWCNTs on polymers cooled after melt mixing has been reported previously and was observed for the unmodified MWCNTs in this study. The non-covalent functionalisation of MWCNTs prior to melt

mixing appears to limit the nucleating effect commonly observed. The increase in T_c is directly related to the extent of MWCNT dispersion which promotes nucleation and favours crystal growth. The results suggest the P[LA] is coating and shielding the MWCNTs from the PP matrix and hence reduces nucleation of the MWCNTs.^[45]

The addition of P[LA] to PP had little or no effect on the T_m and T_c of PP. X_c decreased by ~3 % for the 20 wt% P[LA] filled PP from DSC and by ~ 9% from WAXD. Due to the increased loading of P[LA], the reduction in PP accounts for the decreased crystalline content.

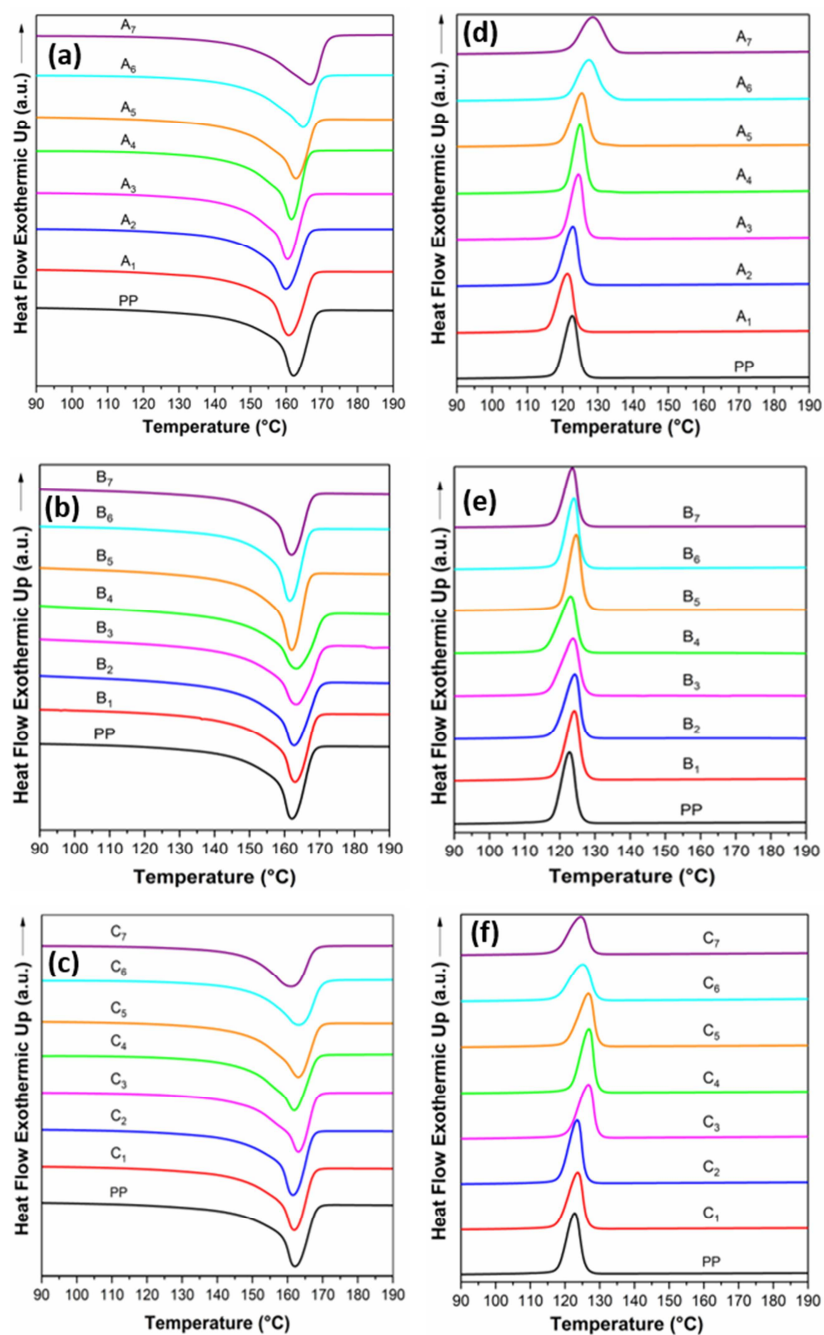


Figure 2. DSC heating curves for unfilled PP and composites of (a) PP and MWCNTs, (b) P[LA] modified PP and (c) PP and P[LA] modified MWCNTs. DSC cooling curves for unfilled PP and composites of (d) PP and MWCNTs (e) P[LA] modified PP and (f) PP and P[LA] modified MWCNTs.

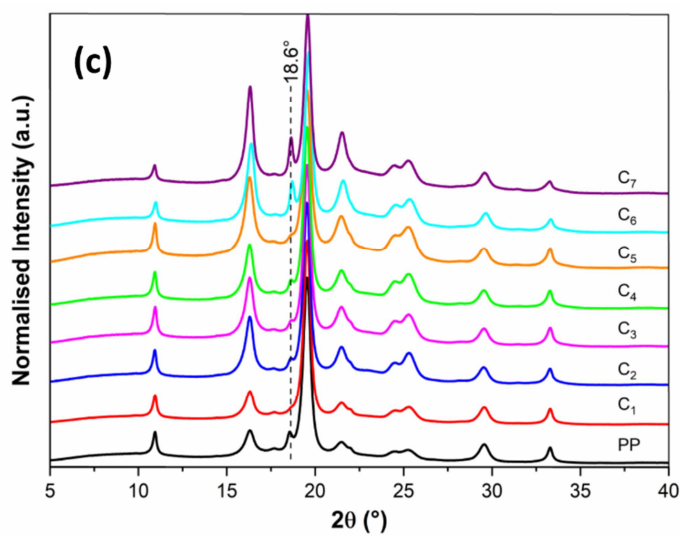
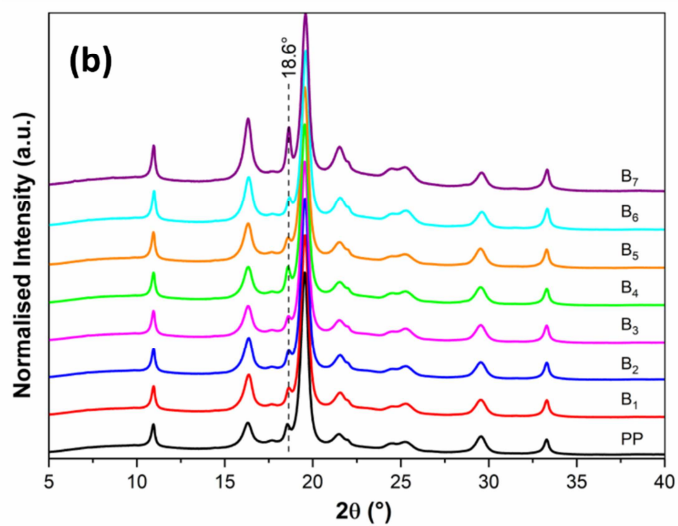
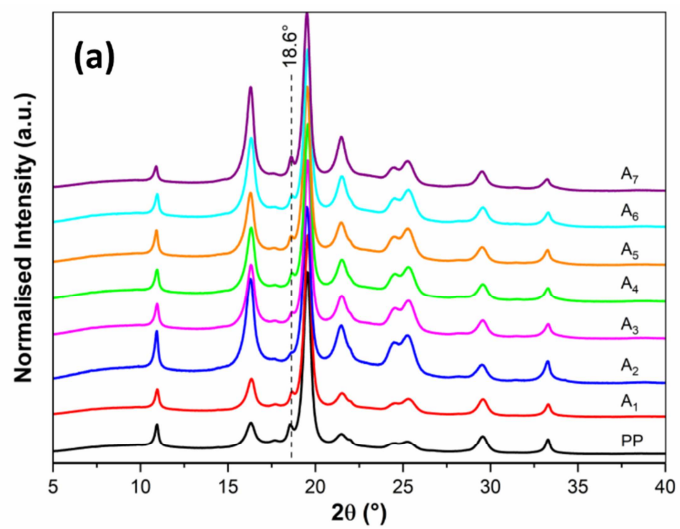


Figure 3. WAXD diffractograms for unfilled PP and for composites of (a) PP and MWCNTs (b) P[LA] modified PP and (c) PP and P[LA] modified MWCNTs.

The normalised diffractograms shown in Figure 3 b) and c) show the evolution of a peak at about 18.6° which is associated with the (300) basal plane of the β -polymorph of PP. This peak is present but at lower intensities in the diffractograms for the composite of PP with as received MWCNTs (Figure 3 a), confirming the co-crystallisation of PP with P[LA], as expected. Moreover, the intensity of the doublet centred around 25° increased with increasing P[LA] content, particular the peak at lower 2θ which is derived from the (301) basal plane of the β -polymorph of PP.

Table 2. Calorimetric data observed from DSC and crystalline content (X_c) determined from DSC and WAXD for PP and composites of PP, P[LA] and MWCNTs.

Sample	T_m^a ($^\circ\text{C}$)	T_c^b ($^\circ\text{C}$)	ΔH_m^c (J/g)	ΔH_c^d (J/g)	X_c^e (%)		FWHM _m ^f ($^\circ\text{C}$)	FWHM _c ^g ($^\circ\text{C}$)
					DSC	WAXD		
PP	163	125	-105.5	104.5	51.0	36.6	12.0	5.9
A ₁	161	122	-104.2	102.0	50.3	36.3	12.7	5.6
A ₂	160	123	-101.5	98.8	49.0	31.2	12.8	5.2
A ₃	161	125	-102.5	100.7	49.6	31.7	12.3	4.7
A ₄	162	125	-103.0	101.6	50.0	32.9	10.7	4.2
A ₅	163	125	-103.2	102.5	50.3	33.0	14.6	5.9
A ₆	165	127	-101.9	101.1	50.7	31.3	15.3	7.7
A ₇	167	129	-100.3	99.1	51.0	28.3	16.1	7.1
B ₁	163	124	-103.5	104.0	50.0	38.4	14.2	5.3
B ₂	164	124	-100.6	103.1	48.8	37.7	18.0	5.7
B ₃	164	124	-98.4	101.8	48.1	37.1	20.0	6.5
B ₄	164	123	-96.6	100.6	47.6	36.7	23.1	6.5
B ₅	163	125	-93.5	98.2	47.0	35.5	12.5	4.5
B ₆	162	124	-85.5	89.8	46.9	32.9	11.7	4.7
B ₇	162	124	-78.5	81.9	47.4	29.0	13.0	4.8
C ₁	163	124	-105.2	103.3	50.8	37.0	12.7	5.2
C ₂	162	123	-103.2	101.2	50.1	33.5	11.5	4.8
C ₃	164	127	-103.3	101.3	50.6	32.2	13.0	5.2
C ₄	164	127	-103.0	101.4	51.0	32.1	13.8	5.4
C ₅	163	126	-101.7	99.9	51.7	28.3	15.2	5.7
C ₆	163	125	-91.9	90.7	52.2	29.7	15.2	8.0
C ₇	163	124	-82.8	82.9	53.3	28.3	15.8	7.2

^a T_m = melting temperature.

^b T_c = crystallisation temperature.

^c ΔH_m = melting enthalpy.

^d ΔH_c = crystallisation enthalpy.

^e X_c = degree of crystallinity computed from equation: $X_c = (\Delta H_m / (1 - W_f) \Delta H_{100}) \times 100$ where W_f is the weight fraction of filler and ΔH_{100} is the melting enthalpy of a theoretically 100% crystalline PP (-207.1 J/g).

^f FWHM_m = full width at half height of melting curve.

^g FWHM_c = full width at half height of cooling curve.

Table S1 lists the Young's modulus, yield strength, fracture strength and elongation at break for composites of PP and unmodified MWCNTs, PP and P[LA] and, PP and P[LA] modified MWCNTs. The addition of P[LA] modified MWCNTs resulted in a reduction in Young's modulus (~ -50%), yield strength (~ -50%) and fracture strength (~ -30%) compared to neat PP. However, an increase in elongation at break (~ 50%) was observed compared to unmodified MWCNTs for 5 wt% loading. With the exception of elongation at break, all other results showed a decrease in mechanical properties compared to the PP matrix. Clearly, the addition of P[LA] results in plasticisation of PP concomitantly assisting MWCNT dispersion and distribution in the PP matrix.

The Young's modulus (E) of PP (1.456 GPa) was not significantly altered by the addition of just MWCNTs up to a loading of 5 wt%, but a 50% increase in fracture strength, little change in yield strength and a 98% reduction in elongation at break was recorded. Unsurprisingly, the addition of unmodified MWCNTs even at modest loadings embrittled the PP as effective stress transfer at the interface between CNTs and polymer matrix is limited. The addition of P[LA] modified MWCNTs to PP resulted in a ~50% decrease in E , yield strength and fracture strength and, a reduction in elongation at break of about 80 %, some 18 % below that obtained when unmodified MWCNTs were added at the same 5 wt% loading. Presumably, the P[LA] is having a plasticising effect on PP as well as promoting interfacial interaction between the MWCNTs and PP chains, facilitated by wrapping/coating of the P[LA] via CH- π interactions, Figure 1 c) and d). To understand this behaviour further the tensile properties of blends of PP and P[LA] (B group) were measured, where the P[LA] content was similar to that for the composites with P[LA] modified MWCNTs. For these blends, addition of P[LA] to PP resulted in a 50 % decrease in stiffness and strength of PP, about a 20 % decrease in fracture strength, but critically

little change in elongation at break until the P[LA] content was greater than 4 wt%. The ductility and toughness of PP is retained upon P[LA] addition. This plasticising effect can be more clearly observed by examining representative stress-strain curves for the three sets of composites, Fig. 4. The area under the stress-strain curves decreased significantly on addition of MWCNTs alone, but is recovered with increasing P[LA] content in the composites. The critical MWCNT loading at which the effect of P[LA] inclusion can be observed to be between 0.5 and 1 wt%, Figure 5. The ductility of PP can be seen to be recovered on addition of 1 wt% MWCNTs and greater than 4 wt% P[LA], Figure 5 d). It is noteworthy that the change in mechanical properties described originate with CNT and P[LA] addition to PP and not as a consequence of thermal degradation of the components during melt mixing. Previously, we have investigated the thermal stability of P[LA] and its composites with MWCNTs.^[26] Our studies confirmed that P[LA] is thermally stable at PP processing temperatures and the addition of P[LA] modified MWCNTs has no effect on the thermal stability of PP at its typical processing temperature of ~ 165 °C. Interestingly, the thermally stability of PP increased on addition of MWCNTs but the addition of P[LA] modified MWCNTs had no effect.^[26] It is likely this behaviour is a consequence of both the known free radical scavenging ability of MWCNTs being altered on P[LA] addition and that P[LA] degrades forming high concentrations of free radicals.

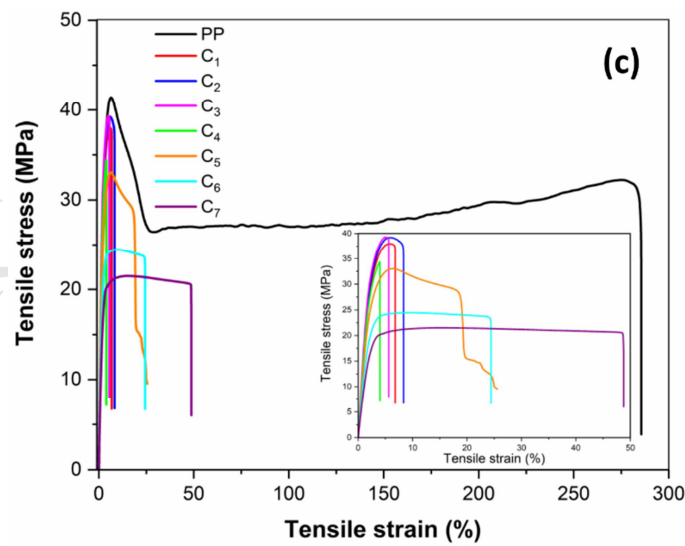
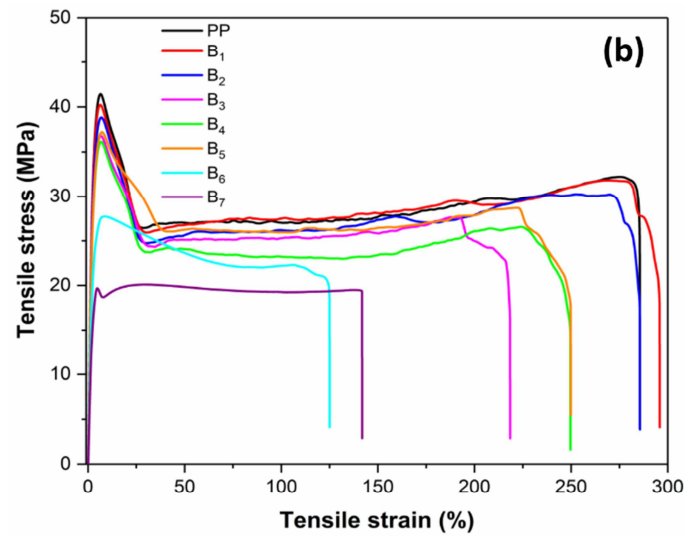
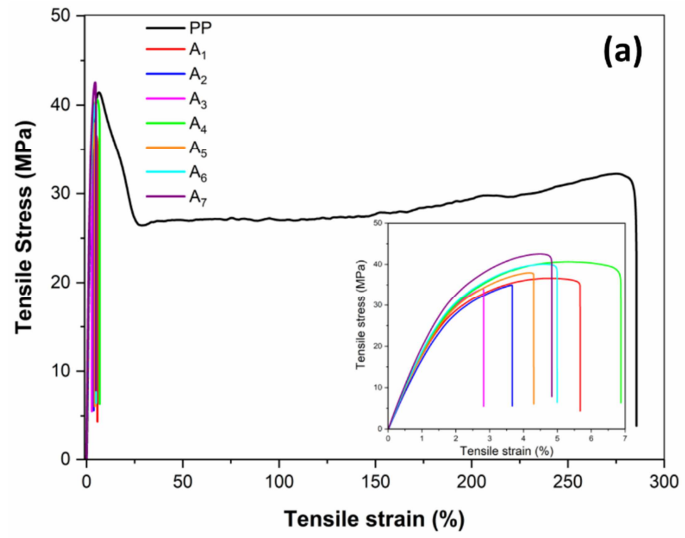


Figure 4. Representative stress vs strain curves for: (a) PP and composites of PP and MWCNTs, (b) P[LA] modified PP and (c) PP and composites of PP and P[LA] modified MWCNTs.

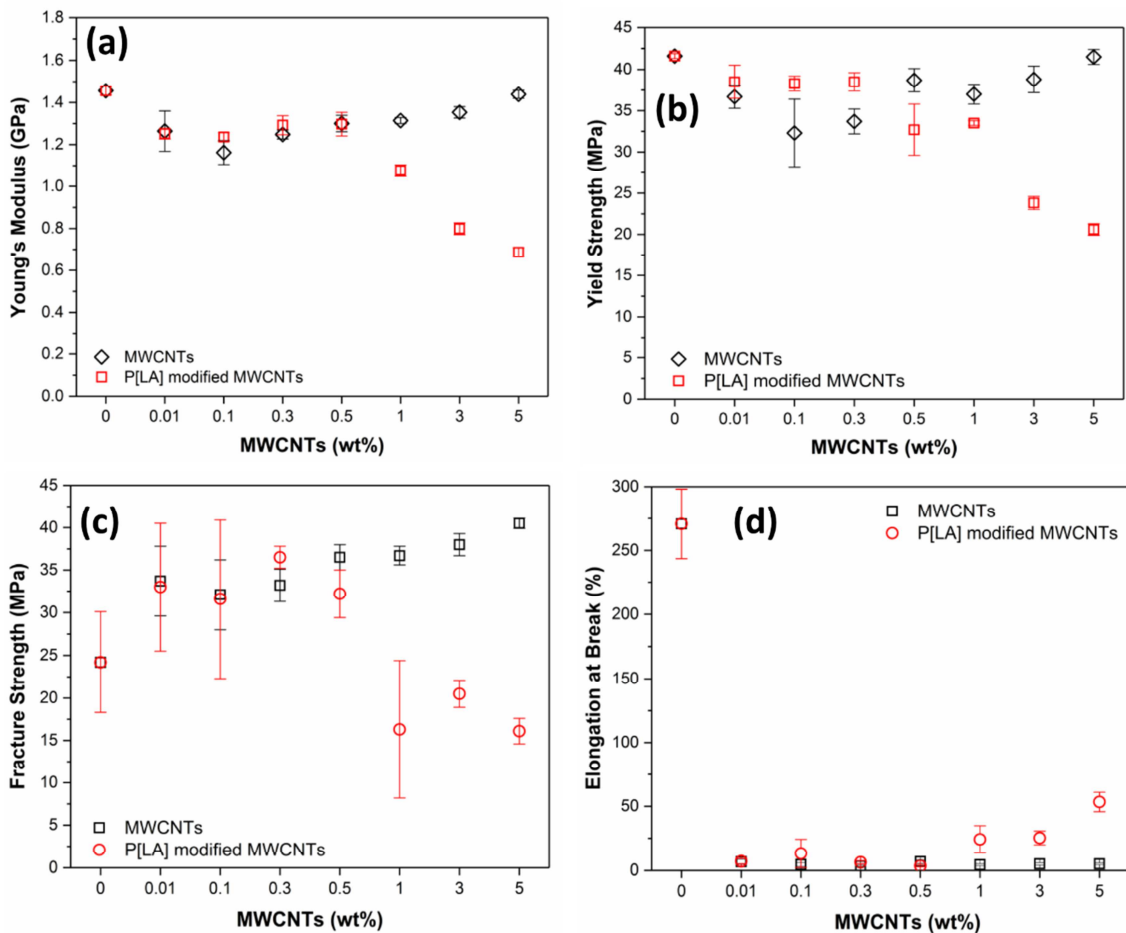


Figure 5. Variation in, (a) Young's modulus, (b) yield strength, (c) fracture strength and (d) elongation break, as a function of MWCNT and P[LA] modified MWCNT loading.

The change in interfacial tension between P[LA] and MWCNTs and the plasticising of PP by P[LA] can also be indirectly proven by studying the changes in the dynamic mechanical properties, in particular the glass temperature (T_g), of PP and composites of PP and MWCNTs on addition of P[LA]. Figure 6 shows the variation in $\tan \delta$, E' and E'' as a function of temperature

for the various composites with and without P[LA] addition. From all three sets of data, irrespective of how the T_g is measured, i.e. peak onset or maxima in $\tan \delta$, corresponding decrease in E' or peak maxima in E'' , the incorporation of P[LA] in to these composite materials results in a significant decrease in T_g , see Figure 7, between 15 °C to 35 °C. The decrease in T_g is first observed when the MWCNT loading is about 0.1 wt% and thus the P[LA] content 0.4 wt%. However, for a loading of 5 wt% MWCNTs, but critically 20 wt% P[LA], the reduction in T_g of PP is shifted to lower temperatures by as much as 35 °C. This result is most interesting given the technological goal of extending the application of PP hitherto hindered by the relatively poor low temperature (< -20 °C) impact properties of PP.

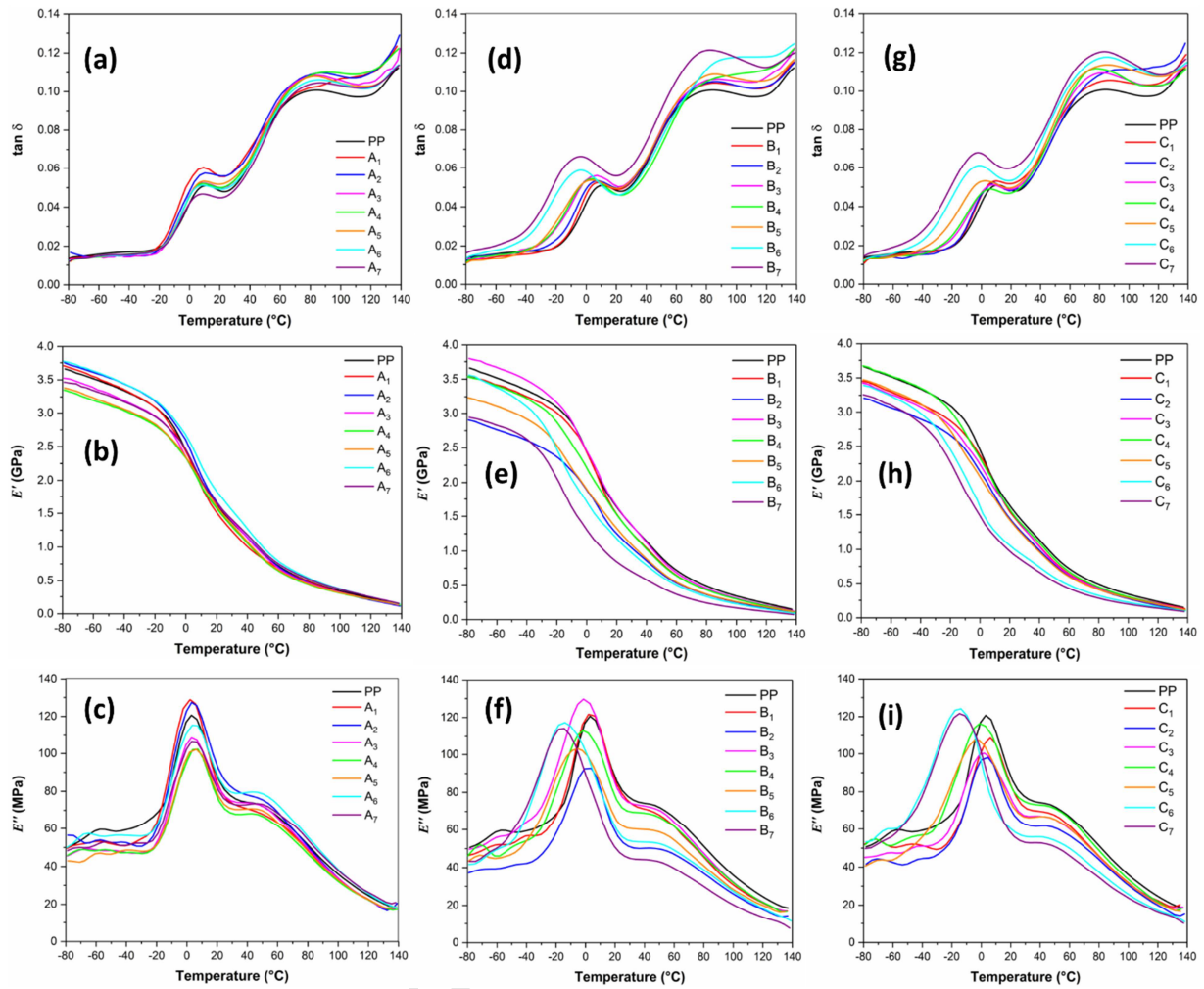


Figure 6. Variation (at 1 Hz) of a) $\tan \delta$, b) E' , c) E'' as a function of temperature for PP and composites of PP and MWCNTs. Variation (at 1 Hz) of d) $\tan \delta$, e) E' , f) E'' as a function of temperature for PP and composites of PP and P[LA]. Variation (at 1 Hz) of g) $\tan \delta$, h) E' , i) E'' as a function of temperature for PP and composites of PP and P[LA] modified MWCNTs.

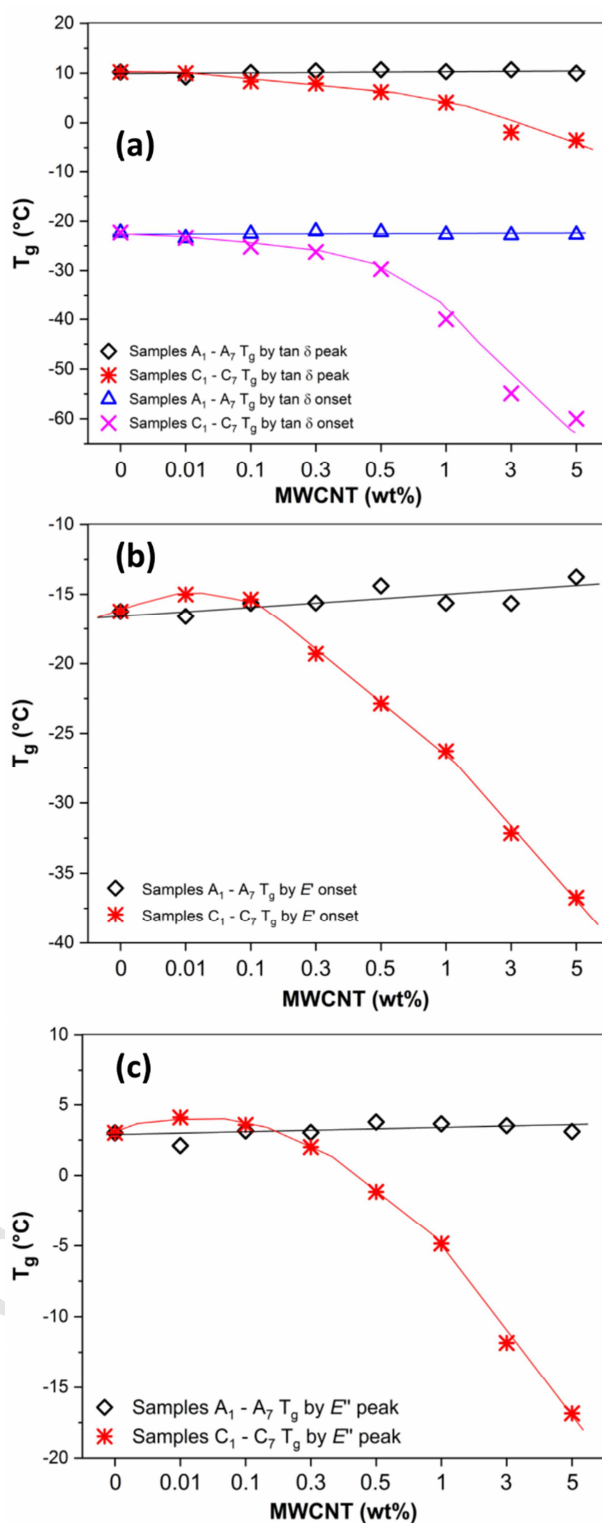


Figure 7. Change in T_g determined from a) $\tan \delta$ peak and $\tan \delta$ onset, b) $\Delta E'$ onset and c) E'' peak for composites of PP and MWCNTs and composites of PP and P[LA] modified MWCNTs.

Clearly the addition of P[LA] alters PP chain dynamics and interfacial interactions between the MWCNT filler and PP resulting in enhanced MWCNT dispersion, Figure 1 and, ultimately, this effects the viscoelastic properties of PP. Since CNTs have an extremely high aspect ratio (length-to-diameter) up to 1000, they have an ability to influence the rheological properties of polymer melts at very low loadings by hindering polymer chain dynamics. On MWCNT addition to polymers a dramatic increase in the storage modulus (G') and complex viscosity ($|\eta^*|$) as well as the detection of an apparent yield strength at low frequencies (< 1 rad/s) is typically observed. A 'pseudo-solid' like behaviour is observed upon formation of a percolated MWCNT network and the extent of filler dispersion, aspect ratio and alignment can all be related to changes in (nano)composite viscoelasticity.^[46]

At low frequencies (e.g. $\sim\omega = 0.1$ rad/s) G' , $|\eta^*|$ and $\tan\delta^{-1}$ all increase with increasing MWCNT loading, G' by about 5 and $|\eta^*|$ by about 3 orders of magnitude on addition of 5 wt% MWCNTs, figures 8 a), b) and c). The formation of a plateau at low frequency for G' and the increase in $|\eta^*|$ and $\tan\delta^{-1}$ as a function of frequency occurred at some MWCNT loading between 0.3 wt% and 0.5 wt%. A more accurate estimate for the rheological percolation can be obtained from constructing Cole-Cole (i.e. G' versus G'' and η'' versus η') and Van Gorp-Palmen (phase angle δ versus $|G^*|$) plots, see figure 8 d), e) and f). The onset in the deviation from the linear relationship between G' and G'' and η'' and η' and the decrease in phase angle δ as a function of $|G^*|$ suggests the rheological percolation is closer to 0.5 wt%. The MWCNTs are relatively well dispersed in the PP matrix and the PP relaxation times increase (see figure 8e)) with increasing MWCNT loading as the MWCNTs hinder polymer chain mobility.

The effect of P[LA] addition on the viscoelastic response of PP and composites of PP and MWCNTs and, rheological percolation can be seen in figure 9. From the plots of G' , $|\eta^*|$ and

$\tan\delta^{-1}$ as a function of frequency, the onset of rheological percolation appears to be closer to 0.3 wt% MWCNTs. Likewise from the Cole-Cole and Van Gorp-Palmen plots for the composites of PP with P[LA] modified MWCNTs (figure 9 d), e) and f)), incorporation of P[LA] enhanced the MWCNT dispersion and distribution in the PP matrix resulting in a lower rheological percolation. Above percolation a large increase in $|\eta^*|$ was also observed, see figure 9 b). The effect of P[LA] itself on the viscoelastic response of the PP used in this study was isolated by performing the same oscillatory rheology measurements, see supporting information Figure S2. As might be expected the addition of up to 20 wt% P[LA] to PP resulted in an decrease in G' and $|\eta^*|$ as a function of frequency as well as PP relaxation times, further confirmation of the plasticising efficiency of P[LA] for PP.

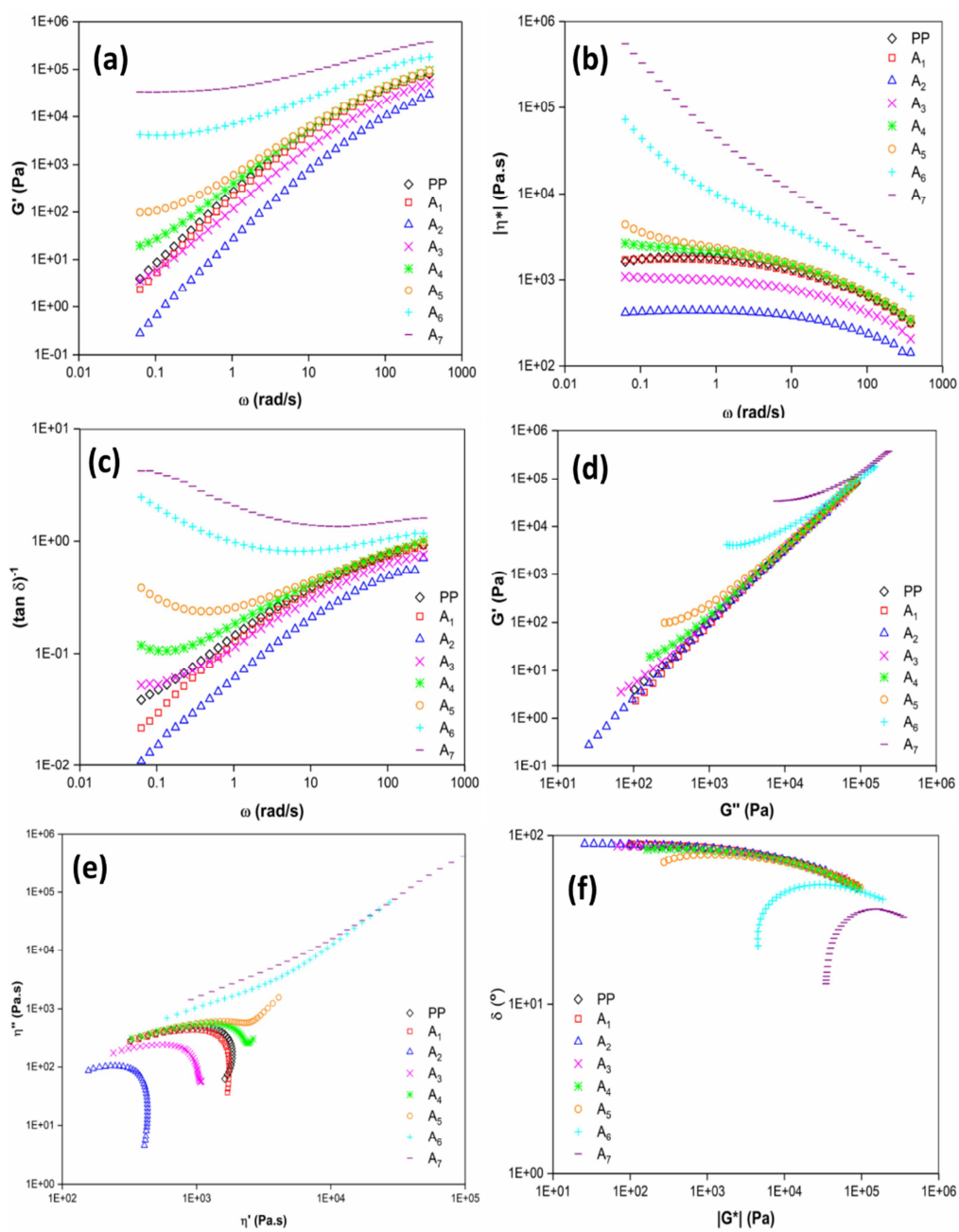


Figure 8. Variation in (a) storage modulus (G'), (b) complex viscosity $|\eta^*|$ and (c) reciprocal of loss tangent ($(\tan \delta)^{-1}$) as a function of angular frequency (ω), (d) Cole-Cole plot (G' versus G''), (e) imaginary viscosity (η'') with real viscosity (η') and (f) phase angle (δ) with the absolute value of ($|G^*|$) (Van Gurp-Palmen plot) for unfilled PP and composites of PP and MWCNTs.

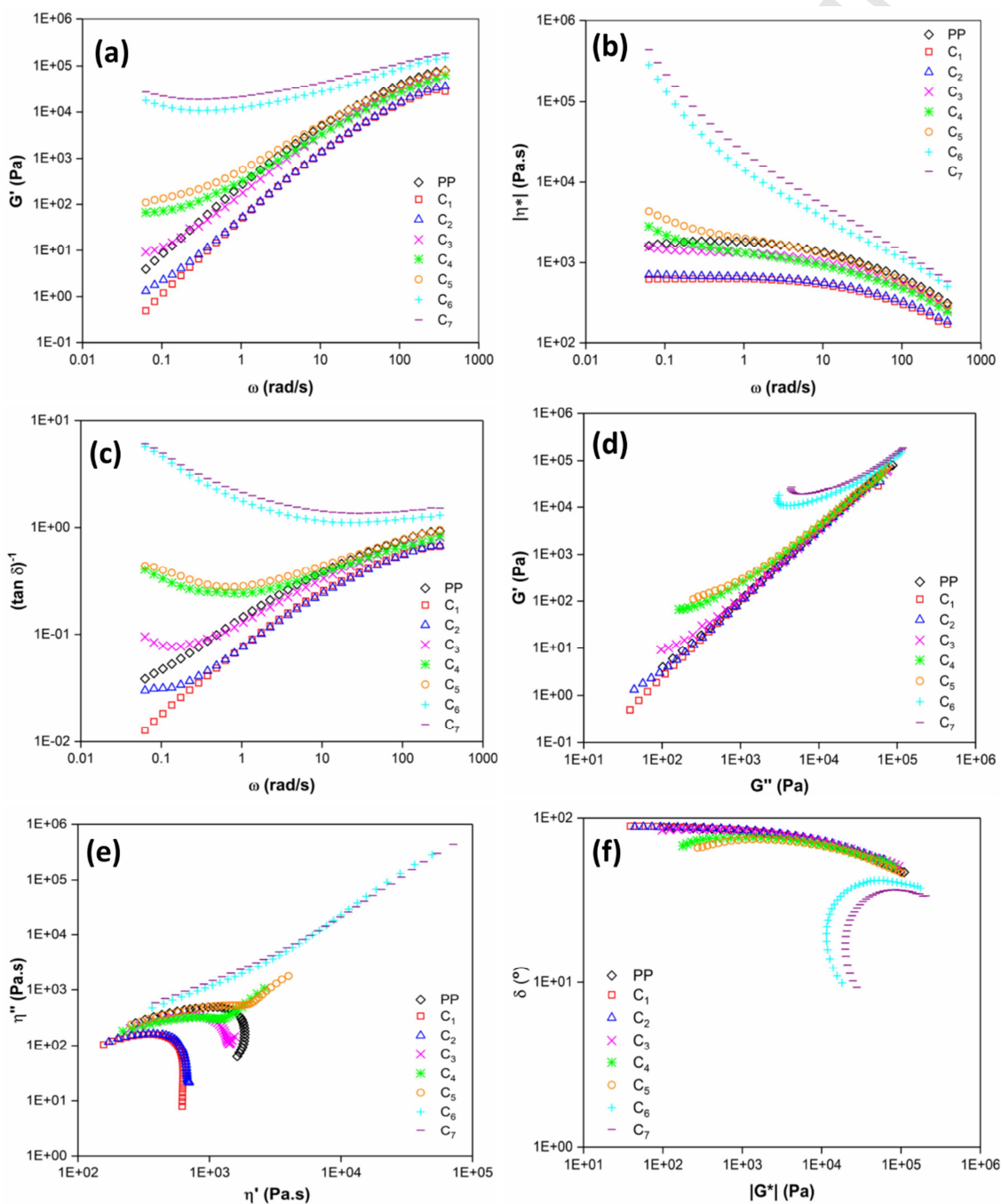


Figure 9. Variation in (a) storage modulus (G'), (b) complex viscosity $|\eta^*|$ and (c) reciprocal of loss tangent ($(\tan \delta)^{-1}$) as a function of angular frequency (ω), (d) Cole-Cole plot (G' versus G''), (e) imaginary viscosity (η'') with real viscosity (η') and (f) phase angle (δ) with the absolute value of ($|G^*|$) (Van Gorp-Palmen plot) for unfilled PP and composites of PP and P[LA] modified MWCNTs.

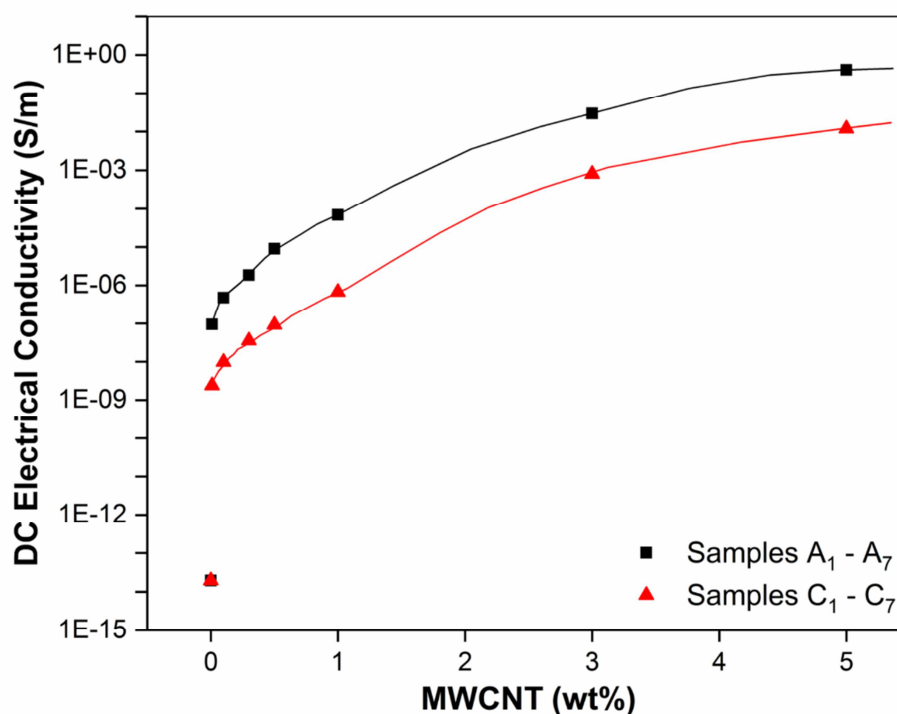


Figure 10. DC electrical conductivity of composites as a function of MWCNT concentration at RT.

If our hypothesis is correct in that non-covalent functionalisation is a route to enhanced interfacial interactions between PP and MWCNTs without altering the intrinsic electron conduction properties of 1D/2D graphitic materials, then it could be expected the introduction of

P[LA] should minimally impact the electrical conductivity of composites of PP and MWCNTs. Figure 10 shows the DC electrical conductivity (RT) of PP itself and composites of PP with MWCNTs and P[LA] modified MWCNTs as a function of MWCNT loading. PP is an insulator ($\sim 1 \times 10^{-14}$ S/m), but the incorporation of 5 wt% MWCNTs resulted in an increase in electrical conductivity of ~ 15 orders of magnitude, to 10^1 S/m. At low MWCNT loading (< 0.3 wt%), there is an initial significant increase in conductivity of about 8 orders of magnitude followed by a further but more gradual increase in conductivity by about 7 orders, suggesting a double percolation phenomenon. Similar behaviour was also observed for the composites with P[LA] modified MWCNTs however, the ultimate values for conductivity were only about 2 orders of magnitude less than that obtained for the composites with unmodified MWCNTs. While the addition of P[LA] improved MWCNT dispersion in the PP matrix, the MWCNTs were in part insulated from each other by the wrapping of the MWCNTs with P[LA] via CH- π interactions.

4. Conclusions

MWCNTs were non-covalently functionalised by surface wrapping of P[LA] synthesised using Cu(0)-mediated LRP and mixed with MWCNTs prior to the manufacture of composites of PP, MWCNTs and P[LA], (1:4, MWCNT:P[LA]). SEM and TEM images showed the MWCNTs were homogeneously dispersed within the PP matrix. Addition of P[LA] appears to improve the extent of MWCNT dispersion and distribution for a P[LA]:MWCNTs of 4:1. HRTEM also confirmed the P[LA] coats or wraps the MWCNTs. This is likely by a combination of CH- π interactions and physical wrapping of the polymer around the CNTs.

The Young's modulus of PP was unaffected on addition of MWCNTs, but decreased significantly with loadings of P[LA] greater than 2 wt% however, the elongation at break

increased by over 50% upon addition of P[LA] modified MWCNTs in a ratio of 1:4 ratio, evidence that P[LA] has a plasticisation effect on PP.

Rheological investigations confirmed the formation of a MWCNT network with a percolation threshold of about 0.5 wt% for unmodified MWCNTs. This percolation threshold was reduced to ~0.3 wt% after the addition of P[LA] modified MWCNTs, again in a 1:4 ratio indicating the P[LA] aided the dispersion of MWCNTs in the PP matrix.

T_m and T_c increased by ~ 4 °C for a loading of 5 wt% unmodified MWCNTs, evidence the CNTs can nucleate PP. Upon functionalisation with P[LA], the P[LA] coating hinders MWCNT nucleation and PP crystallinity decreased at higher filler loadings. The addition of P[LA] resulted in a significant decrease in the T_g of PP, to between 15 and 25 °C. This is further evidence that P[LA] effectively reduced the T_g by plasticising PP.

WAXD results indicate the P[LA] is behaving as a α -nucleating agent though the observed increase in intensity of the peak at $2\theta = 18.6^\circ$ corresponding to the hexagonal $\alpha(300)$ for both composites of PP and P[LA] functionalised MWCNTs and composites of PP and P[LA]. However, the β -polymorph is also present in the composites with P[LA] modified MWCNTs which was induced by the inclusion of the P[LA] and not the MWCNTs. Also, there is evidence from the published literature for the β -polymorph being more prominent in low molecular weight (high MFR) PP, as used in this study.

The DC electrical conductivity of PP was increased by about 15 orders of magnitude on addition of 5 wt% unmodified MWCNTs. However, the electrical conductivity of the composites of PP and P[LA] modified MWCNTs was only 2 orders of magnitude less than that obtained for composites with as received MWCNTs, across the composition range. The data suggests a double percolation effect for both sets of composites.

Author Information

Corresponding author.

E-mail: t.mcnally@warwick.ac.uk

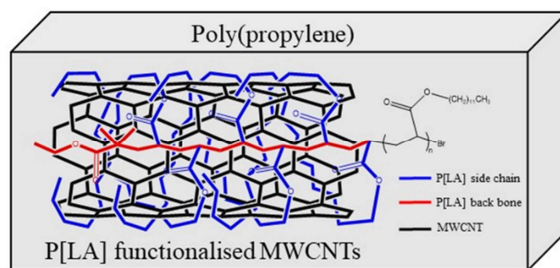
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TOC Graphic

Highlights

- Poly(lauryl acrylate) P[LA] non-covalently functionalised MWCNTs
- P[LA] altered interfacial interactions between neighbouring MWCNTs
- Rheological percolation was reduced by halve on inclusion of P[LA]
- P[LA] plasticised PP and decreased the T_g of PP by up to 25 °C.
- Non-covalent functionalisation of MWCNTs with P[LA] marginally degraded conductivity