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Poly(lauryl acrylate) and poly(stearyl acrylate) grafted multiwalled carbon nanotubes for polypropylene composites

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ABSTRACT

Two new polymer grafts on an industrial grade multiwalled carbon nanotube (MWCNT) were prepared through a non-oxidative pathway employing controlled free radical polymerization for surface initiated polymer grafting. After photochemical introduction of an ATRP initiator onto the MWCNT, polymerizations of lauryl or stearyl acrylate were performed, resulting in two novel polymer modifications on the MWCNT (poly(lauryl acrylate) or poly(stearyl acrylate)). The method was found to give time dependent loading of polymers as a function of time (up to 38 wt% for both acrylates), and showed a plateau in loading after 12 h of polymerization. The modified nanomaterials were melt mixed into polypropylene composites with very low filler loading (0.3 wt%), whereafter both the thermal and electrical properties were investigated by DSC and dielectric resonance spectroscopy. The electrical properties were found to be substantially improved, where poly(lauryl acrylate) was found to be the superior surface modification, resulting in a conductive composite.

1. Introduction

Polymer composites with carbon nanotubes (CNT) are promising candidates for development of new materials with superior properties. A focused development has been going on in the area of nanocomposites during the recent decades, where numerous new materials have been developed [1,2]. However, the major challenges in preparation of nanocomposites are still dispersion or distribution of the filler in the polymer matrix of choice, as well as to obtain good interaction between the filler and the matrix.

The dispersion of the filler can to some extent be improved through mechanical treatments of the composites e.g. through multiple extrusions of the composite mixture. However, this will not improve the interaction with the matrix, since this is related to the chemical difference between the surface of the filler and the polymer matrix. Generally, there is an acceptance that in order to improve the interaction between a filler and the polymer matrix a surface modification of the filler is necessary [3]. Such a surface modification can take place through a number of processes [4,5], where CNTs are modified through either an oxidative (acid treatments) or a non-oxidative approach (e.g. free radical grafting). Both methods have extensively been used, however, both methods also suffer from different weaknesses. The oxidative process conveniently results in the formation of alcohols or acids on the surface of the CNT that can easily be converted to numerous functional groups and thereby create the basis for a better interaction between the filler and the matrix. However, it is also well documented that the oxidative process results in scission of the CNT and substantial defect formation, which causes a reduction in the conjugation length on the CNT as well as a more open structure [6–8]. Comparatively, the non-oxidative methods can be used to introduce functional groups or polymers through radical chemistry. The advantage of this approach is that the conjugation length of the CNT is preserved, though it generally affords lower loading and a less efficient grafting.

In order to improve the efficiency of different surface modifications, polymerization from reactive groups on the surface has been applied to prepare polymer grafted nanoparticles [9,10]. Polymer grafts by controlled radical methods have been prepared through nitroxide mediated polymerization (NMP) [11], reversible addition fragmentation chain transfer polymerization (RAFT) [12,13] and atom transfer radical polymerization (ATRP) [14–19]. However, there are few examples of controlled polymerizations being performed on an activated CNT that has not been oxidized at some point in the preparation [20–22].

The purpose of the present study has been to investigate the efficiency of two different polymer modifications on an industrial grade MWCNT. The approach was based on a non-oxidative radical

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method to obtain polymer composites that would allow the composites to potentially be applied for electronic applications such as e.g. electrostatic charge dissipation. It has earlier been shown that a poly(ethylene-co-butylene) (PEB) modified MWCNT gave improved dispersability as well as improved conductive properties in polypropylene (PP) compared to a non-modified MWCNT [23]. The PEB modified MWCNT was prepared through a grafting to approach, allowing for a moderate loading. Therefore it was interesting to see if an increased loading from a similar type of compatibilizer would result in even further improved compatibility or conductivity. In addition to this, it is well known from the literature that strengthening of PP is closely related to its semicrystallinity. PEB is an amorphous polymer that would be expected to have little influence on the crystallinity and therefore modifications that could influence the crystallization behavior close to the filler would be interesting alternatives.

To complement the findings from the PEB modified MWCNT two different acrylate monomers that would permit a higher loading through polymerization were selected. The long apolar sidechain in lauryl and stearyl acrylate is expected to facilitate good compatibility based on the structural similarity to PP. Poly(lauryl acrylate) (PLA) [24,25], poly(stearyl acrylate) (PSA) [26,27] and copolymers [28] of these have been prepared through controlled radical methods. Both monomers have been grafted onto silica surface through ATRP [29,30], on the other hand there are currently no reports of either monomer being grafted to an MWCNT. In addition to this, PLA and PSA are both semicrystalline and exhibit melting transitions close to room temperature (PLA has $T_m = 0$ °C and PSA has $T_m = 35$ °C for homopolymers) [31]. The hypothesis was that the similarity of the sidechain in the respective acrylates to the PP structure might induce an improved compatibility or synergy with PP. It would also be interesting if the presence of the different types of crystal phases could interact with the crystal phases of PP to improve the interaction between the filler and the matrix.

Here the first preparation of PLA and PSA grafted MWCNT by ATRP is presented. The two different polymer modifications on MWCNT are tested in PP composites to elucidate their efficiency for compatibilization.

2. Experimental

2.1. General methods and materials

MWCNTs with an average diameter of 9.5 nm and average length of 1.5 μm were purchased from Nanocyl S. A. (NC7000, Belgium) and were used as received. Isotactic PP was acquired from Lyondellbasell (HM562S, melt flow rate 30 g/10 min). All other chemicals were purchased from Aldrich and used as received.

Fourier transform infrared spectroscopy (FT-IR) was performed on a Thermo-Fischer is 50 FT-IR with a universal attenuated total reflection (ATR) sampling accessory on a diamond crystal. Differential scanning calorimetry (DSC) was performed on a DSC Q1000 from TA Instruments. The thermal analyses were performed at a heating and cooling rate of 10 K/min. The melting temperatures (T_m) are reported as the peak temperatures of the endothermic melting peaks. Glass transition temperatures (T_g's) were measured at the inflection point on the second heating cycle. Thermogravimetric analysis (TGA) was performed on a TA instruments TGA Q500 from 25 to 700 °C at 10 K/min under nitrogen flow. Scanning electron microscopy (SEM) was performed on a Quanta 200F from FEI Instruments. Ultra sonication was performed with a Hielscher UP200S. Extrudates were prepared on a Haake mini lab extruder (7 min @ 50 RPM). Raman spectra were recorded on a Thermo DXR dispersive Raman microscope with a 780 nm laser. Dielectric resonance spectroscopy (DRS) was performed on a Novocontrol Alpha-A high performance frequency analyzer.

2.1.1. Poly(lauryl acrylate)–MWCNT, general polymerization procedure

Initiator modified MWCNT (MWCNT-Br [22], 0.3 g) was mixed with DMF (30 mL) and sonicated for 30 s to form a stable dispersion. LA (15 mL, 13.26 g, 0.055 mol), CuBr (0.035 g, 0.24 mmol) and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 0.125 mL, 0.104 g, 0.6 mmol) was added to the dispersion and nitrogen was bubbled through for 20 min. The reaction was kept under nitrogen and placed in an oil bath at 90 °C for the polymerization time (24 h). After polymerization the dispersion was diluted with dimethylformamide (DMF, 100 mL) and filtered to remove residual monomer and catalyst. The crude was purified by repeated dispersion in dichloromethane (DCM, 100 mL) followed by filtration (3 times) and finally dried *in vacuo*. The obtained product was a viscous black solid isolated in quantitative yields (polymer loading by TGA was 37.4 wt%, $T_m = 0.7$ °C).

3. Results and discussion

An industrial grade MWCNT was prepared for grafting by atom transfer radical polymerization (ATRP) through a recently developed two step method [22]. Briefly, the pristine MWCNT was dispersed in toluene with benzophenonyl 2-bromoisobutyrate and the slurry was irradiated with a UV source (365 nm) for 30 min. After purification of the tubes the radical modification of the MWCNT was confirmed by Raman spectroscopy, where an increase in the D/G ratio supports the covalent attachment of the initiator [22]. The amount of initiator that is reacted onto the MWCNT can be increased through numerous wetting and irradiation steps. Here a constant irradiation procedure (one wetting and one UV irradiation step of 30 min at 365 nm) was chosen for investigation of the polymer grafting by ATRP. The prepared initiator (MWCNT-Br) could subsequently be used for surface initiated ATRP as illustrated in Scheme 1.

The MWCNT-Br was grafted with LA or SA employing CuBr as the catalyst and PMDETA as the ligand through surface initiated ATRP. The prepared PLA or PSA grafted materials were investigated by scanning electron microscopy (SEM) as shown in Fig. 1, respectively.

As can be seen from the SEMs, there are clearly polymer material covering the MWCNT completely for both PLA and PSA grafted MWCNT. The nature of the polymer grafts was confirmed by FT-IR as shown in Fig. 2.

In the IR spectra shown in Fig. 2 there are peaks originating from the polymer grafting, such as stretches from CH, CH_2, CH_3 at 2800–3100 cm^{-1}, from the carbonyl in the acrylate ester at 1739 cm^{-1} as well as a small peak from the ether stretches in the ester at 1100 cm^{-1}. In addition to this, there are also some common features visible in all spectra, such as the set of peaks at 1900 and 2100 cm^{-1}, which must be originating from the MWCNT and are tentatively assigned to the C–C stretches in the MWCNT structure (as is seen for diamond). For the pristine material (spectra not shown) and the initiator grafted MWCNT (MWCNT-Br) there are additionally a set of low intensity peaks visible at 3900 cm^{-1}. These peaks are too high in wavenumbers to correlate with water or amines, and are speculated to be related to the MWCNT structure and could be an overtone coming from the bands at around 1900 cm^{-1}.

In all the spectra of the grafted MWCNTs significant changes can be observed as the polymerization time is increased. The differences in the spectra clearly correlate to the increase in polymerization time and relate directly to the polymer modification (increases in the ester and CH, CH_2, CH_3 stretches). There is a