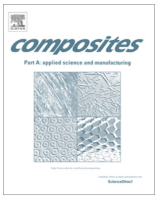
Composites: Part A 80 (2016) 13–20

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa



Conductive polyolefin–rubber nanocomposites with carbon nanotubes

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ARTICLE INFO

Article history:
Received 19 May 2015
Received in revised form 1 October 2015
Accepted 3 October 2015
Available online 8 October 2015

Keywords:
A. Polymer-matrix composites (PMCs)
B. Mechanical properties
B. Electrical properties
D. Electron microscopy

ABSTRACT

Polyolefin–rubber composites of differing compositions were formed by melt mixing linear low density polyethylene (LLDPE) and functionalised rubber particles (FRP) through interactions of pre-functionalised polymers in the interface. Following the incorporation of carbon nanotubes to the polymeric composites the nanocomposites filaments were extruded for fused deposition modelling (3D printing). The mechanical properties of the composites (tensile and flexural modulus, yield stress, tensile strength, elongation at break) were compared with respect to how the test specimens were made: compression moulding versus 3D printing. The results showed that increasing the rubber content concentrated the nanotubes in the LLDPE phase forming electrically conductive pathways. The use of maleic anhydride as a compatibilizer improved the mechanical properties of the composites overall. The 3D printed specimens had lower mechanical properties than the compression moulded specimens, though they had the same electrical conductivity.

1. Introduction

Recycling of rubber tyres has gained importance due to environmental and legislative regulations that restrict and even ban their disposal in landfill. Used tyres have been cryogenically granulated to produce ground tyre rubber (GTR) and successfully down-cycled into various secondary products. The GTR can also be de-vulcanised to form reclaimed rubber which can be up-cycled into value-added product. One way to up-cycle the reclaimed rubber is to incorporate it with thermoplastics such as polyolefins to form thermoplastics elastomers for applications requiring a toughened composition. However, formation of successful composites of polyethylene and reclaimed rubber has been hindered by poor adhesion between the rubber particles and the thermoplastic matrix. The use of various compatibilizers and surface activation of the de-vulcanised rubber particles have been considered as possible solutions.

Meszaros et al. have studied the contribution of poly(ethylene-*co*-vinyl acetate) (EVA) as compatibilizers of low density polyethylene (LDPE) in combination with GTR. They found that increasing EVA content increased tensile modulus and elongation at break; creating tougher more resilient materials. SEM images showed that EVA ensured better adhesion between the matrix and the GTR particles [1]. Qin et al. prepared a range of LLDPE–GTR composites and studied the influence of different copolymer compatibilizers such as poly(styrene-*b*-butadiene-*b*-styrene) (SBS), poly(ethylene-*co*-n-butyl acrylate-*co*-carbon monoxide) (E-nBA-CO), as well as an EVA. Each of the copolymers increased the elongation at break of the composites. The increase was greatest for the SBS copolymer since it has a similar chemical composition to GTR and LLDPE, whereas EVA and E-nBA-CO have polar carbonyl in their structure and are less miscible. It was reasoned that the probable chemical interaction between SBS and GTR may lead to improved compatibility and better dispersion of the rubber particles in the LLDPE matrix, thereby improving tensile properties, especially elongation at break. The morphology and structure of the composites were investigated using atomic force microscopy and differential scanning calorimetry, and revealed interfacial roughening of the rubber particles and good interfacial adhesion between the polyethylene and rubber phases [2].

Ayyer et al. have studied the contribution of a compatibilizer in improving the mechanical performance of a composite of cryogenically ground micronized rubber particles and a polypropylene composites. Yield stress and modulus reduced with increasing compatibilizer content but elongation at break increased. It was hypothesised that either the compatibilizer was assisting interaction between the rubber particles and polypropylene or that it was acting as a toughening agent [3]. Magaraphan et al. have studied the effects of grafted maleic anhydride as a compatibilizer in a composite of LLDPE–natural rubber and showed that the

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http://dx.doi.org/10.1016/j.compositesa.2015.10.002
1359-835X/

in situ copolymer was capable of promoting improved interfacial adhesion and consequently enhanced mechanical properties [4].

Compatibilized polyolefin–rubber composites can be made electrically conductive by means of fillers such as carbon black, carbon nanotubes or graphene for use in a wide range of applications such as antistatic and electrostatic dissipation materials, and electromagnetic interference materials. Because of their high aspect ratio, carbon nanotubes are superior solution to the other fillers and have been used by many researchers to improve the conductivity of inherently insulating polymers. 'Percolation threshold', is the filler volume fraction, where a polymer composite makes a transition from an insulating to a conducting system. It can be controlled by manipulating the polymer blend morphology and the idea has been extensively studied and reviewed [5–7]. Recent studies have shown that much lower concentrations of carbon fibres may be sufficient in polymer composites if the carbon nanotubes are distributed predominantly in one continuous phase and/or preferentially located at the interface between the two polymer phases [8]. Studies of the electrical conductivity of polycarbonate (PC), poly (acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) and multi-wall carbon nanotubes (MWCNT) composites confirmed that localisation of MWCNTs changes from the ABS to the PC phase when the rubber content was reduced from 60% to 5% [9]. At low rubber concentrations of rubber, MWCNT selectively localised in the PC phase and this effective concentration resulted in increased conductivity and a low percolation threshold of around 0.5–1 wt.% [10].

In ternary systems of polycaprolactone (PCL), poly(lactic acid) (PLA) and MWCNT, selective localisation of carboxylic functionalised nanotubes occurs both in the PCL phase and on the phase interface; interfacial adhesion lowers conductive percolation threshold. When the carbon nanotubes are not functionalised they are localised only in the PCL phase and the conductive percolation threshold is relatively higher; the ternary composites show conductivities 3–4 orders higher than binary composites at a MWCNT loading of 1 wt.% [11]. In a similar PCL–PLA composite but with 1%·w/w acid-oxidized MWCNT, carbon nanotubes were selectively localised in PCL and maximum conductivity was observed at 40%·w/w PCL; giving a co-continuous matrix with interconnected carbon nanotubes [12]. Pötschke et al. developed a novel strategy to incorporate carbon nanotubes into thermoplastic matrices of PC and polyamide-6 (PA6) by melt blending the PE based masterbatch with a very high MWCNT loading. This improved the carbon nanotube dispersion in PC and PA6, thereby reduced the percolation threshold limit [13]. Likewise, an additive assisted one-step melt mixing approach was developed to produce a nanocomposite based on LLDPE with high MWCNT loading which showed an excellent carbon nanotube dispersion and highly improved electrical properties compared with composites without the additives [14]. Selective localisation of MWCNT in LLDPE has been the basis of the current research directed towards the development of conductive polyolefin–rubber composites.

The aim is to design and prepare flexible polyolefin–ground tyre rubber composites by melt mixing linear low-density polyethylene (LLDPE) with ground tyre rubber in the form of functionalised rubber particles (FRP). The investigation was part of a project commissioned by Polymeric Powders Company Pty Ltd, who hold patents in the area, supplied the specific FRP used in the project. We report on inclusion of (i) grafted maleic anhydride as a compatibilizer, and (ii) manufacturing processes (compression moulding versus fused deposition modelling) on the mechanical properties of the composites with varying compositions. Introduction of carbon-nanotubes to the LLDPE–FRP, is used to form nanocomposite filaments with the objective of: (i) the carbon nanotubes are proposed to introduce conductivity and (ii) fused deposition modelling (3D printing) is employed to produce composite parts possessing conductivity.

2. Experimental

2.1. Materials

Linear low-density polyethylene (LLDPE) with a melt flow index 3.0 dg/min (ASTM D1238 at 190 °C, 2.16 kg) was mixed with maleic anhydride grafted polyethylene (MA-g-PE). MA-g-PE was Fusabond D226 (E.I. DuPont, Wilmington, DE, USA), which is a linear low-density polyethylene, grafted with maleic anhydride 0.90% w/w, with melt flow index 1.5 dg/min (ASTM D1238 at 190 °C, 2.16 kg). Rubber particles were first reclaimed from recycled rubber tyres in the form of particulates having a de-vulcanised surface area according to a patented process [15]. The de-vulcanised rubber particles were further modified by utilizing aggressive gasses (a combination of ozone, nitrogen and oxygen) to generate an activated surface area by creating oxygen containing functional groups according to another patented process [16]. MWCNT were incorporated into the polyolefin–rubber composites [17] in the form of a masterbatch Plasticyl LDPE2001. Plasticyl LDPE2001, which has a carbon nanotube loading of 20% w/w, is a conductive masterbatch based on low density polyethylene (LDPE) due to its low viscosity and high flow rate, it is ideal for injection moulding and extrusion applications requiring superior electrical conductivity and electrostatic discharge (ESD). Electrical resistivity was measured in accordance with CTM E043 and CTM E402 (Cabot Testing Method), on standard injection moulded IZOD specimens: 3% w/w carbon nanotube loading was identified as the percolation threshold based on the percolation curves for volume and surface resistivity [13,18].

The FRP with an average particle size distribution of around 400 μm was identified as the most suitable feedstock. In fused deposition modelling, which is one of the processing techniques used in this study, composite filaments are extruded through a small nozzle with a nominal diameter of 0.4 mm. Elongation at break of polyolefin–rubber composites was improved by decreasing rubber particle size [3]; hence FRP with a small particle size offered an added advantage of ease of processing with enhanced properties.

2.2. Conductive composite preparation

The polyolefin–rubber composites were prepared using a non-intermeshing, counter rotating Haake Polylab R600 internal batch mixer (Thermo Fisher Scientific, Waltham, MA, USA). The LLDPE, and FRP were melt mixed together with MA-g-PE containing 0.9%·w/w maleic hydride as the compatibilizing agent. Powdered LLDPE was fed into the pre-heated mixer at 180 °C and mixed at 50 rpm for 1 min to ensure complete melting of polymer prior to the introduction of FRP and MA-g-PE to the mixer; all three ingredients were mixed for another 5 min at 180 °C before the mixture was removed and placed in a compression mould to make specimens for mechanical testing. Table 1 shows the compositions of each composite that was prepared to assess MA as a compatibilizer in order to enhance the interaction of LLPDE and FRP at their interface.

Table 1
LLDPE–FRP composite codes and compositions.

Sample code	Composition (% w/w)		
	LLDPE	FRP	MA-g-PE
PB1	70	30	–
PB2	50	50	–
PB3	30	70	–
PB4	65	30	5
PB5	25	70	5