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Effect of crosslinking on the properties of composites based on LDPE and conducting organic filler

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Abstract

New types of composites were prepared using low-density polyethylene (LDPE) filled with modified organic filler, Canadian switch grass coated with polypyrrole (PPy). The grass surface was entirely covered when 10 wt.% of pyrrole was used for the modification, as confirmed by scanning electron microscopy and infrared spectroscopy. LDPE composites filled with modified grass were prepared by melt mixing and their properties were compared with the properties of the composites filled with unmodified grass. The influence of crosslinking, induced by 1 wt.% of peroxide, on mechanical, thermal and electrical properties of the composites was investigated. Crosslinking enhanced the tensile strength of the prepared composites in the entire range of the filler content. The Young's modulus of the composites prepared by crosslinking is slightly lowered when compared with the uncrosslinked composites if the filler content is less than 60 wt.%, for higher filler content it is increased. The conductivity of the uncrosslinked composites containing 40 wt.% of grass modified by PPy was in the range $1 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$, which is a value by 5 orders of magnitude higher than the conductivity of the crosslinked materials. The presence of PPy on grass surface leads to a reduction of crosslinking of the LDPE matrix.

Keywords: Composites; Polypyrrole; Polyethylene; Organic filler

1. Introduction

In recent years, organic fillers have drawn attention as reinforcement in thermoplastics. The advantages, compared with inorganic fillers, are their low-density, low abrasion, availability from renewable resources, low cost and no waste disposal problems. Among them, cellulose-based materials as e.g. wood flour, sisal fibre, flax fibres or cellulose itself [1–5] are of special interest. The disadvantages, in comparison with the inorganic fillers, are the need of the surface treatment of the cellulose-based hydrophilic fillers to improve their adherence to hydrophobic thermoplastic matrices [6–8], the decomposition of the organic fillers at high temperature (about 200 °C) and a lower aspect ratio. In spite of this,

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composites containing organic fillers are used in various applications as decks and docks, window frames or, in the last years, also as materials in the automobile industry.

A possible route to create conducting filler from a non-conducting material is the in situ polymerization of a conducting polymer in the presence of organic or inorganic substances. For example, polypyrrole can coat the surface of conventional organic polymer powders particles such as polyethylene (PE), polypropylene (PP) [9,10], poly (vinyl chloride) [11,12], polystyrene latexes [13], or inorganic colloids [14,15], and nanoparticles such as multi-walled carbon nanotubes [16].

The pioneering paper about the preparation of organic matrix/PPy composites was published in 1984, when Bjorklund and Lundstrom [17] described the synthesis of paper/PPy composites. Porous filter paper was dipped into $FeCl_3$ solution and then directly contacted with pyrrole liquid or vapour. After drying, the paper/PPy composites showed a conductivity of about $2\,S\,cm^{-1}$. Later, the oxidation of pyrrole by iron salts in aqueous solution of methylcellulose resulting in colloidal solution of PPy and cellulose was reported [18]. After the cellulose gelation and drying of the product the conductivity of this material was $0.2\,S\,cm^{-1}$. Recently, production of a new conducting composite material based on polyaniline and wood by a simple one-step synthesis from aniline and wood sawdust was described [19] and Dall' Acqua et al. prepared embedded polypyrrole in natural and man made cellulose-based fibres by means of in situ polymerization [20]. However, the preparation of thermoplastic composites with conducting organic fillers has not been reported in the literature, with the exception of the recent preparation and study of the composites of linear low-density polyethylene, high-density polypropylene and polycaprolactone filled with cellulose fibres coated with polypyrrole [21]. Polypyrrole was chosen for the modification of the organic fillers, because of its high conductivity and good environmental stability. PPy can be used as a substitute for metallic conductors or semiconductors in a wide variety of electrical and electronic devices [22,23].

In this work we prepared and investigated a new type of composites which are based on LDPE matrix and conductive modified grass. Our aim was to obtain a composite with good mechanical and antistatic properties. The influence of crosslinking on the properties of the composites was studied. Crosslinking of polyethylene is a well known process used in cable industry or for production of shrinkable materials [24]. Crosslinking is usually initiated by thermal decomposition of peroxides or by high-energy irradiation, less often by UV irradiation [25]. The main reason for using crosslinking is to increase thermal resistance of the material. In composites or blends, crosslinking frequently leads to an improvement of the mechanical properties; especially a higher Young's modulus can be achieved when compared to the uncrosslinked analogues [24,26]. In our work, the thermal decomposition of peroxide was applied for crosslinking of LDPE matrix. The properties of the crosslinked and non-crosslinked LDPE composites containing grass modified with 10 wt.% PPy (G–10% PPy) were compared with the properties of the composites where unmodified grass (uG) was used as filler, recently published by Chodák et al. [26].

2. Experimental

2.1. Materials

Low-density polyethylene (LDPE, Bralen RA 2-19, $T_m = 109.3\,°C$, MFI = 2.0 g/10 min, ASTM D 12138, Slovnaft, Slovakia) containing a common antioxidizing system (BHT based) was used as polymeric matrix. Dried switch milled grass (G, $135 \times 30\,\mu m$, aspect ratio = 3.5, Canada) was used as organic filler. For the coating of the grass fibres, pyrrole monomer (Merck–Schuchardt, Germany), purified by distillation under reduced pressure and stored in a refrigerator at 4°C, and ferric chloride ($FeCl_3$, Lachema, Czech Republic) were used. (2,5-dimethyl-2, 5-ditertbutyl peroxy) hexyne (Luperox 130, 90 mol.% of active component, Luperox GmbH, Germany) was utilized as the peroxidic initiator of crosslinking.

2.2. Grass–polypyrrole preparation

Hundred grams of grass was dispersed in 1600 ml of distilled water and stirred for 15 min. The oxidant, $FeCl_3$ was then added and the mixture was stirred for 30 min. Pyrrole was dissolved in 50 ml of water and inserted dropwise into the reaction mixture which was then stirred for a further 30 min. The molar ratio $[FeCl_3]/[pyrrole]$ was 2.3, as recommended by Armes et al. [27]. After 4 h, grass coated with polypyrrole was filtered off and rinsed several times with distilled water. Later on it was dried at