



Surfactant effects on poly(ethylene-co-vinyl acetate)/cellulose composites

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ABSTRACT

Cellulose whiskers, isolated from banana waste fibres, were used as a reinforcement in poly(ethylene-co-vinyl acetate) [EVA] matrices, to develop composites. A non-ionic surfactant, poly(ethylene glycol ether), was used to improve the dispersion characteristics of the cellulose whiskers in EVA/cellulose whisker composites. The influence of the surfactant on the morphology, the mechanical properties and the thermal characteristics of the resultant EVA/cellulose whisker composites has been examined. Theoretical models, namely the Halpin–Tsai model and the Nicolais–Narkis model have been used to provide a basis for comparing the results those were derived from investigations of the tensile properties of the composites.

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1. Introduction

Cellulose is a natural polymer consisting of D-anhydroglucose (C₆H₁₁O₅) units joined by 1,4-β-D-glycosidic linkages at C1 and C4 position. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical and chemical properties of cellulose. The fields of application of cellulose microcrystals and/or microfibrils are varied. Microcrystalline cellulose (MCC) is widely used, especially in food, cosmetic and medical product industries. Cellulose whiskers have been used as reinforcements in manufacture of composites [1–3].

One of the major challenges in the use of cellulose whiskers as reinforcements in polymer matrices is the achievement of a uniform distribution of the whiskers in the matrix material. Due to the hydrophilic character of cellulose, the most suitable polymer systems in which to incorporate cellulose whiskers are those that are water-compatible [4,5]. It is known to be difficult to achieve uniform dispersion of cellulose whiskers in a non-polar medium [6]. To achieve a reasonably good dispersion of such whiskers in non-polar media, two routes are generally practiced [7]. One route is the grafting of suitable hydrophobic chains onto the cellulose surface and the other more viable route involves the use of suitable surfactants. These two techniques provide a basis for the preparation of polymer composites by the placing of the relevant suspensions in an

increasingly organic medium. Different researchers have successfully used these methods [8–16]. Among these two options, the use of a surfactant-based approach, with the surfactant acting as a dispersant, is of interest due to its relative simplicity. However, the technique based on cellulose grafting is difficult to implement because of the practical restrictions associated with achieving surface modification alone, without affecting the bulk characteristics.

The modification of composite systems using surfactants has been reported. The coating of cotton whiskers and tunicin whiskers, using a surfactant that was based on a phosphoric ester of poly(oxyethylene-9-nonyl phenyl ether) [PEPNP], gave rise to stable suspensions in toluene/cyclohexane [6] and in chloroform [17]. Kim et al. [18] analysed the dispersion stability of surfactant-coated cellulose whiskers in THF, using turbidimetry as the diagnostic tool. The authors prepared cellulose/polystyrene nanocomposites with the dispersive assistance of the non-ionic surfactant, sorbitan monostearate. The authors found that the addition of the non-ionic surfactant improved the mutual compatibility of the components. They found that the reinforcement–matrix interactions for the system containing the non-ionic surfactant, were much greater than those of the composites in which the cellulose whiskers had not been coated with the non-ionic surfactant. The authors reported that a cellulose:surfactant weight ratio of 1:2 gave the optimal interactions. They also highlighted the possibility of self assembly of the surfactant species at greater loadings.

Poly(ethylene-co-vinyl acetate) is a random copolymer of ethylene and vinyl acetate, which is commonly referred to as EVA copolymer or simply EVA. EVA copolymers represent the largest volume segment of the ethylene copolymer market. Their properties depend on the vinyl acetate content: products ranging from

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2% to 40% vinyl acetate are marketed for different purposes, especially in the production of cables, piping, adhesive tape, packaging films, barrier sheets etc. However, there exists only limited information about the properties of EVA/cellulose based composites. Dikobe and Luyt [19] examined composites of PP/EVA blends with wood powder (WP) and reported that WP influenced the crystallization behaviour of EVA. Mydul et al. [20] studied the mechanical properties of EVA and cellulose acetate (CA)-containing natural fibres (*Sterculia villosa*). They observed that the tensile strength of EVA composites decreased with the addition of fibre, whereas in CA composites, tensile strength increased due to the good distribution of fibres. In another study, the effect of wood fibre (WF) content and wood fibre particle size on the morphology, mechanical, thermal, and water-absorption properties of uncompatibilized and ethylene glycidyl methacrylate copolymer (EGMA) compatibilized ethylene vinyl acetate copolymer–WF composites has been investigated [21]. The authors pointed out that there was an increase in the tensile modulus with increasing wood fibre content; the compatibilized composites had a higher modulus than that of the uncompatibilized ones. Because of better dispersion and filler–matrix interaction in the small wood fibre containing composites, these composites exhibited higher tensile strengths than larger wood fibre containing composites, both in the presence and absence of EGMA.

The present study concerns the use of a non-ionic surfactant, poly(ethylene glycol ether), to enhance the compatibility between cellulose whiskers and poly(ethylene-co-vinyl acetate). The effect of the surfactant on the performance of the composites, in terms of mechanical properties and thermal characteristics, was studied. Two theoretical models were used to provide a basis for the comparison of data from experimental observations with theoretical expectations.

2. Experimental

2.1. Materials

Two different EVA copolymers, namely EVA-1802, (18% vinyl acetate units), coded EVA 18 in this study, supplied by National Organic and Chemical Industries Limited (NOCIL), Mumbai, India and EVA FLEX, (40% vinyl acetate units), coded EVA 40 in this study, supplied by Dupont Mitsui Polychemicals Co., Ltd., Tokyo, Japan were used in the study. The banana fibres were procured from the Fibre Design Centre, Khadi and Village Industries Commission (KVIC), Trivandrum, India. NaOH and NaOCl, used for the pre-treatment of banana fibres, were of analytical purity. Sulphuric acid (>98%) (Fisher Scientific, UK), Tetrahydrofuran (THF) (Sigma Aldrich, UK) and poly(ethylene glycol ether) [EMULDAC/ALCS-100 SC] (Sasol Italy, S.p.A.), used in the study were of commercial grades.

2.2. Preparation of EVA/cellulose composite membranes-with surfactant and without surfactant

Isolation of cellulose whiskers: The cellulose whiskers, derived from the banana waste fibres, were used as the filler in an EVA matrix. The cellulose whiskers were generated from the banana fibres by an acid catalysed hydrolysis. Initially, the ground banana fibres were sieved using a test sieve of 150 μm apertures (Endecotts Ltd., England). The sieved fibres were subjected to an alkaline treatment and then bleaching prior to acid hydrolysis. The pre-treated banana fibres were then dispersed in a 64 wt% sulphuric acid solution, at 45 °C, for 4 h. The aqueous suspensions of the cellulose that was obtained after dialysis and ultrasonication, were freeze dried (LSL Secfruid, Switzerland). The detailed procedure developed for the

isolation of cellulose from banana fibres, using different reaction conditions, has been reported [22].

In a typical fabrication of the EVA18/cellulose composite films, 3 g EVA18 was dissolved in 50 g of THF at 60 °C, for 4 h under vigorous stirring. Care was taken to ensure that there was no loss of THF during the process. In a parallel exercise, a dispersion of the cellulose whiskers in THF was prepared by separately weighing a known amount of the freeze dried cellulose whisker sample and placing these whiskers in THF, with stirring. Dispersions with different wt% (2.5%, 5%, 7.5% and 10%) of cellulose whiskers, in THF, were mixed with the EVA-THF solution. These mixtures each were heated for 10 min at 60 °C, under reflux, whilst being stirred mechanically. Each of the dispersions was cast onto a glass plate (17 cm \times 17 cm \times 0.5 cm) and then slowly dried at room temperature in a fume cupboard. For the fabrication of EVA40/cellulose composite films, 3 g of EVA40 was dissolved in 50 g of THF, with stirring overnight at room temperature, under sealed conditions. To prepare the surfactant-loaded EVA/cellulose composites, each cellulose–surfactant dispersion in THF was individually mixed with the respective EVA–THF solution, stirred well, and cast onto a glass plate. The sample coding that was used for the EVA/cellulose composites is given in Table 1.

2.3. Characterisation

2.3.1. Turbidity measurement

The turbidity of dispersions of cellulose–surfactant solution mixtures, in THF, was monitored using a Digital Nephelo-Turbidity Meter 132 (Systronics). A low turbidity of the dispersion was taken to indicate that a large amount of the cellulose whisker particles had settled due to the precipitation. 20 mL of each cellulose–surfactant dispersion, in THF, was stirred for 24 h and then subjected to the turbidity measurement, with respect to the settling time. The turbidity was measured in Nephelometric Turbidity Units (NTU).

2.3.2. Morphology studies

The morphology of the composite films was investigated by scanning electron microscopy (SEM). The samples were sputter-coated with gold, before analysis by SEM, to avoid subsequent charging during measurement. Images were taken using an electron microscope (JEOL JSM-820). Optical images of the samples were taken using a Motic BA300 optical microscope. The cellulose whiskers were analysed by transmission electron microscopy (TEM) using a JEOL-1011 model transmission electron microscope.

2.3.3. Thermal analysis

The EVA/cellulose whisker composite films were analysed by thermogravimetry (TG) and by differential scanning calorimetry (DSC). In these analyses, a TGA 2050 series analyzer (TA Instruments) was used, across a temperature range from 30 °C to 500 °C, at a heating rate of 10 °C/min, in a nitrogen environment. The melting temperature of each sample was recorded by DSC (DSC 2010 series, TA Instruments), from –50 °C to 150 °C, with a heating rate of 10 °C/min, again under a nitrogen environment.

2.3.4. Mechanical properties' evaluation

The mechanical properties of the composite films were studied by using a Universal Testing Machine (Instron corp., Canton, MA, USA), following the ASTM D 882-88 protocol. The initial grip separation and crosshead speed were set at 40 mm and 50 mm/min respectively. The data reported are the average of at least five experiments.

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