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A study of the effect of acetylation and propionylation surface treatments on natural fibres

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Abstract

Recently, the incorporation of lignocellulosic materials as reinforcing agents or as fillers in polymer composites has received an increased attention. Although natural fibres have a number of advantages over glass fibres, the strong polar character of their surface is a limiting factor, as compatibility with strongly apolar thermoplastic matrices is very low. Such problems of incompatibility may be overcome with fibre pre-treatments, which can enhance compatibility, albeit having a negative impact on the economics. In the present study, two fibre pre-treatment methods, acetylation and propionylation, were applied on flax, hemp and wood fibres. The effect of esterification between the acetyl/propionyl groups and the hydroxyl groups of the fibre was examined by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS), while its extent was assessed by titration. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the crystallinity and the surface morphology of the untreated and esterified fibres. The highest extent of the esterification reaction was achieved for the wood fibres due to their high lignin/hemicelluloses content. The two spectroscopic methods revealed that the fibre surface chemistry was altered after the treatments, as the results indicated that ester bonds are present on the fibre surface. The SEM results revealed that both treatments resulted in a removal of non-crystalline constituents of the fibres, possibly waxy substances, and alter the characteristics of the surface topography. It was also shown that the fibre crystallinity decreased slightly as a result of esterification.

Keywords: Natural fibres; Surface treatments; Surface chemistry

1. Introduction

Over the last few years, there has been an increasing interest in using natural fibres as reinforcing agents in composite materials [1–7]. A combination of properties, such as low cost, low density, non-toxicity, high specific properties, no abrasion during processing, and recycleability, contribute to a rising interest from the manufacturing industry of low cost, low weight composites [8–11]. However, there are a number of problems associated with incorporating such fibres into thermoplastic matrices, most notably fibre-matrix incompatibility where apolar polymers are concerned, and thermal stability of the fibres where relatively high processing temperatures are required. The compatibility problem may be further complicated by dimensional instability of the resulting composites in humid conditions. When water is absorbed the matrix is placed under stress by the swelling of the fibres. Since no significant bonding exists between the fibres and the matrix, when the material is dried a rapid shrinkage of the fibres takes place that results in propagation of debonding cracks and severe deterioration of mechanical properties [12].

Thus, in order to develop composites with good properties, it is necessary to improve the interface between the matrix and the lignocellulosic material. There are various methods for promoting interfacial adhesion in systems where lignocellulosic materials are used as fillers, such as esterification [13–17], silane treatment [18,19], graft copolymerisation [20], use of compatibilisers [21], plasma treatment [22], and treatment with other chemicals [23]. These methods are usually based on the use of reagents,

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which contain functional groups that are capable of reacting and form chemical bonds with the hydroxyl groups of the lignocellulosic material, while maintaining good compatibility with the matrix. Interfacial compatibilisation improves the stress transfer between the two components and leads to the improvement of mechanical and physical properties of the produced composites. On the other hand, the use of surface treatments has the disadvantage of increasing the cost of the final product.

Esterification by means of acetylation is a chemical modification procedure, which has been studied extensively for lignocellulosic compounds [13–17]. In contrast, for propionylation there is only a limited number of studies available in the literature [13,14]. Chemical modification with acetic and propionic anhydrides, substitutes the cell wall hydroxyl groups with acetyl and propionyl groups, rendering the surface more hydrophobic, and thus, more compatible to the polymer matrix. According to Rowell [13], the hydroxyl groups that react with the reagent, are those of lignin and hemicelluloses (amorphous material), while the hydroxyl groups of cellulose (crystalline material), being closely packed with hydrogen bonds, prevent the diffusion of the reagent and thus result in very low extents of reaction, if any. It has been shown that esterification improves the dispersion [11,24,25] of lignocellulosic materials in a polymer matrix [11,26,27], as well as the dimensional stability [28,29], and the interface of the final composite [11,27].

The aim of the present work was to study the effect of a solvent free, catalyst free, anhydride treatment on different lignocellulosic materials, in order to produce cost effective totally biodegradable composites. In particular, the esterification of three lignocellulosic materials, i.e. flax, hemp and wood fibres and its effect on properties like crystallinity and surface morphology was investigated by XRD, XPS, ATR-FTIR and SEM methods.

2. Experimental

2.1. Materials

Three different natural fibres were used in the present study. Flax and hemp fibres were purchased by S.A. Van Robaeys Frères, France, while wood fibres (Pinus silvestris) by WKI, Germany. Acetic anhydride (AA) (98.5%, Merck), propionic anhydride (PA) (97%, Aldrich) and other reagents and solvents were used as received.

2.2. Fibre surface treatment

Prior to treatment, the fibres were dried for 6 h at 100 °C in an oven. Subsequently, 1 g fibres was placed in a 100 ml flask and the appropriate amount of acetic or propionic anhydride was added, so as to ensure that all fibres were totally covered with the reagent. Afterwards, the fibres were placed in a preheated oven at 120 °C for 30, 60, 120 and 180 min. The treated fibres were then Soxhlet extracted using acetone as solvent, in order to remove any remaining unreacted reagent, and acid by-products. Finally, the fibres were left in the air to dry and then put in an oven for 6 h at 100 °C. It should be noted here, that the Soxhlet extraction was carried out only for the fibres used in the determination of the saponification value and ester content, and in this test it was necessary to extract the fibres in order to obtain an accurate value of the extent of the reaction. On the other hand, in the rest of the characterisation tests employed in this study, the fibres used were not Soxhlet extracted, for the reason that the extraction step is an additional step that may increase unnecessarily the cost of the treatments.

2.3. Fibre characterisation

2.3.1. Determination of cellulose, hemicelluloses, lignin

The composition of lignocellulosic fibres was determined according to the Acid Detergent Fibre—Neutral Detergent Fibre (ADF–NDF) method (van Soest and Wine) [30,31]. The equilibrium moisture content (EMC) was calculated by placing treated and untreated fibres in a dessicator (60 and 90% RH) at 20 °C, and then drying them in an oven at 105 °C until constant weight was reached.

2.3.2. Determination of the saponification value and ester content

The total ester content of treated fibres was calculated from the saponification value of the esterified fibres [32].

2.3.3. Attenuated total reflectance-Fourier transform infrared analysis (ATR-FTIR)

Fourier Transform-Infrared spectra were acquired using an Equinox 55, AXS Bruker FTIR spectrometer equipped with a MCT detector. The fibres were mounted on a ATR accessory equipped with Ge crystal prior to scanning. The spectra were obtained with an accumulation of 100 scans and with a resolution of 2 cm^{-1}.

2.3.4. Scanning electron microscopy (SEM)

The effect of modification upon the fibre surface was examined using a SEM microscope (LEO 435VP). Prior to the analysis, the samples were coated with gold (layer thickness ∼30 nm) to avoid sample charging under the electron beam.

2.3.5. X-ray diffraction (XRD)

In order to assess the influence of the treatments on fibre crystallinity, XRD analysis was applied. A Siemens D500 diffractometer, employing Cu Kα ($\lambda = 1.54$ Å) radiation was used. The crystallinity index (CrI) of the fibres was calculated according to the Segal empirical method as follows [33]

$$\mathrm{CrI}(\%) = (I_{002} - I_{\mathrm{am}})/I_{002} \times 100$$