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Mechanical, morphological and thermal properties of chitosan filled polypropylene composites: The effect of binary modifying agents

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ABSTRACT

This work investigates the effects of the binary modifying agents–organosolv lignin and acrylic acid, on the mechanical and thermal properties of chitosan-filled polypropylene (PP) composites. We analyse the mechanical and the thermal properties of the composites by means of ASTM D 638-91, ASTM D 256, thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). Tensile strength of the composites decreases upon the addition of chitosan, but Young's modulus improves. Impact strength is found to increase with the maximum value at 30 php. The chemical modifications do not alter the stress–strain character or the thermal degradation mechanism of the composites considerably; however the results of this study show that the treated composites are found to have better mechanical and thermal properties than untreated composites. Furthermore, the obtained results are comparable to results from previous work. This outcome implies that organosolv lignin could be a potential reagent to partially replace its synthetic counterpart.

1. Introduction

Polymer composites reinforced with natural fibres have become an attractive research field in recent years [1]. These investigations are mainly driven by the low cost of natural fibres, which are a promising alternative to synthetic fibres (e.g. glass fibres) for use as a reinforcing agent in the manufacturing of polymeric composite materials [2]. Additionally, the use of natural fibres could minimise environmental pollution due to their bio-degradability, reducing environmental problems [3]. Currently, many natural fibres have potential as a reinforcing agent in polymer composites [4–8]. The main advantages of using natural fibres in polymer composites include a high strength per unit weight, ease of processing, a lower specific weight (density), and desirable thermal properties [9,10]. However, some disadvantages such as variable quality (which depends on unpredictable influences, such as weather and moisture absorption), low maximum processing temperatures, poor fire resistance and incompatibility with hydrophobic polymer matrices, can limit their potential use as reinforcements in polymer composites for industrial applications [11].

Among the existing natural fibres, chitosan fibre is known to possess excellent mechanical and thermal properties [12]. Chitosan fibre is the second most abundant natural fibre after cellulose; it is extracted from crustaceous shells such as crabs, shrimp and prawns [13]. In solid form, chitosan fibre is a crystalline polymer; it is also non-toxic, biodegradable and biocompatible [14]. A recent study reported that chitosan fibre is a useful reinforcing agent for increasing the mechanical and thermal performances of polymeric composite materials; however, it is not as widespread as synthetic fibres. Research is still required to determine several unknown factors, e.g. the ideal matrices for reinforcements. This factor has limited the application of chitosan as a reinforcing agent, mainly because hydrophobic polymeric matrices repel the polar sites of the chitosan fibre. Such incompatibility results in materials with a low fibre/matrix adhesion in the interface region [15].

To mitigate the issue of adhesion, interfacial interaction is modified in this composite system. Interfacial adhesion can be enhanced by the chemical or physical modification of the chitosan fibre, by means of a surface coating or a coupling agent, which is usually a functionalised polymer. Specifically, maleic anhydride grafted polyethylene (MAPE) was used in a study to enhance the interfacial adhesion between the chitosan fibre and a recycled polyethylene polymer matrix [16]. In other studies, the surface of the chitosan fibre was chemically modified with 3-aminopropyltriethoxysilane (3-APE) and sodium dodecyl sulphate to reduce the hydrophilic character of chitosan enhancing its adhesion with a hydrophobic polypropylene (PP) matrix [17,18]. To date, chemical modification is extensively used for enhancing the interfacial interaction in polymer composite systems, because it is an effective method to reduce the polarity of natural fibres [19]. However, chemical modification adds another step in the preparation of composites, hence increasing the production cost. Ideally, the reagents used in the chemical modifications are inexpensive and

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involve compounds obtained from renewable sources. Alternatively, the use of reagents obtained from non-renewable sources reduces the benefits of using natural fibres [20].

In our previous study, the chemical modification of chitosan fibre was carried out using acrylic acid as the modifying agent. The results demonstrated that the use of 3 wt.% of acrylic acid enhanced the interfacial adhesion between the chitosan and the PP matrix, led to significantly improved composite properties [21]. In the present study, the chemical modification of chitosan was conducted using a binary modifying agent composed of acrylic acid and lignin. Lignin was chosen because of its worldwide availability, and its abundance as a vegetal-derived material [22]. The distinct chemical groups in the macromolecular structure of lignin, such as polar hydroxyls, non-polar hydrocarbon chains, and aromatic rings, can interact individually with the differing fibre surface sites, increasing the possibilities for chemical reactions [23].

In this work, the lignin was extracted from lignocellulosic fibre using the organosolv process. This process consists of extracting lignin from lignocellulosic fibre by an organic solvent with water, normally under acid catalysis; this is advantageous because it results in lignin with a low molecular weight compared to other processes. This process lends lignin a large number of reaction sites, making it a more appropriate modifying agent [24]. The goal of this work was to investigate the effects of the chemical modification of chitosan using a binary modifying agent composed of organosolv lignin and acrylic acid, on the mechanical and thermal performances of chitosan-filled polypropylene composites.

2. Experimental

2.1. Materials

The PP homopolymer used in this study was injection moulding grade S11232 G112 and had a melt flow index (MFI) of 45 g/10 min at 230 °C, from Polypropylenas Sdn. Bhd. The chitosan (Hunza Nutriceuticals Sdn Bhd., Malaysia) used had an average size of 80 μm and a 90% degree of deacetylation (DD). The ethanol (98% v/v) and the acrylic acid were obtained from Aldrich, Penang, Malaysia.

2.2. Extraction of organosolv lignin from lignocellulosic fibre

The extraction of organosolv lignin was carried out using the organosolv method developed by Hage et al [25]. Lignocellulosic fibre was treated with aqueous ethanol mixed with a catalyst, 1.2 w/w% sulphuric acid at 190 °C for 1 h; the solid to liquid ratio was 1:8. The pre-treated fibre was then washed with warm ethanol. The washes were combined, and 3 vol.% of water was added to precipitate the organosolv lignin. The organosolv lignin was centrifuged and dried in an oven at 80 °C for 24 h.

2.3. Preparation of treated chitosan

Chitosan filler was chemically modified through a reaction with a binary solution mixture comprising of acrylic acid and organosolv lignin in an ethanol medium. Initially, the organosolv lignin was dissolved in ethanol to make an organosolv lignin solution; 1 wt.% of filler was used as recommended by Thielemans et al. [26]. Meanwhile, the acrylic acid solution was prepared by diluting 2 wt.% of acrylic acid in ethanol. Chitosan was gradually added to the organosolv lignin solution and stirred for 1 h. Next, the acrylic acid solution was slowly added to the chitosan and stirred for 2 h. The binary solution was then filtered and dried at 80 °C for 24 h.

Table 1
Formulation of untreated and treated PP/chitosan composites at different filler loading.

Materials	Untreated PP/chitosan composites	Treated PP/chitosan composites
Polypropylene (PP) (php)	100	100
Chitosan (php)	0, 10, 20, 30, 40	10, 20, 30, 40
Acrylic acid (wt.%)	–	2
Organosolv lignin (wt.%)	–	1

php = part per hundred of polymer.

2.4. Preparation of PP/chitosan composites

PP/chitosan composites were prepared in a Z-blade Mixer (MCN ELEC Co., Taiwan) at 190 °C and a rotor speed of 50 rpm. PP was loaded first to start the melt mixing. After 12 min, the chitosan was added; the mixing continued for another 3 min. Next, the PP/chitosan composites were removed and sheeted through a laboratory mill at a 2.0 mm nip setting. Samples of PP/chitosan composites were compression moulded in an electrically heated hydraulic press. The hot-press procedure involved preheating at 190 °C for 9 min, compression for 3 min at the same temperature and cooling under pressure for 3 min. A similar procedure was conducted for the preparation of treated PP/chitosan composites. The formulation of untreated and treated PP/chitosan composites is summarised in Table 1.

2.5. Characterisation

Tensile tests were carried out according to ASTM D 638-91 on an Instron 5582. A minimum of five dumbbell specimens of each composition, 1 mm thick were cut from the moulded sheets with a Wallace die cutter. A cross-head speed of 20 mm/min was used and the test was performed at 25 ± 3 °C.

Impact tests were conducted on a Compact Charpy Impact Tester according to ASTM D-256, using notched samples. For each test, five specimens were measured and the average data was reported.

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses were performed with a TGA Q500 (Perkin Elmer Instrument). Samples were scanned from 30 to 600 °C at a heating rate of 20 °C/min using a nitrogen flow of 50 ml/min. Differential scanning calorimetry (DSC) analysis was carried out with a DSC Q 1000 (Perkin Elmer TA Instrument). Samples were scanned from 25 to 250 °C at a heating rate of 20 °C/min using nitrogen flow of 50 ml/min. The melting points and enthalpies of PP/chitosan composites were automatically calculated by the instrument software. The crystallinity of composites (X_c) was manually calculated using the following equation:

$$X_c = \Delta H_f \times 100/\Delta H_f^o \quad (1)$$

where ΔH_f is the heat of fusion of the PP and composites, and ΔH_f^o is the thermodynamic heat of fusion of fully crystalline PP (209 J/g) [27]. A mean value of three samples of each specimen was recorded.

The morphology of the tensile fracture surface of the PP/chitosan composites was investigated with a scanning electron microscope (SEM), JEOL model JSM 6260 LE. The fracture ends of specimens were mounted on aluminium stubs and sputter coated with palladium to avoid electrostatic charging during examination.

Fourier transform infra red spectroscopy (FTIR) was performed on untreated and treated chitosan in ATR mode (Perkin Elmer 1600 Series). Samples were scanned from 650 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

The number average molecular weight (M_n) and weight average molecular weight (M_w) of organosolv lignin were determined by gel permeation chromatography (GPC) after acetylation of the lig-