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Thermal, calorimetric and crystallisation behaviour of polypropylene/jute yarn bio-composites fabricated by commingling technique

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ABSTRACT

Commingled biocomposites based on polypropylene/jute yarns were prepared using commingling technique. The thermal and calorimetric behaviour of these commingled composites were studied with respect to fibre content and various chemical treatments. The thermal stability of the composites was found to be in between that of jute fibre and neat polypropylene (PP). Different chemical treatments increased the thermal stability of the composites due to increased interfacial adhesion between the matrix and reinforcement. Jute yarn acts as nucleating agents and favours the process of crystallisation thereby increasing the crystallisation temperature. Chemical treatments further increased the crystallisation temperature as a result of better interfacial adhesion between jute yarn and PP matrix. The close proximity of jute yarns weakens the mechanical bonds between PP molecules resulting in marginal lowering of melting temperatures. Polarized optical microscopic studies revealed the formation of transcrystalline layer around the jute fibre after 6 h.

1. Introduction

Natural fibre based composites have witnessed a number of successful applications in the automotive, electronics and engineering sectors during the last few years [1,2]. The low density and good mechanical performance of natural fibres offers a promising alternative to other reinforcing fibres presently available like glass and carbon fibres (which are synthetic in nature). Natural fibres have low abrasive properties and hence their processing is easier compared to those of harder inorganic fillers, such as glass fibres or mica [2,3]. In order for the natural fibres to show good reinforcing ability in composite materials a strong interfacial adhesion between the natural fibre and the synthetic matrix is required [2,4]. The materials that have been used to prepare bio composites include natural cellulose fibres such as jute and kenaf, byproducts of food crops such as wheat straw, poultry feathers, proteins and oils from soybeans, starch based polymers and biodegradable synthetic polymers such as poly(lactic acid) [5–15,16]. Even red algae fibre and bacterial cellulose fibres have also been recently reported as potential reinforcements for bio composites [16–18].

Reddy and Yang have reported that both partially green composites where either the reinforcing or the matrix materials are biodegradable and completely green composites where both the reinforcing and matrix materials are biodegradable and obtained from renewable resources have been developed [16]. Extensive use of natural fibres during the last few years in composite manufacture can be justified by its low cost and density, easy biodegradability, nontoxicity and its ability to be recycled [19].

The conventional methods like injection moulding, internal mixer, etc. are normally used to prepare composites, and involves the natural fibres or yarns being subjected to very high shear forces at higher loadings resulting in damage to natural fibres and a consequent reduction in properties. Joseph et al. have reported that during melt mixing natural fibres undergo considerable damage like splitting and peeling as a result of the high shear force at higher fibre loadings [20]. In order to counter these shear forces “commingling” technique is used here to make PP/jute yarn composites from PP yarn and jute yarn. The process of commingling involves the polymer fibre and reinforcement fibre to be intermingled together at the filament level [21–25]. The matrix fibre will have a lower melting temperature than the reinforcing fibres and will melt and fills the space between the reinforcing fibres during the compression moulding process. The biggest advantage of this method is that, the reinforcing natural fibres are not subjected to high shear forces as in melt mixing (injection moulding, internal mixer etc.). Very small quantities of solvents are required for mixing the polymer with the reinforcement fibre during the processing stages (acetone and chloroform, during the chemical treatments only). Another advantage is that, the percentage loading of the

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reinforcing fibres could be increased up to 60%. A uniform distribution of the matrix and reinforcement fibres or yarns can be achieved by commingling technique without inflicting much damage to the reinforcing natural fibres during the processing stages. A very good homogeneous distribution of the reinforcement in a non molten state prior to the processing steps is obtained as a result of commingling. Commingling is also one of the most cost effective ways of mixing reinforcing fibres with very good alignment. The reinforcing fibres and matrix fibres are blended intimately at the filament level.

The cost-effective, renewable, versatile, non-abrasive, viscoelastic, biodegradable, combustible, compostable nature and better insulation against noise and heat makes jute one of the most versatile natural fibre that has excellent potential in bio composite manufacture [26]. Structure–property relationships can be understood using thermal analysis technique. In the case of fibre reinforced composite the thermal stability of the composite is an important factor and it can be determined using thermal analysis. Thermal analysis can also be used to determine the amount of moisture and other volatiles present in the system, which can cause deterioration to the composite properties [27]. In most of the natural fibres cellulose and lignin are the major constituents, of which lignin degradation starts at around 200 °C, whereas other polysaccharides, mainly cellulose, are oxidised and degraded at higher temperatures [27]. Natural fibres tend to lose their strength at around 160 °C [27]. The effects of crystallinity, orientation and cross-linking on the thermal behaviour of cellulose have been reported by previous researchers [28–30]. Doan et al. reported that the overall thermal resistance of PP/jute composites was found to be in between that of neat PP and jute fibre [31]. Also the thermal resistance of PP/jute composites decreased with increase in fibre content which is in accordance with the higher thermal resistance of neat PP than jute fibre. Sinha and Rout reported that chemical treatments increase the thermal stability of PP/unsaturated polyester composites due to the resistance offered by the closely packed cellulose chain in combination with the resin [32]. However most of these previous works were based on injection moulding technique, extrusion or mixing both the fibres and matrix in an internal mixer and then moulding. All these techniques involve high shear forces and hence might damage the natural fibre. In commingling both the matrix (in fibrous form) and reinforcement (here jute yarn) are wound onto a metal plate and then compression moulded. Hence the fibre integrity is excellent compared to other methods and techniques.

Isotropic spherulites are normally formed in the bulk on cooling the semi-crystalline melt matrix (here polypropylene matrix). A crystalline morphology is induced at the natural fibre surface in some cases when the natural fibre is inserted in between the semi-crystalline polymer matrix. This induced crystalline morphology is different from the spherulites in the bulk. Natural fibres are good nucleating agents and hence the nucleation sites present along the fibre surface restricts the growth of spherulites in lateral direction only. As a result of this lateral growth a column layer develops around the fibre surface and encloses the fibre. This anisotropic layer is called transcrystalline layer (TCL) [33].

The transcrystalline layer of polyethylene (PE) and polypropylene (PP) has been reported to be having less ductile nature and higher Young's modulus, compared with the spherulites in the bulk by several researchers [34,35]. Thomason and Van Rooyen [36] investigated the isothermal crystallisation of PP in the presence of a large variety of fibres using hot-stage microscopy and differential scanning calorimetry (DSC). They observed that the occurrence of transcrystallisation was found to depend on the type of fibre used and the crystallisation temperature (T_c). Similarly Jose et al. conducted transcrystalline studies on PP/cotton commingled composites and found out that thickness of TCL and radius of the spherulites increase with the increase in the crystallisation temperature [37]. Jose et al. also reported that fibre surface roughness and thermal stresses facilitate the growth of transcrystallinity on cotton fibre [37].

The aim of the present work is to investigate the effect of fibre content and various chemical treatments like {Stearic acid (ST), Toluene diisocyanate (TDI), Potassium permanganate ($KMnO_4$) and Maleic anhydride modified polypropylene (MAPP)} on the thermal, calorimetric and crystallisation behaviour of PP/jute yarn bio-composites fabricated by novel commingling technique.

2. Experimental

2.1. Materials

Polypropylene (PP) a thermoplastic was used as the matrix and was supplied by Bonus Plastics Private Ltd., Gujarat, India in the form of continuous yarn. The supplied yarn had a specific gravity of 0.90–0.91 and melt flow index of 9 g/10 min. The reinforcement used was jute yarn and was supplied by Gloster jute Mills, Kolkata, India in the form of continuous yarn. The individual jute fibres in the yarn had a length of 1.5–3.5 m. The supplied jute yarn had a thickness of 0.6 mm (the thickness of individual jute fibre was in between 0.015 and 0.02 mm). The main constituents of jute are cellulose (59–61%), pentosan (15–17%), lignin (12.5–13.5%), polyuronide (4.8–5.2%), acetyl value (2.8–3.5%), fat (0.9–1.4%), nitrogenous matter (1.56–1.87%) and mineral substances (0.5–0.79%) [38]. Stearic acid (Qualigens), potassium permanganate (Merck), toluene diisocyanate (E Merck, Germany) and maleic anhydride modified PP (MAPP), were of AR grade.

2.2. Fabrication of commingled composites

PP and jute yarns were wound onto a metal plate using a fibre winding machine specifically designed for commingling purpose [39,40]. The plate with the commingled PP and jute yarns was then compression moulded at 205 °C, 0.2 MPa pressure and 9 min holding time (optimum conditions) [39]. The compression moulded commingled samples were then allowed to cool at room temperature and after that samples were taken for thermal studies. The winding pattern used for thermal studies is shown in Fig. 1 (with 55.89 wt.% jute content). The fibre content (weight percentage) was varied by altering the above mentioned winding pattern.

The winding pattern mentioned above contains 55.89 wt.% jute content which is the maximum weight fraction of jute that can be incorporated into the PP matrix, above which the properties start to decrease due to the insufficient wetting (covering) of jute yarn by polypropylene (PP). The above mentioned pattern yielded the best mechanical and dynamic mechanical properties during this study [39,40].

2.3. Fibre surface treatments

Polypropylene is hydrophobic (non-polar) in nature whereas most of the natural fibres including jute are hydrophilic (polar) in nature. This leads to low compatibility between them and hence the interfacial adhesion between the two will be minimal. Chemical treatments like stearic acid, $KMnO_4$, toluene diisocyanate and maleic anhydride modified polypropylene (MAPP) were done on PP and jute yarns in order to increase the compatibility between the two.

(a) Stearic acid treatment: A 2% solution of stearic acid in acetone was applied onto each layer of PP and jute yarns during the winding process itself. The metal plate with the treated commingled PP and jute yarns was then kept in a hot air