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Effect of quenching process on mechanical properties of flax/polypropylene composites

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Flax/polypropylene needle - punched nonwovens (550 g /m^2) have been produced and then used as a preform for the production of composites. In this study, better infiltration of polypropylene melt into the flax fibres has been achieved by altering the crystal structure of polypropylene in the preform. A modified sequence of production of composites is also proposed. The proposed method yields composite with 25, 98 and, 91% improvement in tensile, flexural and short beam strength properties as compared to the conventional method of manufacturing.

Keywords: Composite, Crystal structure, Flax, Needle - punched nonwoven, Polypropylene, Quenching process

1 Introduction

Composites are used in wide range of applications, such as aerospace, automobiles, consumer & electronic packaging and for other domestic applications[1-4]. Among them, thermoplastic based composites have gained significant ground because of shorter processing cycles, shelf life, storage, recyclability and sustainability. Thermoplastic composites are lighter in weight, which, in turn, increases the process performance [5]. Compared to thermoset resins, the cost and environmental advantages make it a suitable choice for wide range of applications[6].

Most of the matrices used in the preparation of thermoplastic composites are in the form of solid or liquid. The resin may be in the form of powder, fibre, film and fabric[7, 8]. The fibrous form of the resin is usually blended with the reinforcement either manually by hand mixing or by preparing nonwoven fabrics using technologies such as needle - punching, hydro- entangling, stitch bonding and adhesive bonding. The preform thus prepared is then hot pressed to form the composites[9].

The performance of the composites depends on the strength which is influenced by various factors. Among them, the bonding between the melted thermoplastic resin and reinforcement plays a significant role. Better bonding of the thermoplastic resin with fibre can be achieved by better wetting of reinforcement with the melted thermoplastic resin[10]. This in-turn depends on the process conditions deployed for hot compaction, as it influences the flow behaviour of the polymer melt. It has been observed in our various preliminary trials that most of the fracture in the composites occurred by delamination[11]. Previous works to improve the interfacial strength is by adding silane coupling agent, benzoylation, peroxide treatment steam explosion process, plasma, corona treatment, dielectric barrier techniques, ultrasound, ultraviolet treatment and with enzymes[12–15].

Limited literature is available on changing the crystal structure of the polypropylene during composite manufacturing. The altering of the crystal structure changes the amorphous content of the polypropylene fibre. This is likely to aid in better melting, leading to the better realization of improved mechanical properties.

Needle - punched nonwovens with flax and polypropylene (PP) fibre have been prepared for this study. During consolidation process, the sample was heated at varying temperature followed by sudden quenching to obtain the β form. The samples were further hot pressed at varying temperature to obtain the composites. The influence of the quenching process on the mechanical properties and failure behaviour was analysed.

2 Materials and Methods

2.1 Raw Materials

Polypropylene (PP) fibres and flax were procured from Zenith fibres, Vadodara, Gujarat, India and Aditya Birla Nuvo Ltd., West Bengal, India respectively.

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2.2 Composite Preparation

The prepared nonwoven web is made of flax and polypropylene in 30:70 ratio having 550 gsm weight. Composites were prepared by compression moulding process as per the line diagram given in Fig. 1. Six layers of the cross - laid nonwoven mat of the dimensions 25×25cm^2 were used for the preparation of composites. The mat was further placed in a spacer of 4 mm thickness between the two platens and was compression moulded at a varying temperature 180°, 190° and 200°C. The pressure for consolidation was maintained at 7.8 MPa. The control samples were hot pressed for 10, 15 and 20 min. The quenched samples were prepared by first heating for 5, 7.5 and 10 min followed by quenching in water cooled bath maintained for 1 min. The samples were further reheated for 5, 7.5 and 10 min. The composite samples prepared at 200°C for 10 min yielded better mechanical properties.

Further, to study the effect of reheating temperature on composite properties, the consolidation temperature was fixed at 200°C for 10 min. The quenched samples were prepared first by heating for 5 min at 200°C followed by quenching in water cooled bath for 1 min. The samples were further consolidated at varying temperature ranging from 140°C to 200°C .The prepared samples were coded as RH-140°C, RH -150°C, RH -160°C, RH -170°C, RH -180°C and RH -200°C.

2.3 Characterisation

2.3.1 Tensile Test

The tensile test was carried out on Instron 3369, USA tester according to ASTM standard test procedure D638-10. The tensile test specimen dimensions were 165×13×4 mm and the machine speed was set at 5 mm/min. The average tensile strength (MPa) was determined from five specimen results based on the formula given below:

$$\text{Tensile strength} = \frac{\text{Maxmium tensile load applied}}{\text{Original cross} - \text{setion area}} \quad \ldots (1)$$

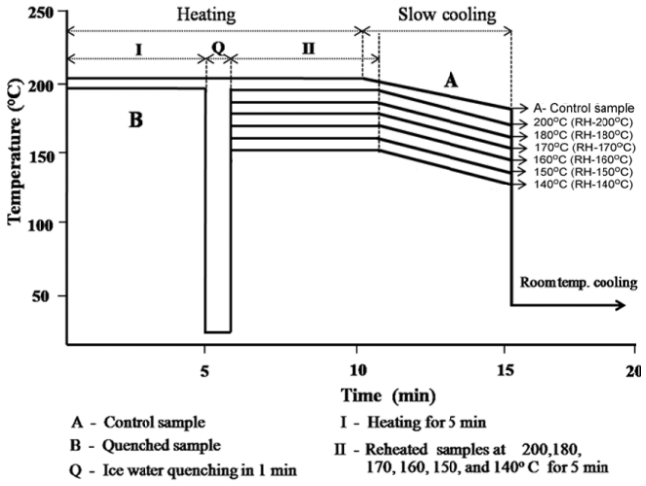

Fig. 1 — Line diagram of composite preparation process

2.3.2 Flexural Test

The flexural test was carried out on the specimens as per ASTM D790-10 standard using Instron 3369. The flexural test specimen dimensions were 125×13×4 mm and the machine speed was set at 2 mm/min. The average flexural strength (MPa) was determined from five specimen results based on the formula given below:

$$\text{Flexural strength} = \frac{3PL}{2bt^2} \quad \ldots (2)$$

where P is the maximum load; b, the width of the specimen; and t, the thickness of the specimen.

2.3.3 Short Beam Strength (SBS)

The short beam strength tests were performed on the composite samples at room temperature to evaluate the value of interlaminar shear strength. It is a 3-point bend test, which generally promotes failure by the interlaminar shear test. The short beam strength test was carried out on the specimens as per ASTM D 2344/D2344M -13 standards using Instron 3369. The average short beam strength (MPa) was determined from five specimen results based on the formula given below:

$$\text{Short beam strength} = \frac{3P}{4bt^2} \quad \ldots (3)$$

The data recorded during the 3- point bend test is used to evaluate the flexural strength also. The test specimen dimensions were 24×8×4 mm and the machine speed was set at 1mm/min.

2.3.4 X- Ray Diffraction (XRD)

Wide angle X- ray diffraction (WAXS) experiments were performed on a PAN analytical X'Pert³ Powder diffractometer with a Cu anode operating at 45 kV and 30 mA, and equipped with a monochromator and a scintillation detector. The intensity versus 2θ peaks was plotted and the crystallinity of the samples was calculated as per the literature reported[16].

2.3.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry experiments were performed on a Netzsch DSC 7 Differential Scanning Calorimeter by varying the cooling rate. To analyse

the effect of quenching on the melting profile, the sequence followed is given below:

(i) Heating from -40°C to 200°C at a rate of 10°C/min.

(ii) Cooling from 200°C to -40°C at a rate of 50°C/min.

(iii) Heating from -40°C to 200°C at a rate of 10°C/min.

(iv) Cooling from 200°C to -40°C at a rate of 10°C/min.

2.3.6 Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR analysis of the control and quenched polypropylene samples was performed on Perkin Elmer Spectrum RX1 (Massachusetts, USA). The resolution for the collection of spectra was fixed at 4 cm^{-1} (24 scans collected) and the scanned wavenumber ranged from 4000 cm^{-1} to 400 cm^{-1}

2.3.7 Thermogravimetric Analysis (TGA)

Thermal stability of control and quenched samples of polypropylene was studied using thermogravimetric analyzer (TA Instruments, TGA 7, USA). The sample weight taken was 5 mg and the measurements were carried out in nitrogen atmosphere with temperature ranging from room temperature to 700°C at a heating rate of 10°C/min.

3 Results and Discussion

Needle - punched nonwovens with flax and polypropylene have been prepared and then the webs are hot pressed to form composites. The composites thus prepared are tested for various mechanical properties, such as tensile, flexural and short beam strength properties. It is observed from the study that the failure in majority of the thermoplastic composite specimens is due to poor adhesion between fibre and matrix. The major goal of the present work is to improve the mechanical strength of composites by better infiltration of PP melt into the nonwovens.

Polypropylene fibre is known to exist in four different crystal structures, namely α, β, ϒ and smectic structure[17]. The crystallinity of PP is around 75%. It has been reported in the literature that quenching of PP at 5°C would yield fibres with high amorphous content[18]. The same concept has been extended in the present work and the flax/PP fibres in the mats are exposed at varying temperatures and then quench cooled to room temperature. Finally, the mat is further hot pressed. The hypothesis is that the quench cooled mat will be amorphous in nature and on further hot pressing the PP fibres will melt with ease and have better adhesion with the flax fibres.

3.1 Tensile test

The tensile strength is directly related to the ability of the materials to transfer stress from the matrix to the reinforcing fibres. The control samples are hot pressed at 180 - 200°C. It can be seen that with an increase in temperature for hot pressing, an increase in tensile strength is observed. At 200°C, a maximum tensile strength of 27 MPa is obtained in the case of control sample. The modulus of the samples is also increased with the increasing temperature of hot pressing; the modulus obtained at 200°C is 1.54 GPa. The strain (%) at 200°C is found 5%. As the maximum tensile properties are achieved at 200°C, for further studies the temperature of consolidation is fixed at 200°C for studying the effect of quenching.

The nonwoven mat is initially hot pressed at 200°C for 5 min followed by quenching in ice water. The samples are further hot pressed at varying temperature from 140°C to 180°C. The quenched composite samples on further hot pressing show higher tensile modulus and strength. Figure 2 (a)

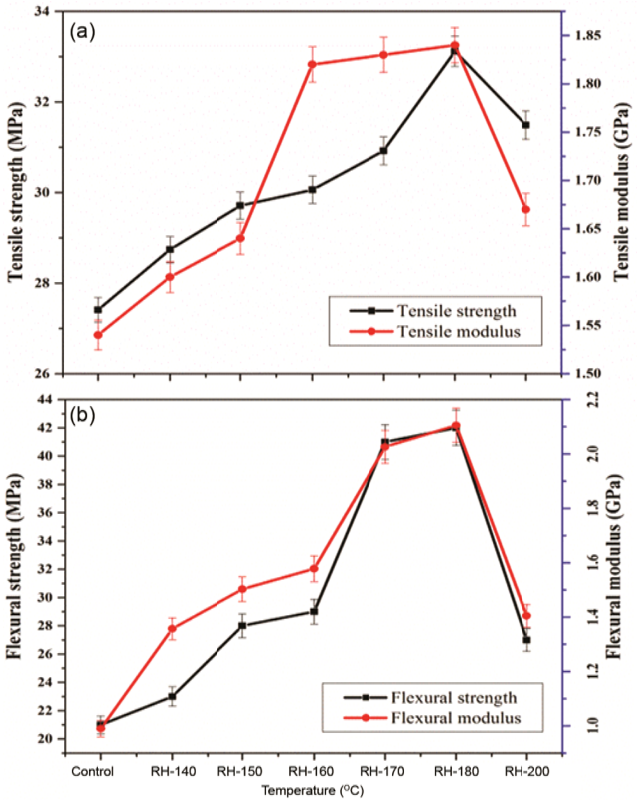

Fig. 2 — (a) Tensile properties of composites and (b) Flexural properties of composites

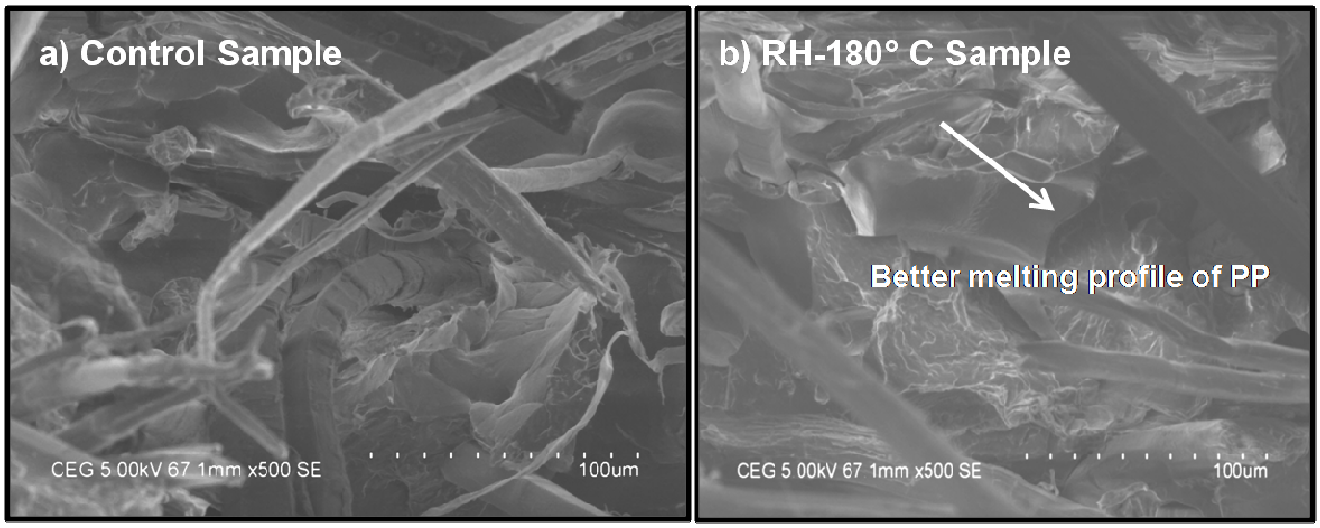

Fig. 3 — SEM micrograph of the tensile fracture surface

shows the tensile properties of composites. A 19 % and 20.83 % increase in tensile modulus and strength has been observed for Q- 180°C samples. This is due to the better infiltration of the PP melt and better adhesion of PP with flax fibre.

3.2 Flexural test

Flexural strength of the composite is the ability to resist deformation under load. The bending of the composites involves both bending and shear displacement. Both tensile compression and shearing take place simultaneously during flexural loading. Figure 2(b) shows the flexural modulus and strength of the samples prepared at varying temperatures. The maximum flexural modulus and strength are obtained at RH 180°C. It should also be noted that for all the quench cooled samples, the flexural modulus and strength values are found to be higher as compared to the control sample. No delamination into separate layers is observed during flexural testing. The increased flexural modulus and strength values suggest that the fibre is fully enveloped by the matrix and efficient stress transfer occurs between the matrix and the fibres. Moreover, during hot pressing, the entanglement of fibres also increases in the nonwoven, thereby improving the strength properties.

Figure 3 shows the SEM images of flax/PP thermoplastic composites. It can be seen from the images that better encapsulation of flax fibres has occurred in quench cooled samples.

3.3 Short Beam Strength (SBS)

The mechanical properties of a composite depend not only on fibre arrangement but also on the

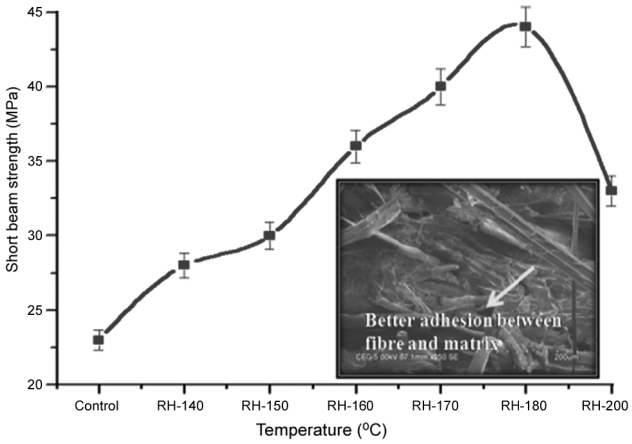

Fig. 4 — Short beam strength properties of composites

adhesion between the fibre and the matrix. This is quite relevant for nonwoven based composites. The interlaminar shear strength is a measure of bonding between reinforcement and matrix. The SBS results of the composite specimens are given in Fig. 4. It can be seen from the graph that SBS of the quenched cooled composites is higher than the control samples. This may be due to the better infiltration of the molten polypropylene and better interlocking of the fibres and matrix owing to hot pressing which can be clearly seen from the SEM images provided as an inset. The short beam strength increases by 91% for reheated samples after quenching as compared to control samples.

3.4 XRD Analysis

Figure 5 shows the XRD peaks of polypropylene taken before and after quenching. The characteristics

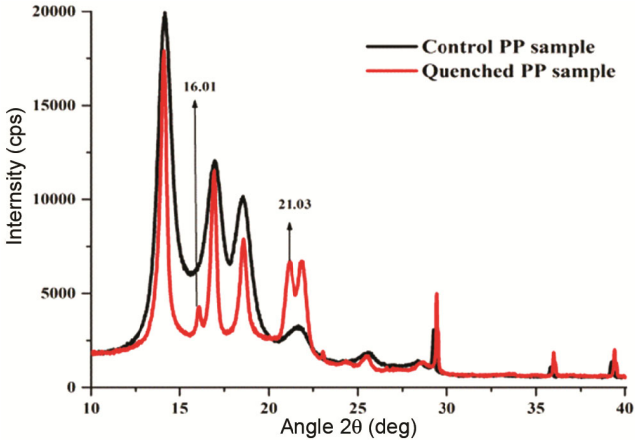

Fig. 5 — X- ray diffraction spectra of polypropylene samples

peaks appear at 14.16, 17.06, 18.65, 21.34 and 21.91° (in 2θ) to that of α-monoclinic crystal structure corresponding to the (110), (040), (130), (111) and (131) planes. No noticeable peak occurs in control sample at 2θ = 16° which is characteristic of the β-hexagonal phase and it can be confirmed that no hexagonal phase (β) is detected. β -hexagonal form appears in quenched polypropylene samples and can be seen from peaks appearing at 2θ = 16° and 21.03°. The appearance of β-phase confirms the structural modification that has occurred due to quenching. The crystallinity % of the quenched cooled samples is found 37% compared to the control samples which has a crystallinity of 54%. This could be advantageously used while preparing the composites.

3.5 DSC Analysis

DSC analysis of the samples has been carried out to study the influence of quenching on melting behaviour of polypropylene. DSC thermograms are taken during heating and cooling cycle of the specimens as shown in Fig. 6. In the case of a heating cycle, the melting point of the polypropylene fibre is observed at 173°C. The onset of the melting occurs at 152°C and it ends at 178°C. The area under the melting peak is 88.92 J/g. The same sample is then quenching cooled in the DSC itself with a scanning rate of 50°C/min and this is followed by the heating of the specimens. This is carried out to simulate the experimental process involved in the work. On the further heating quench cooled samples, the melting peak occurs at 166°C. A shift of 7°C compared to first heating cycle is observed. The onset and end of the melting peaks are 155°C and 166°C. The area under the thermogram

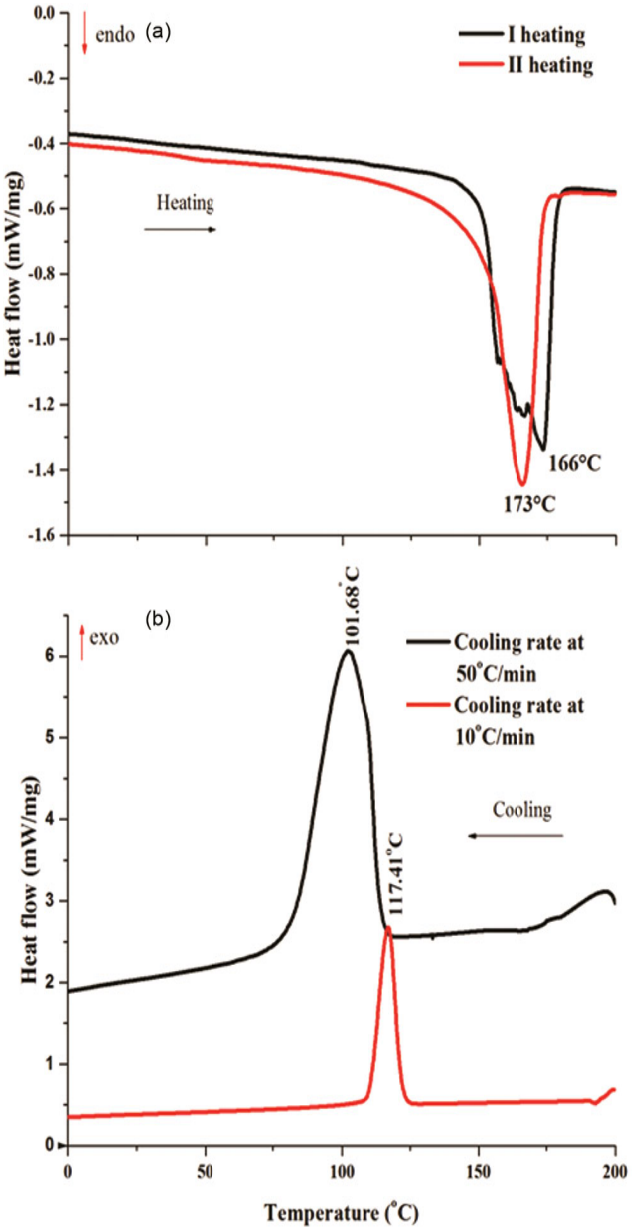

Fig. 6 — DSC thermogram of polypropylene samples

reduces to 62.15 J/g. This suggests that the amorphous content of the sample has increased and is reflected in a decrease in melting temperature. It is well known that PP in the β-phase crystal form melts at a lower temperature compared to α crystal[19]. The cooling profile of the control and rapidly quenched samples is given in Fig. 6(b). The exothermic peak is obtained broadened at a lower temperature with a shoulder at an elevated temperature similar to the results obtained in the literature [20]. This also confirms the formation of a β-phase crystal. However, during normal cooling

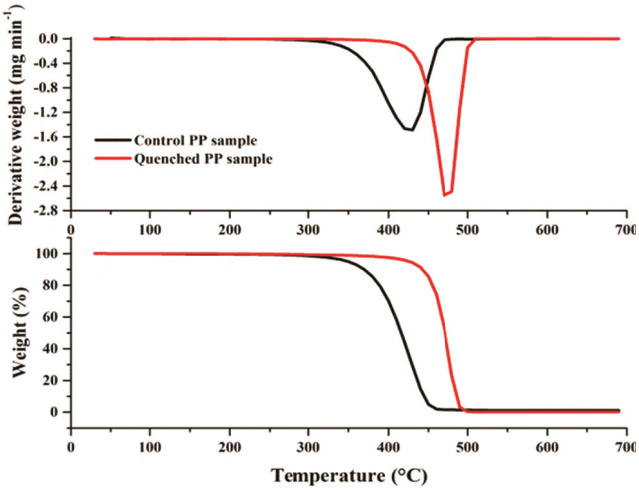

Fig. 7 — Thermogravimetric analysis of polypropylene samples

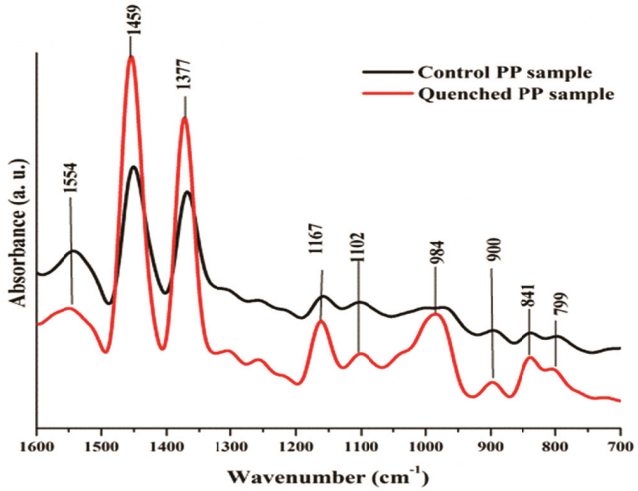

Fig. 8 — Absorbance spectrum of polypropylene samples

(10°C/min), a narrower crystallization profile is obtained. Rapid cooling polypropylene sample crystallizes at 102°C, which indicates that the defective crystals are formed by rapid cooling. A shift in 13°C is observed in crystallisation temperature during normal cooling (10°C/min) in comparison with rapid cooling (50°C/min). This also confirms the formation of a β-phase crystal.

3.6 TGA Analysis

The thermal degradation profiles of pristine and quench cooled PP fibres are given in Fig. 7. In the case of quenched cooled samples, the onset of degradation temperature is 40 – 50°C higher than that of the control sample. In quench cooled samples both α and β crystals are present. The weight loss of the control sample of polypropylene occurs at 260°C, while that of the quenched polypropylene samples occurs at 354°C. Moreover, during quenching, there is an increase in amorphous content in the polymer. During reheating in TGA, the β crystals are converted into α crystal, resulting in increased thermal stability. During reheating, thermal induced crystallisation occurs, and this is also one of the reasons for improved thermal stability.

3.7 FTIR Analysis

To correlate the XRD and DSC results, infrared spectroscopy studies are carried out (Fig. 8). The peaks at 841cm^{-1} and 900 cm^{-1} are due to C-C stretching coupled with C-H deformation, CH_2 and CH_3 rocking. The peak at 1167 cm^{-1} is due to C- C stretching and CH_3 wagging. The peak at 1377 cm^{-1} is due to symmetric C-H bending and the peak at 1459 cm^{-1} can be attributed to bending and asymmetric, in plane CH_3 bending. On comparison with the pristine PP samples, the quenched sample shows an increase in the intensity of peaks and a slight shift occurs between 984 cm^{-1} and 1167 cm^{-1} . This can be correlated to the structural changes occurred in the crystal structure. The appearance of these bands confirms the formation of amorphous phase.

4 Conclusion

The major problem faced in the preparation of flax/PP needle punched - nonwoven based thermoplastic composite is delamination. In the present work, the above limitation is addressed by altering the crystal structure of polypropylene which results in increased β – crystal structure. On further reheating, composites with improved mechanical properties are achieved. The proposed green method can be deployed very easily in various composites manufacturing units and is scalable.

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