Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Bhattacharya, S. K. and Shembekar, V. R.(1995) 'Study of Transcrystalline Morphology of Polypropylene in Composites Containing Polypropylene and Jute Fibres', Journal of Macromolecular Science, Part A, 32: 2, 485 — 497

To link to this Article: DOI: 10.1080/10601329508019194

URL: http://dx.doi.org/10.1080/10601329508019194

MACROMOLECULAR REPORTS, A32(SUPPL. 4), 485-498 (1995)

STUDY OF TRANSCRYSTALLINE MORPHOLOGY OF POLYPROPYLENE IN COMPOSITES CONTAINING POLYPROPYLENE AND JUTE FIBRES

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Abstract:

Development of morphology of Polypropylene(PP) at the jute fibre-PP interface in jute / PP composite systems was studied using thermal, optical and X-ray diffraction techniques. The transcrystallinity was found to develop at the jute/PP interface only on the application of shear & involved the formation of β crystals of PP which were characterised by the presence of endothermic melting peaks at 152°C in differential scanning calorimetry and diffraction peaks corresponding to d-spacings of 5.539Å and 3.302Å respectively in wide angle X-ray diffraction studies. The overall crystallinity of PP in the composite systems was found to decrease on 10 % incorporation of jute but it increased with further increase in jute incorporation level. The surface modification of jute was found to have a beneficial effect on transcrystallinity as well as overall crystallinity of PP in the composites. It is hypothesised that partial compatibility between the matrix and the substrate increases the drag between them under conditions of shear, thereby enhancing the extent of heterogeneous nucleation responsible for development of transcrystalline morphology.

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Introduction:

Transcrystallinity of polymeric materials in fibre reinforced composite systems involves crystallisation of the polymers on the surface of the fibres with or without the application of shear.[1] The chemical nature of the fibre is reported to play an important role in determining the possibility of transcrystallisation.[2] Surface energy of the substrate is also reported to be important in determining transcrystallinity.[3] Development of transcrystalline morphology of Polypropylene (PP) in composites containing various types of fibres e.g. carbon fibre, glass fibre, Kevlar and various other polymeric fibres are reported in literature.[4,5] However, there are not many reports in literature on the development of transcrystalline morphology of PP in contact with lignocellulosic fibres like jute.

Jute is a lignocellulosic fibre containing 72 % cellulose, 13 % hemicelluloses and about 13 % lignin(on dry basis). Because of the presence of cellulose and hemicelluloses jute is a polar, hydrophillic material. On the other hand PP is a paraffinic, hydrophobic, non-polar polymer. Therefore jute and PP are mutually incompatible in nature. The jute surface, however, can be modified to make the surface more hydrophobic. Typical chemical modifications of jute surface include bleaching,[6] acetylation of hydroxylic groups in cellulose / hemicelluloses[7] or grafting of polymeric chains such as polymethyl methacrylate (PMMA)[8] on the cellulose backbone. The interaction between unmodified or chemically modified jute fibres and PP can be reflected on the development of transcrystalline morphology, if any, at the matrix-fibre interface in case of composites containing PP and unmodified or various types of chemically modified jute fibres.

PP is known to exist in three different crystal modifications namely α, β & γ . Among these, the monoclinic α form is thermodynamically the most stable form and PP crystallised from melt under ordinary conditions, crystallises predominantly in α form.[9] The nucleation of the hexagonal β form in the bulk sample is usually rare. But under certain conditions, crystallisation of PP in this form is also reported in literature.[10,11] In case of jute-PP composites, the interaction between jute & PP at the interface &/or effect of shearing during processing of the composites can result in formation of crystal modifications other than the conventional α form in the transcrystalline morphology. In the present study, the development of transcrystalline morphology at the interface of PP and unmodified or different types of chemically modified jute fibres was studied by thermal, optical and wide angle X-ray diffraction studies.

Experimental:

Corchorus olitorius variety of jute and PP powder (MFI=9, from IPCL, India) were used for the preparation of jute/PP composites. Apart from raw jute, bleached, acetylated and PMMA grafted jutes were also used for the same purpose. Bleaching of jute was carried out by treatment with hydrogen peroxide in presence of sodium phosphate and sodium silicate. Acetylation was carried out using acetic anhydride as acetylating agent under various conditions to obtain jute samples with acetyl yields of 2 % & 20 %. PMMA grafting was carried out using hydrogen peroxide and ferrous ammonium sulphate redox initiator system and typical add-on was 5%.[12]

The composites were prepared at National Chemical Laboratory, India, by extrusion blending of the respective fibres with PP and granulating the extrudates. Raw jute was blended in 10 %, 25 %, & 40 % w/w proportions, bleached jute was blended in 10 % & 25 % w/w proportions, acetylated and grafted jutes were blended in 10 % w/w proportion with PP. The granules and the films prepared by melt pressing of the granules were used for thermal and X-ray diffraction studies respectively. Films prepared by melt pressing of the extruded granules were very thick and unsuitable for microscopic studies. For microscopic studies, microcomposite films were prepared by melting PP on a glass slide alongwith a few jute fibres, pulling the fibres when the PP was in molten condition to apply shear and rapidly cooling the films to ambient temperatures.

The interaction of jute fibres and the PP matrix was evaluated by determining the melting and crystallisation behaviour of the composites by a Perkin Elmer Differential Scanning Calorimeter (DSC-7) and comparing them with those of PP homopolymer. The heating and cooling rate employed was 10^0 min^{-1} and scans were carried out in N_2 atmosphere. No glass transition temperature could be detected for either PP homopolymer or composite samples even when scanned from -70^0C and at very low rate of heating / cooling of 2^0C min^{-1}. Heat of fusion values obtained from DSC heating scans were normalised on the basis of the weight fraction of PP present in the composites. Wide angle X-ray diffraction studies were carried out with a Siemens X-ray Diffractometer using Cu-Kα radiation and the typical range of scattering angles studied was 5^0-35^0. For optical microscopy Axioplan Polarising Microscope made by Zeiss was used.

RESULTS & DISCUSSIONS:

Figure 1 shows the crystalline microstructure of PP homopolymer. The spherulitic texture characteristic of crystalline PP was very clearly visible in the picture. The development of crystallinity on the surface of jute fibres in jute/PP microcomposites was also observed in polarising microscopic studies. Figure 2 (a) & 2 (b) show the textures of microcomposites of PP containing raw jute & bleached jute respectively. In both the cases, the birefringent, crystalline texture along the surface of the fibre could be clearly distinguished from the texture in the bulk. The number / amount of crystals on the surface of the fibres was certainly greater than those in the bulk of the microcomposites. In case of those microcomposites where the PP melt was not sheared by pulling off jute fibres while making the films, no transcrystallinity was observed. But in those microcomposites where the fibres were pulled away from the film, transcrystals were even found to form in the displacement path of the fibres. In case of extrusion blended composite granules, the development of transcrystallinity was probably because of shear during processing. Figures 3 (a) and 3 (b) show the textures of the PP microcomposites reinforced with PMMA grafted jute and acetylated (20 % acetyl yield) jute respectively. It can be qualitatively seen that surface modifications of jute fibres, like acetylation or PMMA grafting resulted in enhancement in the amount of transcrystallinity in the system.

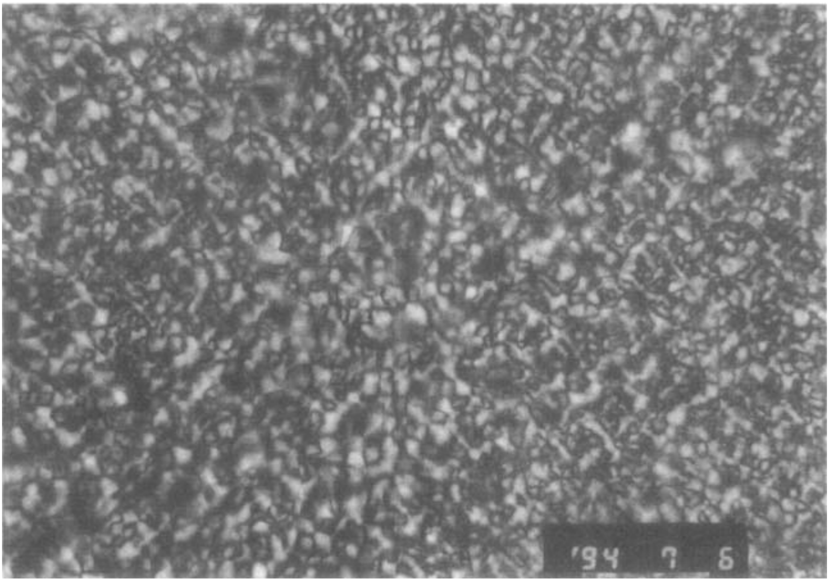

Figure 1:
Crystalline microstructure of Polypropylene. (X 325)

Figure 4 gives the DSC scans of PP homopolymer and jute/PP composite materials containing 25% bleached jute in the first heating cycle. It can be seen from the thermograms that apart from the main melting endotherm occuring at around 164°C, there were smaller peaks at around 142°C to 152°C in the endothermic melting region of PP. The origin of these peaks can be traced to the phenomenon of transcrystllinity.[13] The main endothermic peak represented the melting transition of the α crystal form & the peak at 152°C indicated the melting transition of β-crystal form of PP in transcrystalline samples.[14,15] Similar small melting endotherms around 152°C were also visible in case of composites containing other types of jute fibres. Thus while the PP homopolymer crystallised from melt constituted mostly the α form of crystals, in case of composites β form was also detected along with the α form. The development of transcrystallinity in case of jute / PP composites only on application of shear was also supported by two other observations. The crystallisation

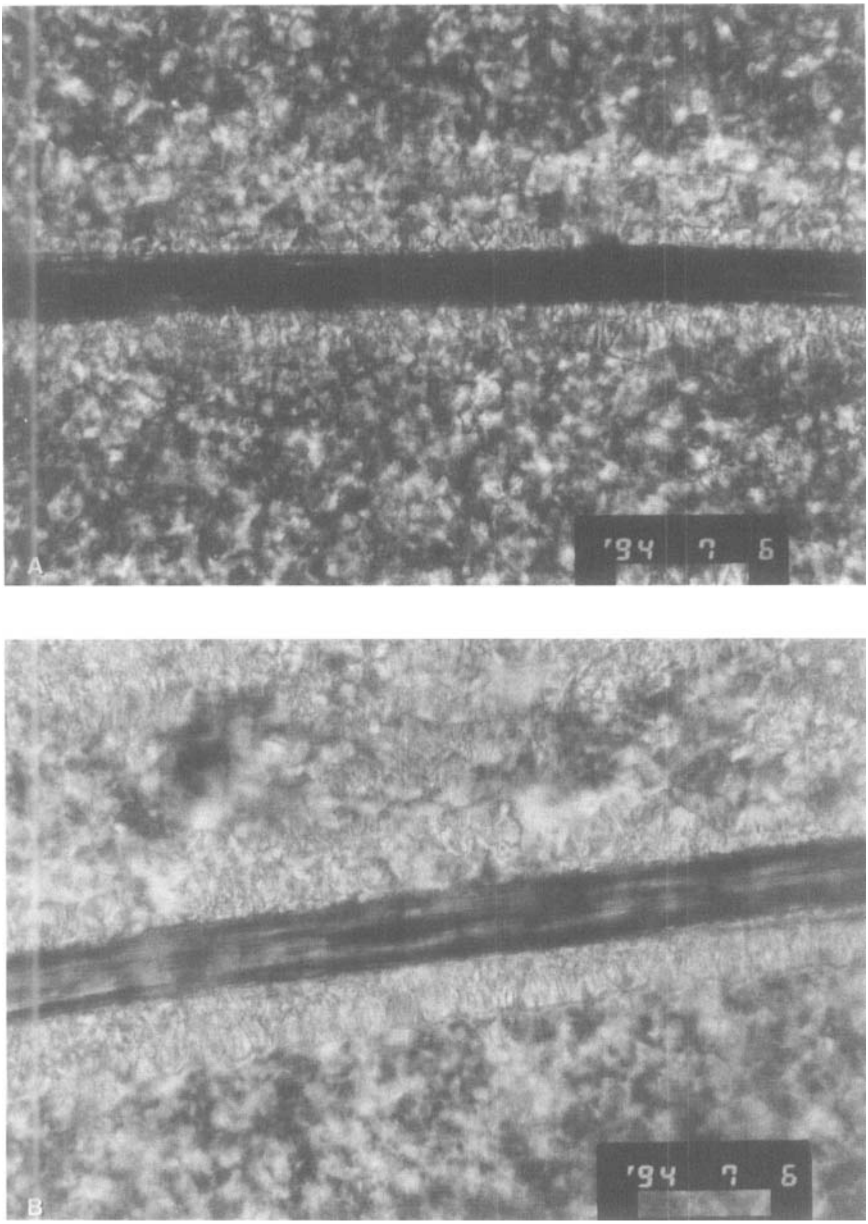

Figure 2:
(a) Transcrystalline morphology developed in a Raw jute / PP microcomposite sample. (X 325)

(b) Transcrystalline morphology developed in a Bleached jute / PP microcomposite sample. (X 650)

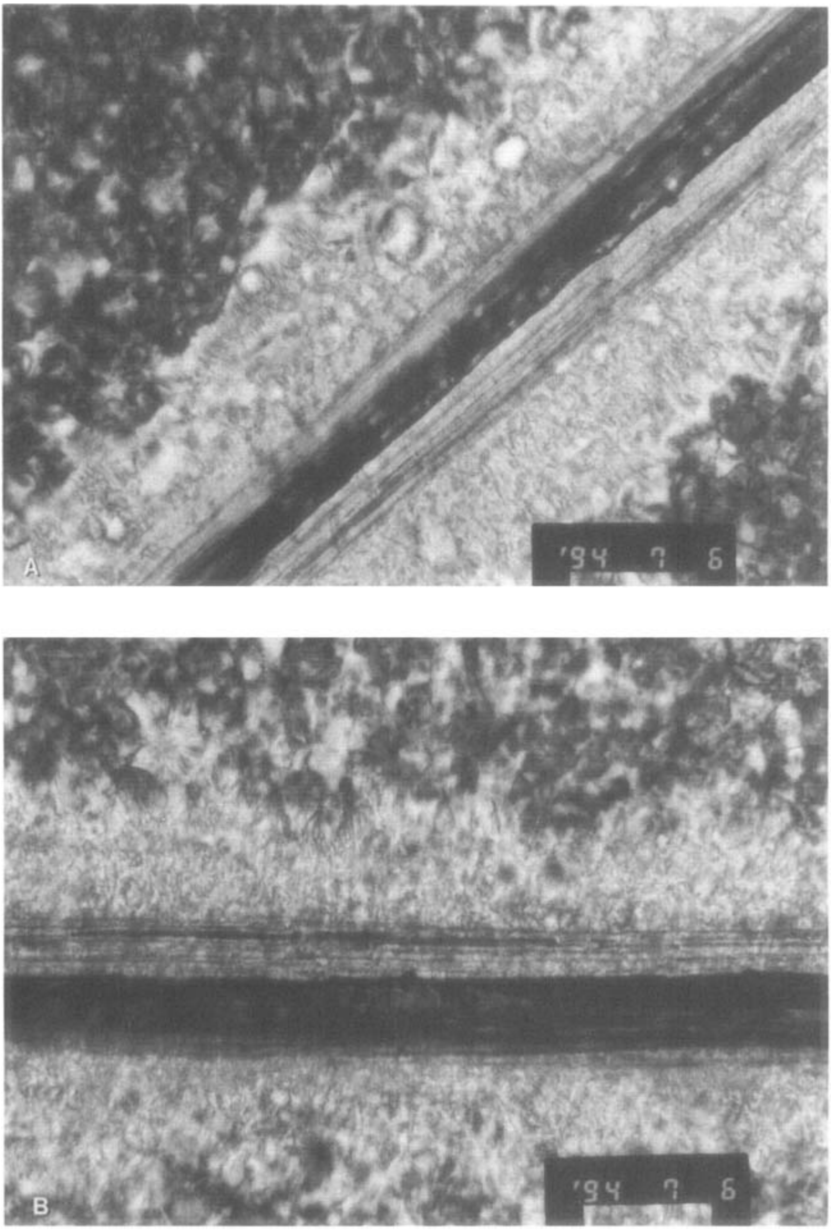

Figure 3:
(a) Transcrystalline morphology developed in a Grafted jute / PP microcomposite sample. (X 650)

(b) Transcrystalline morphology developed in an Acetylated jute / PP composite sample. (X 650) (Acetyl Yield of jute = 20%)

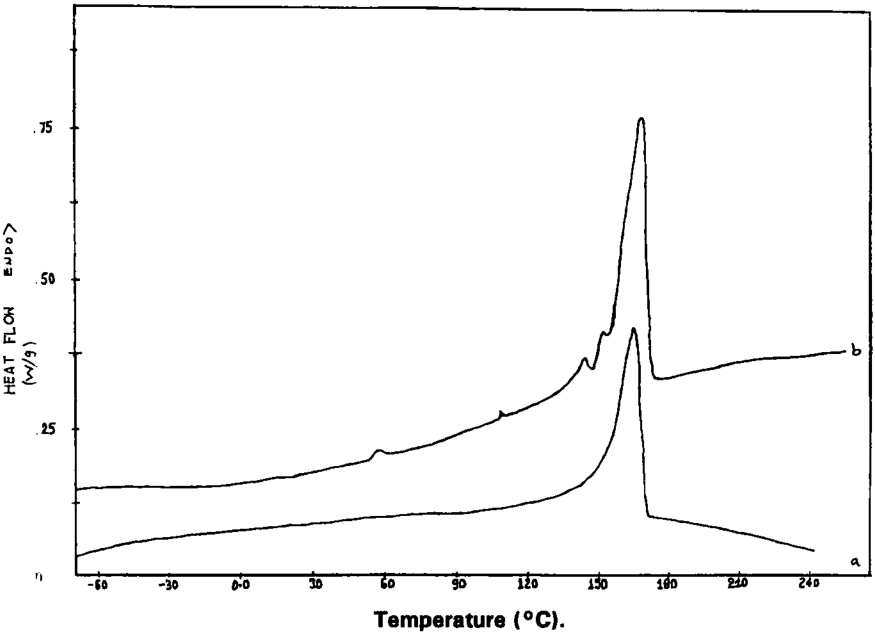

Figure 4:
Differential Scanning Calorimetric scans of (a) Polypropylene (b) Jute / Polypropylene composite.

exotherms of the composite granules in the cooling cycle of DSC, depicting their crystallisation behaviour from melt without the application of any shear, showed no indication of any peak corresponding to transcrystallisation. Secondly, small endotherms corresponding to the melting of the transcrystals were present only in the first heating cycle of DSC of the extrudate granules and were absent in the second heating cycle, which involved melting of PP crystallised without shear.

The wide angle diffraction scans of PP homopolymer, jute and jute / PP composite systems containing 25 % bleached jute are shown in Figure 5. The diffraction peaks at $2\theta=16^0$ and $2\theta= 27^0$ in case of PP / jute composites, which corresponded to d-spacings of 5.539Å and 3.302Å respectively, were clearly absent in case of PP homopolymer thus indicating that they are related to the

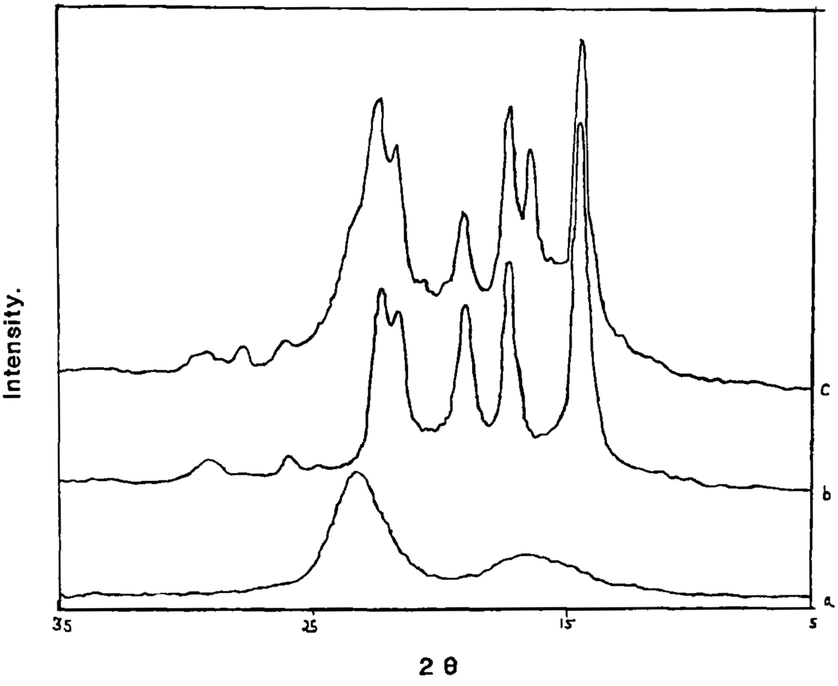

Figure 5:
Wide angle X-ray diffraction scans of (a) Jute (b) Polypropylene and (c) Jute / Polypropylene composites.

transcrystalline growth in the composite system. The diffraction peaks at $2\theta = 16^0$and 27^0 agreed with the observations made in literature on the diffraction pattern of β crystal form found in case of PP rapidly cooled from melt.[16] They also corresponded to the presence of arcs in the wide angle X-ray diffraction patterns related to the hexagonal β crystal form as reported by Draguan and coworkers.[17]

These observations indicated that the dragging of PP molecules on the jute fibre surface due to shearing, caused orderly arrangement of the molecules resulting in nucleation of β crystals along with the ordinary α crystals. When shear was applied during the melt crystallisation of PP in jute / PP composites, a columnar growth in β phase was probably induced

Table: 1

Normalised heat of fusion values of PP in various jute reinforced composites.

Sr. No.	Sample	Normalised Heat of Fusion(J/g).
1.	PP	98.9
2.	PP+10% Raw jute	81.8
3.	PP+25% Raw jute	93.8
4.	PP+40% Raw jute	102.1
5.	PP+10% Bleachedjute	97.0
6.	PP+25% Bleachedjute	114.4
7.	PP+10% Grafted jute	89.6
8.	PP+10% Acetylatedjute (Ac.Yield=2.0%)	87.3
9.	PP+10% Acetylated jute (Ac.Yield=20.0%)	101.5

from the fibre surface, producing a transcrystalline morphology while spherulites nucleated far from the fibres grew in the α form.[14] The extent of transcrystallinity was obviously found to increase with increase in fibre incorporation in the composite. The increase in transcrystallinity in case of microcomposites containing surface modified jute fibres in comparison to those containing raw jute fibres could be explained by the fact that transcrystallinity being a surface induced phenomenon, was affected by the nature of the surface. Partially compatible systems probably enhanced the surface drag between fibre & matrix polymer, thus enhancing the extent of β nucleation resulting in higher transcrystallinity.

Table 1 lists the normalised heat of fusion of PP in various jute containing composites.

The normalised heat of fusion values of PP in case of various composites indicated that incorporation of 10% jute in PP lowered

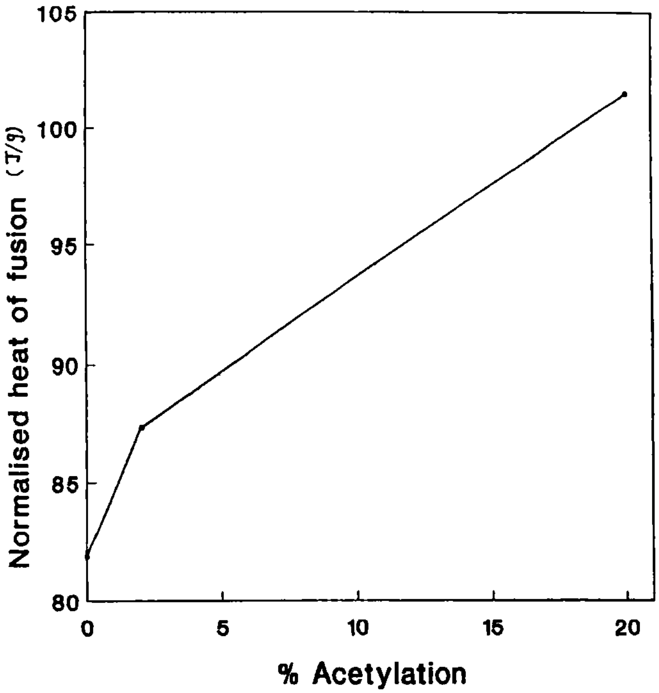

Figure 6:
Heat of Fusion of PP vs. Acetyl Yield of Jute in PP/Ac. Jute composites containing 10% jute.

the heat of fusion, the lowering is less in case of chemically modified (bleached, acetylated, & PMMA grafted) jutes. In fact in case of incorporation of 10 % grafted jute and 10% acetylated jute (Acetyl yield = 20%), the heat of fusion values are Osimilar to that of PP homopolymer within the limits of experimental error. The heat of fusion of PP in the composites was also found to increase with increase in jute incorporation level. As heat of fusion of a semi-crystalline polymer like PP can be directly correlated to it's degree of crystallinity, so it can be said that incorporation of 10% jute lowered the total crystallinity of the system. No certain explanation can be given for this decrease in crystallinity at this moment. However, at higher level of incorporation of fibres, high density heterogeneous nucleation for the ß modification occuring at the jute/PP interface resulted in increase in crystallinity. Surface treatment of jute resulted in surface modification leading to enhanced ß nucleation at low incorporation levels. Figure 6 plots the heat of fusion of PP in jute / PP composites as a function of level of acetylation of incorporated jute & it can be seen that the increase in heat of fusion of PP tended to level off at higher values of acetyl yield of incorporated jute. However, the few number of data points in this case makes any assumption regarding the trend somewhat qualitative.

CONCLUSIONS

Trnscrystallinity develops at the fibre-matrix interface on application of shear in jute/PP composites, involving the formation of ß crystals. The propensity of heterogenous nucleation depends on the alignment of the molecules of the matrix polymer on or in the vicinity of the surface of substrate brought about by shear. The extent of transcrystallinity also depends on the chemical nature of the surface of jute fibres. The partial compatibility between the matrix and the substrate probably increases the drag between them under conditions of shear thereby enhancing the extent heterogenous nucleation. The overall crystallinity of PP in the composite systems decreases with incorporation of low amount of jute fibres but increases upon further increase in the amount of fibres.

ACKNOWLEDGEMENT

The authors wish to thank National Chemical Laboratory, India, for supplying the extrusion blended composite samples used for these studies. They also wish to thank Dr.P.Aravindakshan for supplying PMMA grafted jute fibers.

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