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Structural modification of polypropylene-Bijoypur white clay (PP-BWC) composites

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Abstract Polypropylene-Bijoypur White Clay (PP-BWC) composites were prepared at different compositions of PP and BWC of Bangladesh by extrusion technique. The X-ray diffraction (XRD) studies of the PP-BWC composites reveal that the intensity of the characteristic reflections of BWC increases and that of PP decreases gradually as the BWC proportion increases. The apparent doublet at 21.9° in the XRD pattern of PP becomes two distinct intense reflections in the composites with higher BWC concentrations. The fractional crystallinity, f_c of the composites decreases up to 23 (wt%) BWC and then increases. The crystallite size, t, varies in the opposite manner to that of f_c with BWC concentration. These indicate a change in the composite structure. It is seen from Infrared (IR) spectroscopic studies that the C-H and C-C bonds are affected by BWC. It can be noticed from the Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) that the melting temperature of the composites is found to change from 430 to 435 K with increasing BWC. The change of the melting temperature, exothermic peak temperature and weight loss (%) with BWC content indicates the modification of PP-BWC structure with BWC concentration which supports the observations of XRD and IR.

Keywords Polymer composites, XRD, IR, DTA/TGA

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1. Introduction

A large amount of work has been dedicated to improve the properties and quality of composite materials to meet engineering requirements. Various technical demands of the modern technology of such materials depend on their structural, electrical and optical behaviours. A survey of literature on these composites indicated that although a lot of work has been done on the preparation of polymer ceramic composites but more work on the structure – property relation [1] of these materials are needed to explore for suitable application. The investigation of the structural properties of polymer composite may find particular interest because of their use in electronic applications [2]. Several authors have reported the structure and optical absorption behaviour of polypropylene (PP) [3], biaxially oriented PP [3-5], Polyethylene [6] and other polymers [7-9]. The interaction of additives with polymers may result the formation of molecular aggregates [10-11].

Bijoypur white clay (BWC) is being used in ceramics, insulators and sanitary industries. Several authors [12-14] have reported the chemical analysis of BWC. Chowdhury and Bhuiyan [15] carried out an investigation on the structural modification of BWC on heat treatment at high temperature and found that BWC modifies on heat treatment to a possible mullite phase.

This work is an attempt to elucidate the structural properties of PP-BWC composites using X-ray Diffractometry (XRD), Infrared (IR) spectroscopy and Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). From XRD and DTA/TGA the crystallite size, crystallinity, exothermic peak temperatures in the DTA and corresponding weight losses observed in the TGA trace of different composites have been determined. The IR spectroscopic analyses were done to substantiate the XRD observations.

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2. Theory

2.1 X-ray diffractometry (XRD) :

The Bragg equation for the first order diffraction is

$$d_{hkl} = \frac{}{2 \sin \theta} \tag{1}$$

where d_{hkl} is the interplanar spacing, θ is the angle of diffraction, λ is the wavelength of the X-ray radiation.

The fractional crystallinity, f_c , is expressed as

$$f_c = \frac{I_c}{I_a + I_c} \tag{2}$$

where I_c is the total area attributable to crystalline diffraction (which includes the areas of all crystalline peaks), I_a is the area under the amorphous curve.

The crystallite size was calculated using Scherrer's relation [16].

$$t = \frac{K\lambda}{\beta \cos(\theta_{hkl})} \tag{3}$$

where t is the crystallite size that is perpendicular to the *hkl* plane, β, the peak width at full width half maximum (FWHM) in radians and θ_{hkl} is the Bragg angle. The coefficient K normally takes a value close to 0 9.

2.2 Infrared (IR) spectroscopy :

In the IR spectroscopy intensity of absorption or transmission is directly proportional to the energy of the vibration of molecules. Band intensities are expressed either as transmission (T) or absorption (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance, *i.e.* $A = \log_{10}(1/T)$.

3. Experimental details

3.1 Sample preparation :

Composites used in this work were prepared from PP (NOVOLEN 1100L 2510025, BASF, Germany, density = 900 kg/m^3, melting temperature = 338K, glass transition temperature = 270K) Refractive index, μ = 1.3, Molecular weight, M_w = 184700 g/mole) and the uncompressed hard and solid BWC was collected from the mine at Bijoypur, Netrakona, Bangladesh. To collect the sample in the form of hard lumps, overburden of about 5m thickness was removed. Two kilogram of BWC lumps was manually crushed into coarse powder using mortal and pestle and BWC powder was then sieved through a 200 mesh sieve. At first five batches with different compositions of PP and BWC powder were prepared according to the formula are 10 PP:x BWC where x = 1, 2, 3, 4, 5. The samples are represented as

Sample designation	A	B	C_1	C_2	C_3	C_4	
Composition	PP	BWC	10:1	10:2	10:3	10:4	10.5

The different mixtures were mixed during passing through an extrusion machine. The molten material was collected through the die in the form of rod. The rods were cooled in a water bath during collection. These were then cut by a hacksaw to pellets. The pellets were then polished by a metallographic polisher (MSP-2 of Shimadzu Scientific Instrument Company Ltd , Japan) Then the composite pellets were pressed using a hydraulic pressing unit at a pressure of 34 MPa at 398 K for five minutes. The samples were then stored in a dessicator. A pure PP and BWC samples were also prepared following the same procedure

3.2 Measurement techniques :

An X-ray diffractometer (Model JDX-8P) of JEOL LTD., Tokyo, Japan was used. The target is Cuk$_\alpha$ and the wavelength of X-ray radiation is 1.5418Å. The XRD patterns of the samples mentioned in Section 3.1 were recorded as a function of 2θ from 3 to 73° using the above mentioned diffractometer

The IR spectra of all the samples at room temperature were recorded in the wave number region 400-4000 cm^{-1} using an IR 470 double beam spectrophotometer of Shimadzu Corporation Japan

All DTA and TGA scans were taken from 300-800 K in air at the heating rate 10K/min. DTA was performed using Shimadzu micro DTA system model DT50, Shimadzu Corporation, Japan Mettler M3 balance, TG 50 furnace and microprocessor TA-3000 system were used for TG analysis.

4. Results and discussion

4.1 XRD analysis :

X-ray diffraction patterns of the samples A, B, C_1, C_2, C_3, C_4 and C_5 are presented in Figure 1. These diffraction patterns are represented respectively by diffractograms a, b, c, d, e, f and g The details of the X-ray scans (2θ and d_{hkl}) are depicted in Tables 1 and 2.

From the XRD pattern of sample A (PP), it is observed that the intense diffraction maxima appear at the 2θ values of 14°, 17°, 18.6°, 21.9°, 25.6°, 29.4°, *etc*. These values are matched very closely with the values reported by several authors [17, 18] indicating that the PP used in this experiment is isotactic The X-ray scans of PP indicate monoclinic α form crystallites with some peaks absent. The absence of some peaks could be due to orientation of the crystalline phase [19]. The first very broad peak around 7.2° may be due to the defects between crystallites in fibrils or regions between the fibrils, and/or imperfections in

Table 1. 2θ and d_{hkl} values of samples A (PP) and B (BWC).

PP		BWC	
2θ (degree)	d_{hkl} (Å)	2θ (degree)	d_{hkl} (Å)
7 2	12 277	9.2	9.612
14 0	6.325	12.6	7.030
17.0	5.215	20.0	4 440
18 6	4.770	21.0	4 230
21 9	4.058	25 0	3.560
25 6	3 479	26 8	3 320
29 4	3 038	36.6	2.455
33 8	2.652	38.0	2 370
43 4	2.085	39.4	2 286
47 8	1 903	42.4	2.132
48 8	1 866	45 8	1 981

the ordered phase, together with background noise at the low diffraction angles.

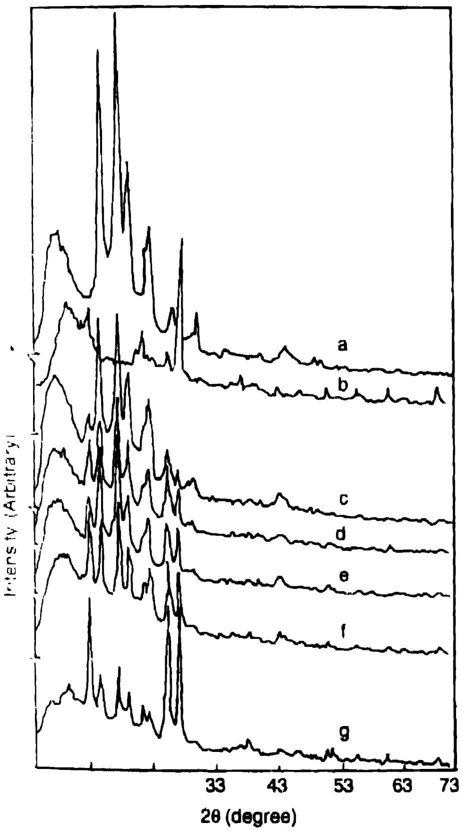

Figure 1. The XRD patterns of all the samples represented by A(PP), a; B (BWC) b, C_1, c; C_2, d; C_3, e; C_4, f ; and C_5, g.

Table 2. Summary of the peak intensities of XRD patterns of PP-BWC composites.

2θ	C_1		C_2		C_3		C_4		C_5	
	PP	BWC	PP	BWC	PP	BWC	PP	BWC	PP	BWC
12 6		S	–	M	–	M	–	M		L
14 0	VL	-	M	-	M	–	M	-	S	–
17 0	VL	–	L	.	L	–	M		M	–
18 6	L	–	M	-	M	–	S	-	S	-
20 0	–		–	–	-	-	–	–	–	–
21 0	–		–	–		–	–	S	–	S
21 9	L (doublet)	-	M (doublet)	–	M (doublet)	-	M	–	S	-
25 0	–	S	-	M	–	M	–	M		L
25 6	S (merged)	–	-	-	-	–	–	–	–	–
26 8	-	S	–	S	–	M		M	-	L
29 4	S	-	VS	–	VS	–	VS	-	VS	-
43 4	S		VS	.	VS	-	VS	-	VS	

VL–Very large, L–large, M–Medium, S–Small, VS–Very small

The XRD pattern of the sample B (BWC) shows the main position of diffraction peaks at the 2θ values of 12.6°, 20°, 21°, 25°, 26.8°, 36.6°, 38°, 39.4°, 42.4°, 45.8°, 55°. The XRD analysis shows the presence of kaolinite (7.03, 3.56 and 1.45 Å), silicon oxide (4 44, 2.44 and 1.45 Å), iron oxide (1.67, 1.38 and 1.28 Å), potassium aluminium silicate hydroxide (4 93, 3.56, 2.53 and 2.37Å), aluminium silicate (9.61 and 4.44Å), *etc*. Very small amount of oxides of potassium, calcium, sodium, *etc*. may also be present as reported by Biswas and Basak [12] and Chowdhury and Bhuiyan [15].

The XRD patterns of samples C_1 to C_5 containing different amount of BWC shown in Figure 1 exhibit most of the major characteristic reflections present in the XRD patterns of PP and BWC. It is observed that the intensity of the characteristic reflections (2θ = 12.6°, 20°, 21°, 25°, 26.8°, *etc*) of BWC are increasing and that of PP (2θ = 14°, 17°, 18.6°, 21.9°, 25 6°, 29.4°, *etc*) are decreasing gradually as the BWC proportion increases (Table 2). The apparent doublet at 2θ = 21.9° in the XRD pattern of PP becomes a clear doublet and appears as two distinct intense reflections (Table 2) in case of becomes a clear doublet and appears as two distinct intense reflections (Table 2) in case of composites with high BWC concentrations These variations in the XRD reflections indicate a definite effect of BWC in the PP structure.

The fractional crystallinity, f_c, was calculated using the eq (2) from the XRD patterns of A, B, and composites C_1 to C_5 samples. The crystallite size, *t*, was calculated using eq. (3).

The variations of f_c and *t* as a function of BWC concentration are presented in Figure 2. It is observed that f_c decreases up to 23 (wt%) BWC and then increase and *t* varies in opposite manner to that of f_c with BWC concentration. This kind of behaviour was also observed in the metal filled PP composites [16] and polypropylene/styrene-ethylene butylene-styrene triblock copolymer blends [20].

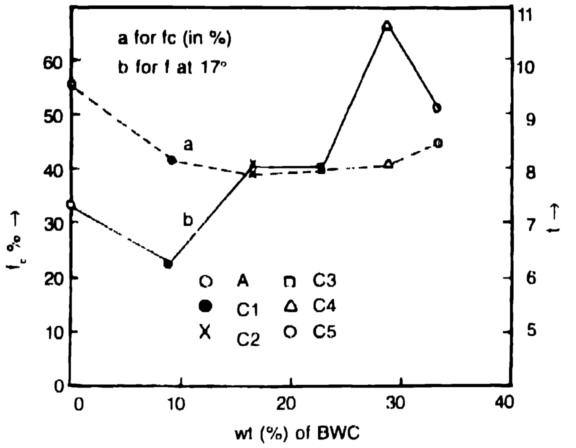

Figure 2. The crystallinity, f_c, and crystallite size, t, of all the samples The samples designations are as in Figure 1

4.2 Infrared (IR) spectroscopy .

The IR spectra of all the samples are shown in Figure 3. The IR spectra for the samples, A, B and composites C_1 to C_5 are represented as a, b, c, d, e, f and g, respectively.

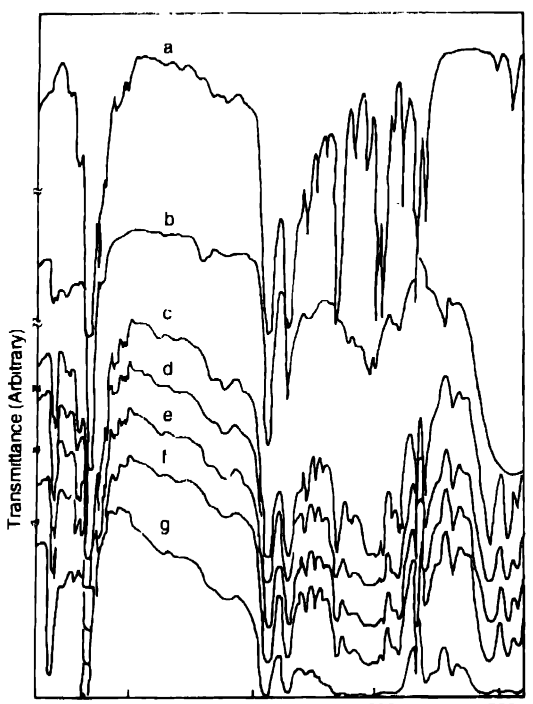

Figure 3. The IR spectra of all the samples. The samples' designations are as in Figure 1

In the spectrum a for PP, it is observed that there is a broad band around 3000 cm^{-1} which may be assigned to C-H stretching in alkane. The absorption bands at 1446 and 1365 cm^{-1} may be due to the presence of CH_3 group in polypropylene. The absorption band at 1251 cm^{-1} may be due to the C-H out of plane bending. The absorption band at 995 cm^{-1} may be assigned to C-C stretching and 838 and 806 cm^{-1} absorption bands arise due to the presence of C-H rocking group. The absorption bands 897, 995, 1163 and 1253 cm^{-1} are the characteristic of isotactic polypropylene [4], Thus, the IR spectrum is well matched with the reported IR spectrum of isotactic polypropylene except for a few extra bands.

The major absorption bands in the IR spectrum b for sample BWC are summarized in Table 3. The spectrum b shows a close similarity to a standard kaolinite [21, 22] along with other absorption bands. The minor departure in the absorption features of this clay with that of standard kaolinite may be attributed to the variation of kaolinite content, degree of crystallinity presence of other constituents, *etc*.

Table 3. The IR absorption bands of the major constituents of sample B (BWC)

Constituents of BWC	Wave number (cm^{-1})
Kaolinite	691,911, 1005, 1031, 1115, 3660
Silicon oxide	768, 790, 935

In the IR spectra c to g for composites C_1 to C_5 respectively given in Figure 3, it is observed that all the composites exhibit all the major characteristic IR bands of PP and some new peaks The overall transmittance decreases with increasing BWC The addition of BWC results in the appearance of a band at 3660 cm^{-1} corresponding to kaolinite the intensity of which is increased with the increase of BWC concentration. The bands at 995 and 1163 cm^{-1}corresponding to C-C decreases gradually and then disappear for higher concentration of BWC The absorption band at 838 cm^{-1} for C-H decreases with the increasing percentage of BWC. It is seen that the C-H and C-C bonds are affected by the increasing amount of BWC in PP whereas the CH_3 bond is not affected by the addition of BWC Thus this observation substantiated the XRD observation which reflects a variation in the PP structure on inclusion of BWC

4.3 Differential thermal analysis and thermogravimetric analysis :

The DTA and TGA traces of the samples A, B, C_1, C_2, C_3, C_4 and C_5 are presented in Figure 4 (a-g). The DTA thermogram of sample A (PP) shows an endothermic peak at about 430 K and two exothermic peaks at about 550 and 635 K. The endothermic peak at about 430 K is due to the melting of PP [23] The two exothermic peaks at 550 and 635 K may be related to dehydrogenation and oxidative reaction. The corresponding TGA trace from room temperature to 773 K shows a gradual weight loss up to about 505 K, a step weight loss between 505 and 650 K and then a small weight loss above 650 K. The TGA trace can be divided into three regions each associated with different rate of weight loss. The amounts of weight losses at the three regions are about 10, 81 and 7%. The first region of

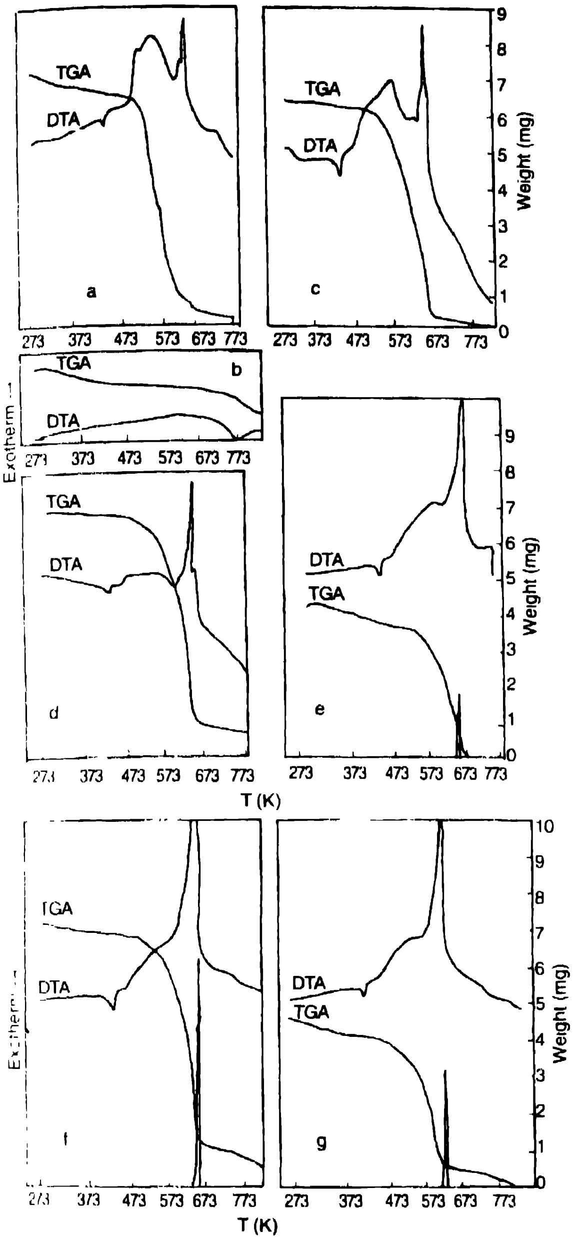

Figure 4. The DTA and TGA traces of all the samples The samples' designations are as in Figure 1.

weight loss from room temperature to 505 K may be due primarily to the expulsion of absorbed water and other gaseous species. The DTA endothermic peaks corresponding to melting of PP in this region supports this argument. The second region of weight loss, from 505 to 650 K could be responsible for major thermal degradation of the polymer as the DTA trace exhibits two exothermic peaks in this region. These may be associated to two different types of reaction. The first wide exotherm may be attributed mainly to the dehydrogenation of the polymer together with some oxidative reactions. The second sharp exothermic peak may be related to oxidative thermal breakdown of the polymer backbone. The third region of weight loss above 650 K may be caused by further oxidative thermal breakdown of the polymer backbone.

The DTA thermogram of sample B (BWC) shows an endothermic peak at about 773 K. The endothermic peak is attributed to the expulsion of water of crystallization or interlayer water [15]. The corresponding TGA trace from room temperature to 873 K shows a gradual weight loss around the DTA endotherm

The DTA and TGA trace of composite samples C_1 to C_5 are shown in Figure 4 (c-g). The DTA thermograms show a common endothermic peak between 430-435 K which are around the melting temperature of PP as observed in Figure 4 (a). The exotherm doublet is reduced gradually to a sharp exothermic peak corresponding to the high temperature exotherm in the DTA of PP Figure 4(a) with the increasing amount of BWC in the composites. The endothermic and exothermic peak temperatures and weight loss (%) for all the samples are depicted in Table 4. It is seen that the melting temperature increases slightly with the addition of BWC up to 23 (wt%) and then remains unchanged. This may be attributed to the formation of polymer BWC agglomerates in the composites and the agglomeration may attain a saturation after 23 (wt%). The increase of exothermic peak temperature with greater intensity also implies the formation of agglomerates in the PP-BWC matrix. As a result the degradation of the matrix and evolution of the different gases take place at higher temperatures at a time. It is seen that the main loss has taken place in the middle region. It is observed

Table 4. The Endothermic and Exothermic peak temperatures in DTA and the weight loss (%) calculated from TGA traces for all the samples.

Samples	Endothermic peak temperature (K)	Exothermic peak temperature (K)	Weight loss (%) in the main region	
			Temperature (K) region	Weight loss (%)
A	430	550 and 635	505-650	81 50
B	773		735-875	11 00
C_1	430	560 and 645	510-650	88.00
C_2	433	647	490-665	85.00
C_3	435	651	510-655	84 00
C_4	430	656	506-656	77.00
C_5	430	648	497-657	74 00

that although the weight loss temperature region is almost same, the weight loss decreases with the addition of BWC in PP. It is seen in Figure 4(b) that the weight loss for BWC in different temperature ranges is less as compared to that of PP. Thus, this may be one of the reasons of reduced weight loss as the amount of BWC increases in the composites. These results corroborate the observation of structural change in the XRD and IR investigations discussed earlier.

5. Conclusions

An analysis of the XRD patterns of the PP-BWC composites reveals that the intensity of the characteristic reflections of BWC increases and that of PP decreases gradually with BWC. The apparent doublet at 21.9° in the XRD pattern of PP is changed to separate intense reflections in the composites in the higher BWC concentration. The f_c of the composites decreases up to 23 (wt%) BWC and then increases. The t varies in the opposite manner to that of f_c with BWC concentration. These observations indicate a definite effect of BWC on the PP-BWC structure. The overall IR transmittance of the composites decreases with increasing BWC. It is seen from IR spectroscopic studies that the C-H and C-C bonds are affected by BWC.

The melting temperature of the composites is found to change from 430 to 435 K on BWC inclusion. The exotherms around 550 and 635 K in the DTA trace of PP and corresponding weight loss observed in the TGA trace may be due to dehydrogenation accompanied by some oxidative reaction. The change of the melting temperature, exothermic temperature and weight loss (%) with BWC content indicate the modification of PP-BWC structure due to inclusion of BWC that supports the observations of XRD and IR studies.

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