Int. J. Chem. Sci.: 10(3), 2012, 1235-1245
ISSN 0972-768X
www.sadgurupublications.com

STUDY ON EFFECT OF VARIATION OF DIISOCYANATE AND NCO/OH MOLAR RATIO ON THERMAL PROPERTY AND CRYSTALLINITY OF INTERPENETRATING POLYMER NETWORKS DERIVED FROM BIOMASS

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ABSTRACT

Polymers derived from biomass are now a matter of the utmost importance from both commercial and academic points of view. Using annually renewable biomass, agricultural waste and a low cost natural oil, the production of new cross-linked polymers can have both economic and environmental benefits. The production, modification, property enhancement and new applications of these materials are an important concern. Interpenetrating polymer networks were synthesized from glycerol modified linseed oil, an aliphatic or aromatic diisocyanate and phosphorylated cardanol. Characterizations of these polymers were performed by spectral and thermal analysis techniques. The kinetic parameters such as activation energies and order of reactions were estimated by using Freeman-Anderson's method. Crystallinity of these polymers was determined by XRD study. The choice of diisocyanate and the variation of NCO/OH molar ratio of polyurethanes on the properties of such polymers are the scope of the present investigation.

Key words: Hydroxyl modified cardanol, Modified linseed oil, Polyurethanes, Interpenetrating polymer networks.

INTRODUCTION

Fossil fuels used in the manufacture of plastics account for about 7% of worldwide oil and gas[1]. These resources will be depleted within the next few hundred years, and within

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the next few decades, the peak in global oil production will occur[2]. Polymers from biomass not only solve the problem of shortage of petrochemical products but also help in waste disposal. Currently, the disposal of polymers derived from petrochemical sources is a major concern, especially in populous countries. Therefore, there is considerable demand for the development of biodegradable and ecofriendly polymers. In fact, many of the polymers derived from renewable resources can also be biodegradable under the appropriate conditions. The work on interpenetrating polymer networks (IPNs) from renewable resources was initiated by Sperling[3,4] and reported later on by others[5-8]. The aim of our work is to utilize our natural and agricultural resources to produce cost-effective and relatively eco-friendly polymers with significantly improved properties. Cardanol having an unsaturated side chain at meta position was isolated from the Cashew Nut Shell Liquid (CNSL) by decarboxylation of its major component that is anacardic acid[9]. It was then modified into a new monomer by reacting it with orthophosphoric acid. Such biomonomer and an isocyanate polyurethane obtained from glycerol modified linseed oil, in different weight ratios were reacted to form a number of interpenetrating polymer networks, a novel enolic class of polymer blend in network forms in which at least one component is polymerized and/or crosslinked in presence of the other. The structural evaluation of these polymers was performed using Fourier transform infra red (FTIR) spectral data. Thermal analysis techniques such as Thermogravimetric analysis (TGA), Derivative thermogravimetry (DTG) and Differential thermal analysis (DTA) were used to study the thermal properties such as the decomposition temperature, temperature of maximum decomposition and relative thermal stability of polymers. Such polymers exhibit significantly large thermal stability and find applications in various fields with better and more improved properties. In the recent past, a large number of research papers, articles and reviews have come out in the field of work with cardanol which is a biomonomer derived from cashew nut shell liquid (CNSL)[10,11]. However, synthesis of interpenetrating polymer networks using phosphorylated cardanol and modified linseed oil based polyurethanes (PUs) is very limited[12]. So in the present study, linseed oil, a drying oil was modified with glycerol. The polyol modified linseed oil (PL) was allowed to react with hexamethylene diisocyanate (HMDI)/toluene diisocyanate (TDI) in different NCO/OH molar ratios to produce a series of polyurethanes by polycondensation polymerization.

EXPERIMENTAL

Synthesis of polyurethanes (PUs)

Linseed oil was heated to 250-260°C in an inert nitrogen atmosphere with 0.1568 g of PbO i.e. 0.05% litharge (Oil basis) as catalyst and 80 mL (1.5 times stoichiometric quantity) of glycerol with constant stirring to obtain polyol modified linseed oil (PL). 0.708 g of polyol modified linseed oil was reacted with 0.672 g of hexamethylene-1, 6- diisocyanate (HMDI) at 45°C in methyl ethyl ketone (MEK) as solvent with constant stirring for 45 min until a viscous prepolymer (polyurethane) separated out with NCO/OH molar ratio at 2.0. The same procedure was followed to prepare PUs using toluene-2, 4-diisocyanate with NCO/OH molar ratio at 2.0 and 1.2.

Synthesis of interpenetrating polymer networks (IPNs)

Anacardic acid (2-carboxylic-3-pentadecadienylphenol), the major component of Cashew Nut Shell Liquid was decarboxylated to cardanol by vacuum distillation. A mixture of 150 g (0.5 mol) of cardanol and 49 g (0.5 mol) of ortho-phosphoric acid was condensed at 175°C under vacuum to obtain phosphorylated cardanol(PC). The mixture of polyurethane (PU) and phosphorylated cardanol (PC) with a constant PU/PC weight – to – weight ratio (50 : 50) for different NCO/OH molar ratios were separately taken in MEK in a reaction vessel in presence of benzoyl peroxide (BPO) and ethylene glycol dimethacrylate (EGDM). The mixture was constantly stirred at room temperature by means of a magnetic stirrer for 15 min to get a homogeneous solution and thereafter the temperature was raised to 75°C to initiate the polymerisation and stirring was continued for about 1 h to get a viscous mass which was poured into a glass mould and kept in a preheated oven at 75°C for 24 h. The thin film thus formed was cooled and removed from the mould and labelled. The feed composition data of the IPNs are furnished in Table 1.

Table 1: Feed composition data of IPNs

Sample code	Composition	NCO/ OH molar ratio	PU / PC (wt. ratio)
IPN-1	PL[a] + HMDI[b] + PC[c]	2.0	50 : 50
IPN-2	PL + TDI[d] + PC	2.0	50 : 50
IPN-3	PL + TDI + PC	1.2	50 : 50

[a]Polyol modified linseed oil, [b]Hexamethylene diisocyanate,
[c]Phosphorylated cardanol, [d]Toluene diisocyanate

RESULTS AND DISCUSSION

FTIR spectral analysis

The infrared spectra of the Interpenetrating Polymer Networks (IPNs) were obtained using Perking Elmer FTIR spectrometer model Paragon 1000.

The FTIR spectrum was used mainly to confirm the presence of component materials in the IPNs. The characteristic absorptions of IPN-1 corresponding to N-H stretching of >NH group at 3488.15 cm^{-1}, C-H stretchings (ss/as) of >CH_2 and –CH_3 groups at 2900.01 cm^{-1} and 2926.11 cm$^{-1,}$ N≡C stretching of –N=C=O for isocyanate terminating PU unit at about 2444.00 cm^{-1}, C=O stretching of >C=O group of urethane linkage at 1738.95 cm^{-1} were observed (Fig. 1). Similar characteristic absorption peaks were observed for IPN-2 and IPN-3 as shown in Fig. 2 and Fig. 3 respectively.

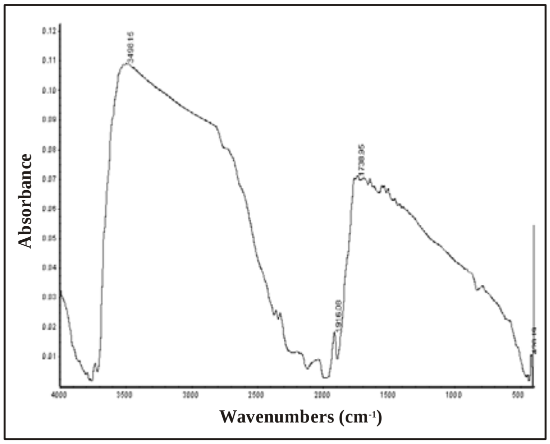

Fig. 1: FTIR Spectra of IPN-1

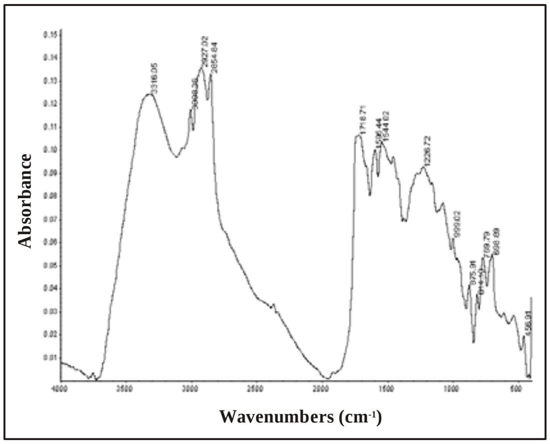

Fig. 2: FTIR Spectra of IPN-2

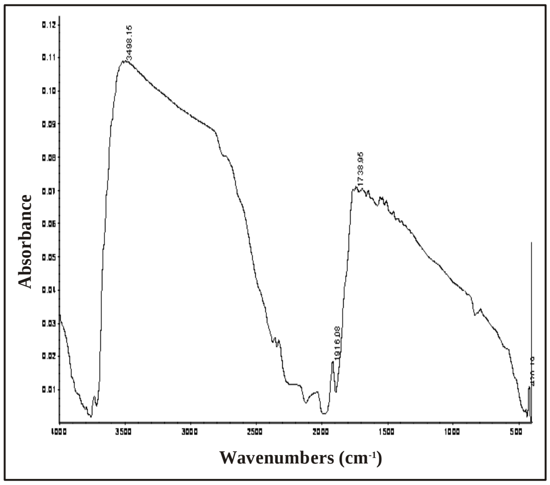

Fig. 3: FTIR Spectra of IPN-3

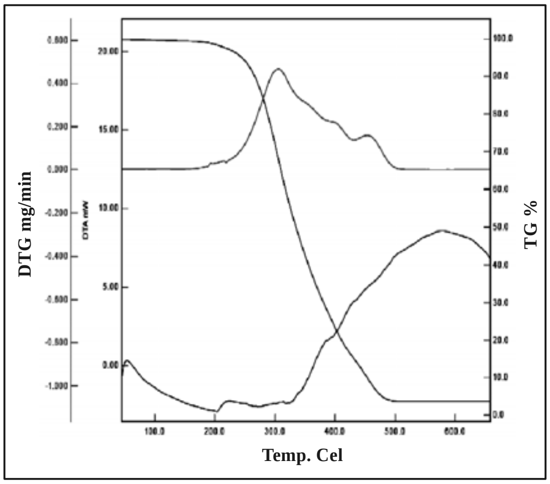

Fig. 4: TG/DTG/DTA of IPN-1

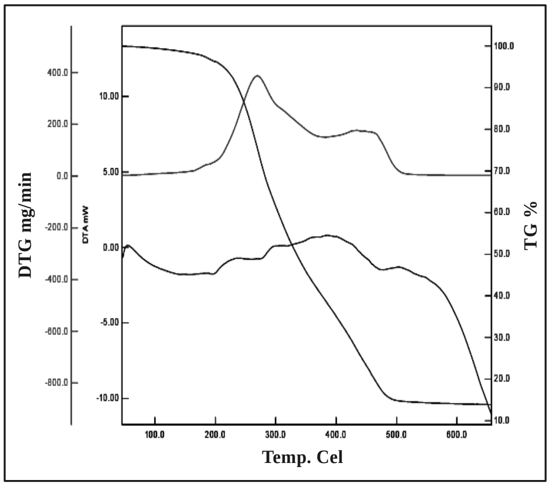

Fig. 5: TG/DTG/DTA of IPN-2

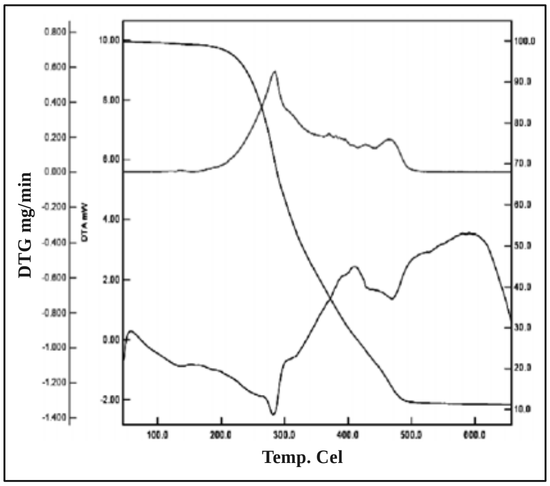

Fig. 6: TG/DTG/DTA of IPN-3

Thermal analysis

The Table 2 describes the percent of thermal decomposition of the IPNs at different temperature ranges. The IPNs are thermally stable upto 200°C with minor weight losses of 1.4%, 3.75% and 1.89% corresponding to the IPN-1, IPN-2 and IPN-3 due to loss of moisture and elimination of solvent molecules embedded in the samples. Significant weight losses of 86.48%, 70.66% and 77.81% corresponding to the IPN-1, IPN-2 and IPN-3 are observed in the temperature range of 250°C-500°C, which can be attributed to the decomposition of benzene ring and decomposition of cross linking with EGDM between PU and PC units. The minor weight losses between 500°C and 600°C are due to complete decomposition of crosslinkings with EGDM between PU and PC units. It is observed that IPN-2 is thermally more stable than IPN-1 (except in the temperature range of 250°C-300°C) where self crosslinking occurs in the long aliphatic chain of diisocyante which may be due to the presence of an aromatic ring in the diisocyanate. It is further observed that IPN-3 is thermally more stable than IPN-2 up to 250°C and thereafter there is no substantial change in the relative stability of the two IPNs which may be due to the increase in oil content of the PU component in the IPN-3 and both the IPNs having the same PU/PC weight-to-weight ratio. The increase in oil content of the PU component result in greater unsaturation leading to enhanced degree crosslinkgs.

The study of TGA is supplemented by the study of its first derivative (DTG) curves. The DTG curves show the rate of thermal decomposition (μg/min) with respect to temperature. The DTG curve in Fig. 4 shows that the IPN-1 has two peaks at 307°C, 456.5°C with corresponding 466.05 µg/min, and 158.03 µg/min rate of decomposition The DTG curves in Fig. 5 and 6 show similar peaks at 270.15°C with 387.02 µg/min and at 438.64°C with 175.00 µg/min rate of decomposition for IPN-2 and at 285.19°C with 577.12 µg/min, 381.36°C with 208.23 µg/min and 466.01°C with 186.00 µg/min rate of decomposition for the IPN-3. Overall, all the three IPNs showed similar behaviour, however IPN-3 recorded highest rate of decomposition 577.12 µg/min at 285.19°C. DTA thermograms of the IPN-1 show two endothermic peaks at 214.42°C and 307.00°C in the temperature range of 250°C to 450°C, but in range of 450°C to 600°C only one exothermic peak at 562.62°C is observed. Similar exothermic and endothermic peaks are also recorded for the IPN-2 and IPN-3 which are listed in the Table 3. The DTA curves indicate that the thermal decomposition process for all the three IPNs is a single step reaction.

Table 2: Percentage of thermal decomposition of the IPNs at various temperatures (°C)

Sample code	100	150	200	250	300	350	400	450	500	550	600	650
IPN-1	0.27	0.48	1.4	5.79	27.98	57.4	76.66	89.18	96.27	96.37	96.37	96.4
IPN-2	0.52	1.42	3.75	14.49	38.51	54.16	64.92	76.78	85.15	85.69	85.93	86.12
IPN-3	0.37	0.81	1.89	10.42	38.65	58.76	70.03	79.97	88.23	88.56	88.71	88.82

Table 3: Thermal data of IPNs

Sample code	Composition	NCO/OH molar ratio	PU/PC wt. ratio	Temp. °C	DTA Peak/°C		% of Decomposition
					Endo	Exo	
IPN-1	PL+HMDI+ PC	2.0	50 : 50	150-250	214.42		5.31
				250-450	307.00		83.39
				450-600		562.62	7.19
IPN-2	PL+TDI +PC	2.0	50 : 50	150-250		137.25	13.07
				250-450		398.81	62.29
				450-600	471.10		9.13
IPN-3	PL+TDI + PC	1.2	50 : 50	150-250	282.14		9.61
				250-450		409.10	69.55
				450-600		591.36	8.74

Kinetic parameter calculation

The calculation of kinetic parameters was performed by the Freeman-Anderson method. The equation used for the Freeman-Anderson method is given as -

$$\Delta \log \left(-\frac{dw}{dt} \right) = n\ \Delta \log w - (E_a/2.303\ R)\ \Delta\ (1/T)$$

Where (-dw/dt) is the rate of decomposition determined from DTG data, w is the residual mass calculated from TG value at constant difference in 1/T, ‘n’ is the order of reaction and Ea is the energy of activation. Freeman-Anderson plots, Fig. 7 and Fig. 8, for kinetic parameters in the temperature ranges of 200°C to 315°C and 315°C to 500°C respectively were obtained by plotting Δ log (-dw/dt) against Δ log w corresponding to a constant difference in 1/T i.e. 0.1 x 10^{-3}. The kinetic parameters such as activation energy (E_a) and order of reaction (n) for the thermal decomposition are given in Table 4. The kinetic data clearly show that the activation energy values for the decomposition process of all the IPNs are large indicating their high thermal stability. Moreover IPN-3 having the highest energy of activation in the temperature range of 315°C – 500°C, exhibits the greatest thermal stability which is in good agreement with experimental thermal decomposition data.

Table 4: Kinetics parameters of thermal decomposition of IPNs crystallinity of IPNs

Sample code	Temperature range °C	E*(KJ mol $^{-1}$)	n	Xcr
IPN-1	200-315	104.08	2.64	27.48
	315-500	94.84	2.64	
IPN-2	200-315	97.67	2.16	22.61
	315-500	48.17	2.16	
IPN-3	200-315	103.66	2.48	23.25
	315-500	127.96	2.48	

X-ray diffraction (XRD) study

The degree of crystallinity of IPNs has been calculated from XRD method. The scanning regions of the diffraction angles were 10° to 30° which covered most of the significant diffraction peaks of the polymer crystallites. The equation for degree of crystallinity is as follows $X_{cr} = A_c / (A_c + A_a)$, X_{cr} refers to degree of crystallinity, A_c refers to crystallised area and A_a refers to amorphous area on the x-ray diffractogram. The relatively sharp peaks were due to the scattering from crystalline region and the broad underlying hump is due to scattering from non crystalline regions. A horizontal base line was drawn between the extremities of the scattering curves to remove the background scattering. The degree of crystallinity of the IPNs is calculated from the Fig. 9 to Fig. 11 are about 22% and are given in Table 4. The degree of crystallinity of IPNs varies with the nature of the diisocyanates used as well as the NCO/OH molar ratio. IPNs prepared from PU of HMDI have higher degree of crystallinity than the IPNs prepared from PU of TDI which may be due to the linear nature of HMDI. IPNs with higher NCO/OH molar ratio have lower degree of crystallinity which may be due to the decrease in oil content.

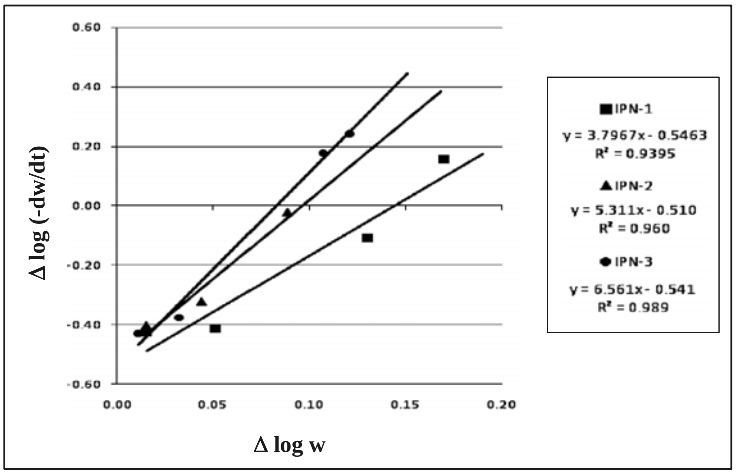

Fig. 7: Freeman-Anderson plots for the temperature range of 200°C to 315°C

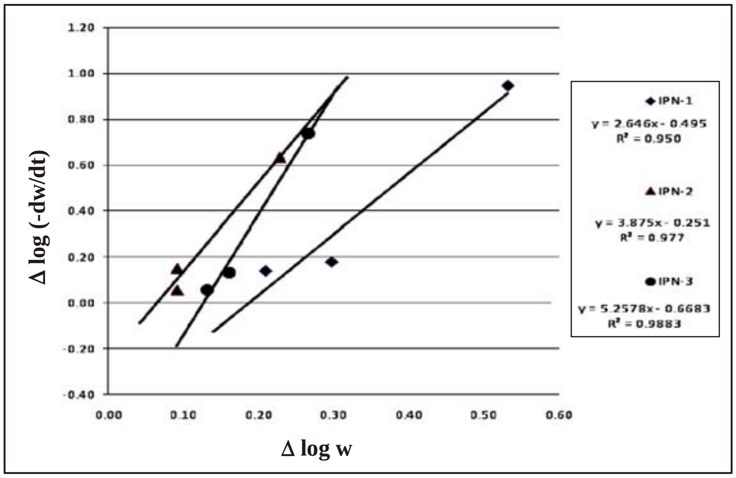

Fig. 8: Freeman-Anderson plots for the temperature range of 315°C to 500°C

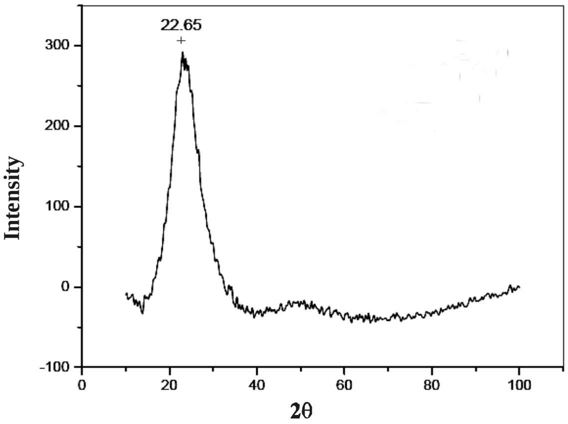

Fig. 9: XRD of IPN-1

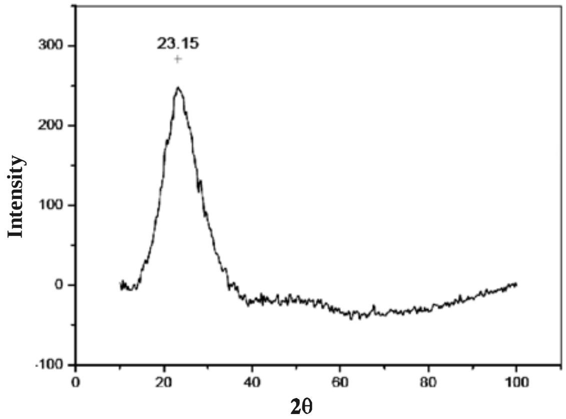

Fig. 10: XRD of IPN-2

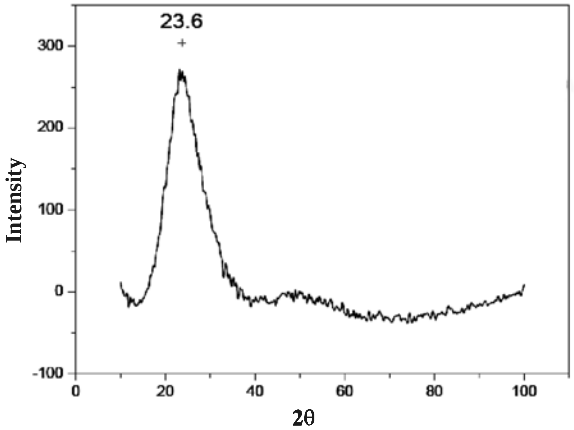

Fig. 11: XRD of IPN-3

CONCLUSION

In the present context the biopolymers have many advantages compared to polymers prepared from petroleum based monomers and are expected to be comparatively ecofreindly and cost effective than petroleum based polymers. Interpenetrating polymer networks prepared from polyol modified linseed oil based polyurethanes and hydroxyl modified cardanol crosslinked to a great extent. Their thermal stability and mechanical strength are very high with improved property for commercial applications. The major conclusion derived from this article is the choice of diisocyante has a profound effect on the thermal stability of the polymer blend. Moreover the effect of variation of NCO/OH molar ratio of the PU unit of the polymer blend has noticeable change in the thermal stability of the IPN. Also the IPNs prepared from modified cardanol show improved mechanical and thermal properties over unmodified cardanol based IPNs. Thus it is possible to design materials with suitable compositions of the IPNs for various specific applications.

ACKNOWLEDGMENT

The authors are thankful to the authority of the Ravenshaw University for providing necessary facility for doing our research work and also obliged to the IIT Kharagpur for characterization of the samples.

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Accepted : 21.04.2012