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Research Article

EFFECT OF CONCENTRATION VARIATION OF HYDROXYL AND ISOCYANATE MOIETIES ON MECHANICAL PROPERTIES OF FLY ASH REINFORCED POLYURETHANE COMPOSITES AT CONSTANT INDEX RATIO

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ABSTRACT

Polyurethane (PU) based foams/composites shows versatile utility and are designed as per the end use by varying Index ratio (IR; NCO/OH), or the filler functionalities or its concentration thereof. The present research work focuses on the study of extent of polymerization of PU system by varying the weight ratios of binary components of cross linking agents (Tepanol and castor oil) in their homogenous mixture and is found to be independent of their weight ratios but depends on the weight of homogenous mixture of cross linking agents, as revealed by the SEM images of fly ash reinforced polyurethane composites.

Variations in mechanical properties of PU foam/composites can be studied by varying IR. In present study, fly ash reinforced polyurethane composites designed at IR 1.1 keeping higher concentration of curing agent (2,4- Toluene diisocyanate) shows better mechanical properties (TS;26MPa & YM;13GPa) compared to, when binder (polyethylene glycol-600,) concentration was decreased at constant IR *i.e* 1.1 (TS;13MPa & YM;6.5GPa) or lowering the concentration of cross linking agents (TS;11MPa & YM5.5GPa) at same IR *i.e* 1.1. The study also reveals that composites designed at IR0.9 shows better mechanical properties (TS;22MPa & YM;11GPa) at higher concentration of cross linking agents as compared to composites designed at same IR but with higher concentration of binder (TS;10MPa & YM;5GPa) or lower concentration of curing agent (TS;8MPa &YM;4GPa).

Keywords: Polyurethane composites, Crosslinking agents, Index ratio, Fly ash, Binders.

1. INTRODUCTION

Polyurethanes due to their easy modification are considered as versatile materials in the field of polymer science [1-3]. Polyurethane's monomeric unit selection *viz.* types of binders, cross linkagers, chain extenders, curing agents and their properties too like hydrophilicity, crystallinity, degradability, their degree of polymerization, degree of cross linking/branching, chain length between branching nodes, are the important parameters which ascertain the physico chemical properties of the designed polyurethane like their mechanical strength, sorption, degradability, crystallinity etc]4-8].

PU have intrinsic segmented structures having HS (hard segment) and SS (soft segment) wherein SS are due to macrodiols blocks and HS are due to diisocyanates and chain extenders, the proximity of HS and SS imparts variation in their mechanical behavior which too can be varied as per the requisite values [9-12], apart from this the variation in the IR value, the amount and functionalities of the filler in terms of filler reinforced PU composites are also the key factors in tailoring the composites as per the required physico chemical properties [13-17].

The present research work focuses on the study of extent of polymerization at various weight ratios of crosslinking agents *viz.* Tepanol and castor oil and the study of mechanical properties of Fly ash-reinforced PU composites (FA-r-PUC) at various concentrations of polyols and isocyantes keeping IR constant.

2. MATERIAL AND METHODS

2.1. Material

Polethylene glycol PEG-600 (Sigma Aldrich) as binder (BN), 2,4- TDI (2, 4 isomer, Toluene diisocyanate, (Sigma Aldrich) as curing agent (CRA), homogenous mixture of castor oil (CL) and Tepanol (TL) (commercial grade) as cross linking agent (CLA) and fly ash (FA) as filler from KTPS (Kota thermal power station, Rajasthan, India) were used in designing FA-r-

PUC, Casting was done on wooden molds pre treated with Silicon Spray (ALFA-40, JIVIKA company). Casted material after curing (curing time; 24 hours, room temperature) was crafted as per the ASTMD 638 Type I standards. Universal Test Machine UTE-40(FiE make, India) was used to evaluate mechanical properties of FA-r-PUC.

2.2. Methodology

Liquid polyol system *viz.* PEG-600, CL and TL was homogenized with mechanical agitator; 10g of filler FA was then added to make a viscous paste in which CRA (pre dried at 105°C in vacuum oven) was added for synthesis of FA reinforced pre polymer, which later casted in the wooden mold lined with mold release. Curing was done for 24 hours thereafter; samples were removed to evaluate their mechanical properties.

The experiments were designed to study (1) the extent of polymerization of PU matrix by varying the weight ratios (1:1, 1:2 and 2:1) of the binary components (TL and CL) of CLA at constant weight ratios of BN and CRA as 3:2 respectively. (2) Mechanical properties of FA-r-PUC composites, designed at IR-1.1, 1.0 and 0.9 wherein each index ratio was formulized by varying one component's concentration keeping the other component's concentration constant.

2.3. Characterization Techniques

FTIR is a good analytical tool for determining chemical composition of the raw material and the finished end products. FT-IR (TENSOR27, Bruker, USA) and FTIR-ATR (ALPHA, Bruker USA) was used for characterization of Filler, CLA, CRA, BN and FA-r-PUC.

Powder X-ray diffraction studies of filler FA was done by using Philips X'pert analytical diffractometer (monochromatic CuK_{α} radiation; $\lambda = 1.54056$ Å; 2θ range of 5-65°). The fly ash samples were scanned in 2θ range of $0\text{-}80^{0}$ with scanning rate of $0.04^{0}s^{-1}$.

SEM (ZEISS, Germany (EHT=20KV, WD=16.5mm, Mag=150KX) was used for analyzing the FA and FA -r-PUC for revealing the FA distribution in the matrix and to witness the extent of polymerization.

UTM (UTE-40, FiE, India) has been used for evaluating Mechanical Properties (tensile strength; TS and young modulus; YM) of FA-r-PUC at rate 0.05mm/min.

3. RESULTS AND DISCUSSION

3.1. Spectroscopic Characterization of, CLA, CRA, BN, FA and FA-r-PUC

Tepanol shows IR band at 2925cm^{-1} ($-CH_3$), 1446 cm^{-1}, 1584 cm^{-1} (aromatic ring str.), 1650 cm^{-1} to 2000 cm^{-1} (aromatic overtones), broad band around 3200 cm^{-1} (-OH), (Fig.1). Castor oil shows IR bands around 3200-3600 cm^{-1} (-OH), 1707 cm^{-1} (C=O), 1640 cm^{-1} (C=C) and 2925 cm^{-1} ($-CH_3$), (Fig.2). The IR spectra of 2,4-TDI shows bands at 2249cm^{1} (-N=C=O), 1522cm^{-1}, 1578cm^{-1}, and 1611cm^{-1} (ring str. bands), 1650 cm^{-1} to 2000 cm^{-1} (overtones), (Fig.3). IR bands around 3200-3600 cm^{-1} (-OH) in IR spectra of PEG-600, broad band with shoulder at frequency around 2925cm^{-1} ($-CH_3$ symm. and asymm.str.) reveals the methylene group of binder (Fig.4). The FT-IR spectra of FA shows a band around 3400-3000 cm^{-1} (-OH of -Si-OH) and at 1650 cm^{-1}(-OH bending) bands at 913, 1090, 1160 cm^{-1} and at 798 cm^{-1} (asymm. and symm. Str. of Z-O-Si (Z=Al, Si), (Fig. 5) Urethane links -NHCOO- of PUC is characterized by bands 1711 cm^{-1} (C=O) and 3309 cm^{-1} (N-H str.) (Fig. 6).

Spherical shape with smooth surface of solid or hollow cenospheres of filler FA has been characterized by the SEM technique, (Fig. 7). The internal structural aspects of FA was studied by XRD technique (Fig. 8) showing crystallite size ranging 33nm to 60 nm and amorphous phase coexistence by gibbousity pattern at 2θ in between 15-35°.

3.2. Effect of binary component ratios of CLA on extent of polymerization

Experiments were designed in synthesizing FA-r-PUC wherein wt ratio of binary components of CLA *i.e* TL and CL were kept 1:1, 1:2 and 2:1 with constant wt ratio of BN and CRA as 3:2. The maximum possible extent of polymerization with 0.5g and minimum with 1g of CLA was noticed at wt. ratios of TL and CL in CLA as 1:1, 1:2 and 2:1. The results were justified with the SEM images (Fig. 9-A, B, C) of FA-r- PUC wherein uniform distribution of filler FA in PU matrix with 0.5 g of CLA was noticed depicting maximum possibility of linking OH with NCO moieties in their equivalent ratio while with 1 g of CLA possibility of linking NCO with OH moieties at equivalent ratio was ruled out as revealed with SEM images (Fig.10-A, B, C) showing the non uniform distribution of filler in the PU matrix.

The above experimental facts can be explained on the basis of monomer molar equivalency concept by equation (1)

$$\left[\left(\frac{w}{M}\right) f.\ N\right]_{OH} = \left[\left(\frac{w}{M}\right) f.\ N\right]_{NCO} \quad \text{...........Equation (1)}$$

where w=wt.(g), M(mol.wt), f=functionality, N= Avogadro number, monomer molar equivalency is unity for maximum possible linkages of NCO and OH moieties as seen with 0.5g of CLA while with 1g of CLA, unity value is not achieved. The weight ratios of binary components of CLA are not as significant as the gross wt of CLA in establishing the maximum possible extent of polymerization. The above experimental facts have been shown in the fig.11 wherein $[\left(\frac{w}{M}\right) f.N]_{OH} = [\left(\frac{w}{M}\right) f.N]_{NCO} = 1$ with 0.5g CLA while $[\left(\frac{w}{M}\right) f.N]_{OH} = [\left(\frac{w}{M}\right) f.N]_{NCO} = 0.7$ with 1.0g CLA despite of any wt. ratios of binary components of CLA.

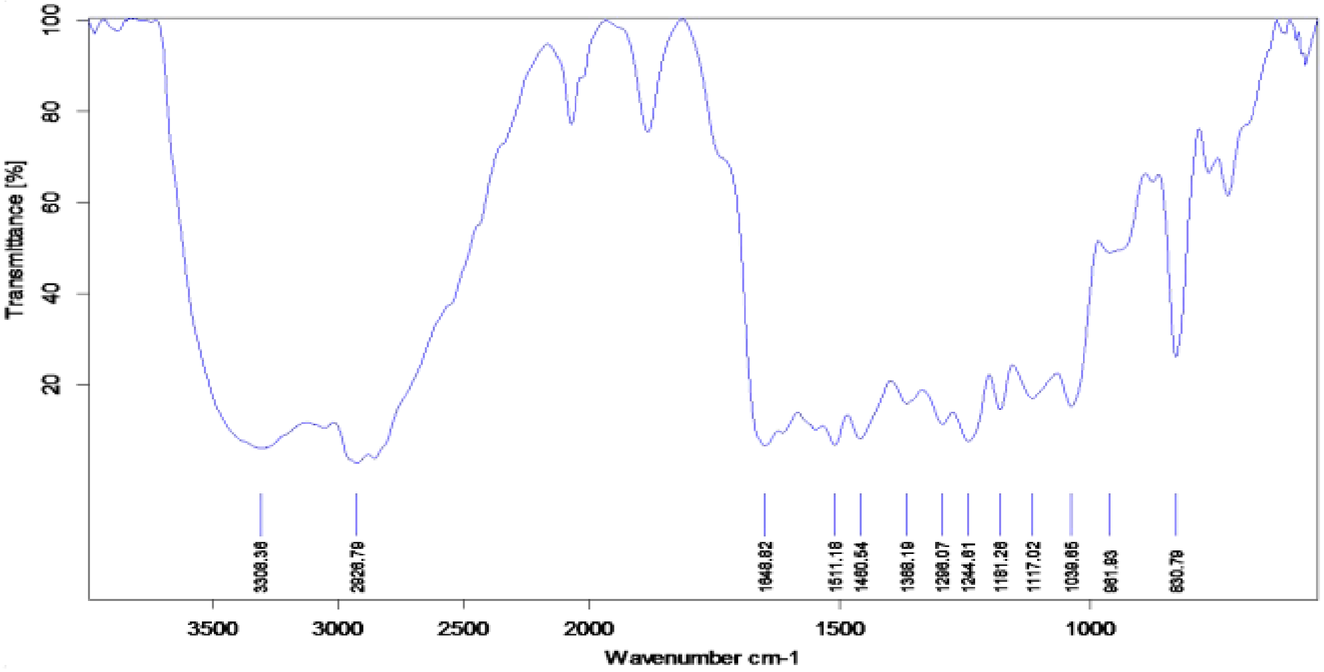


Fig. 1: IR spectra of Tepanol

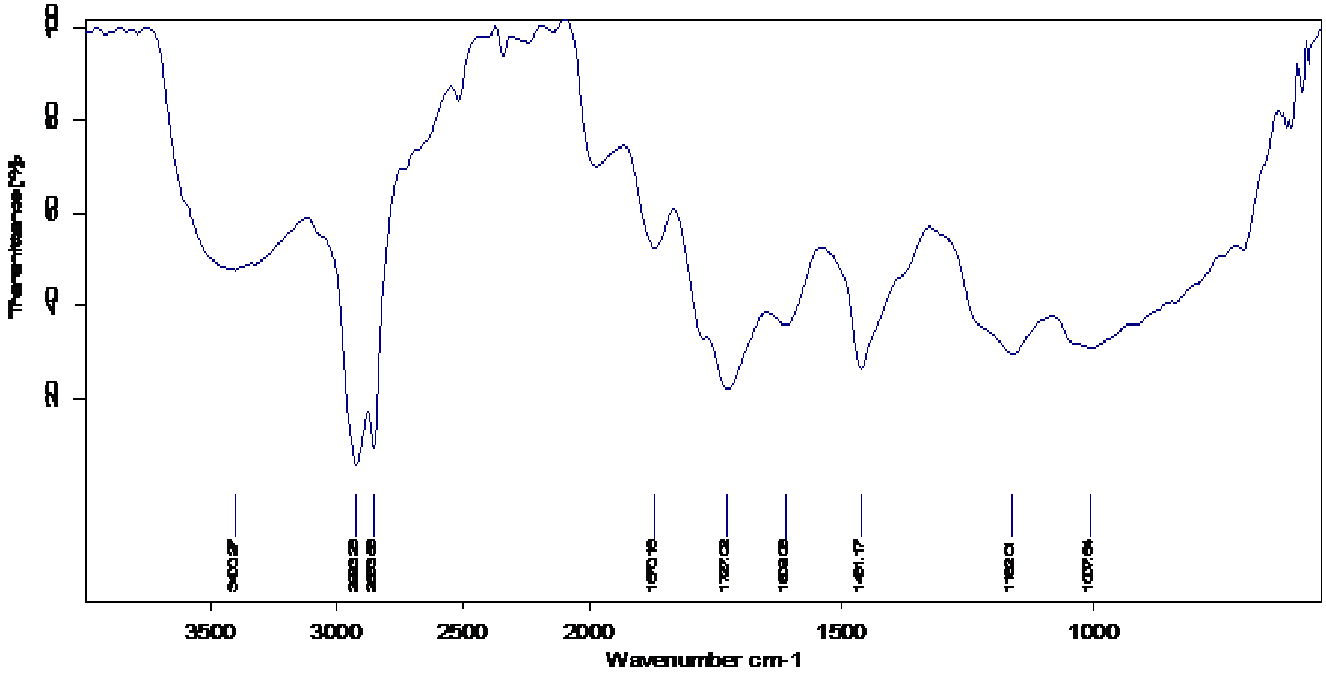


Fig. 2: IR spectra of Castor oil

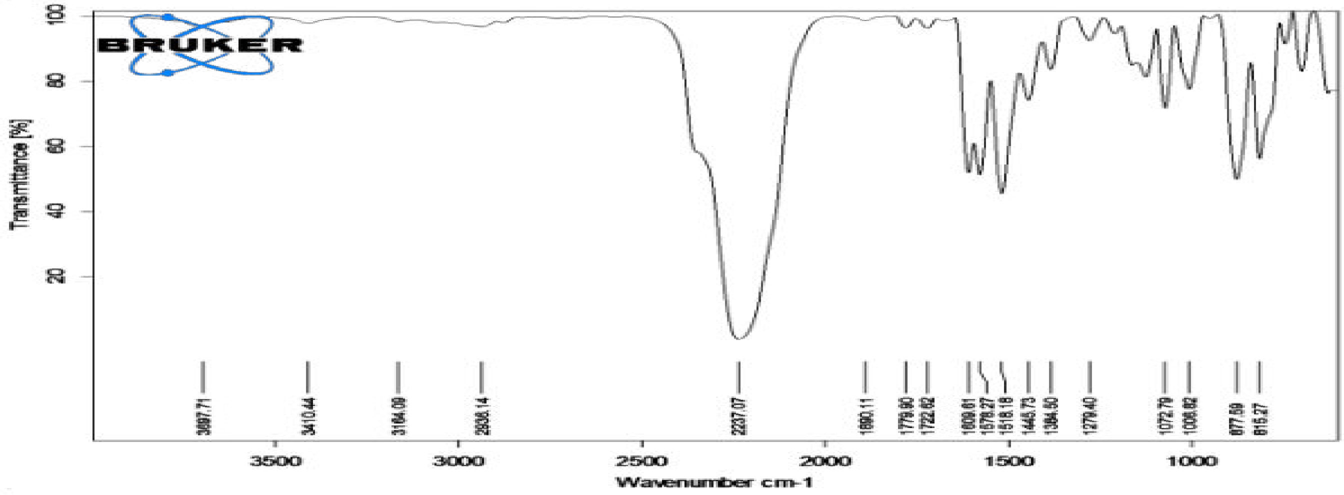


Fig. 3: IR spectra of TDI

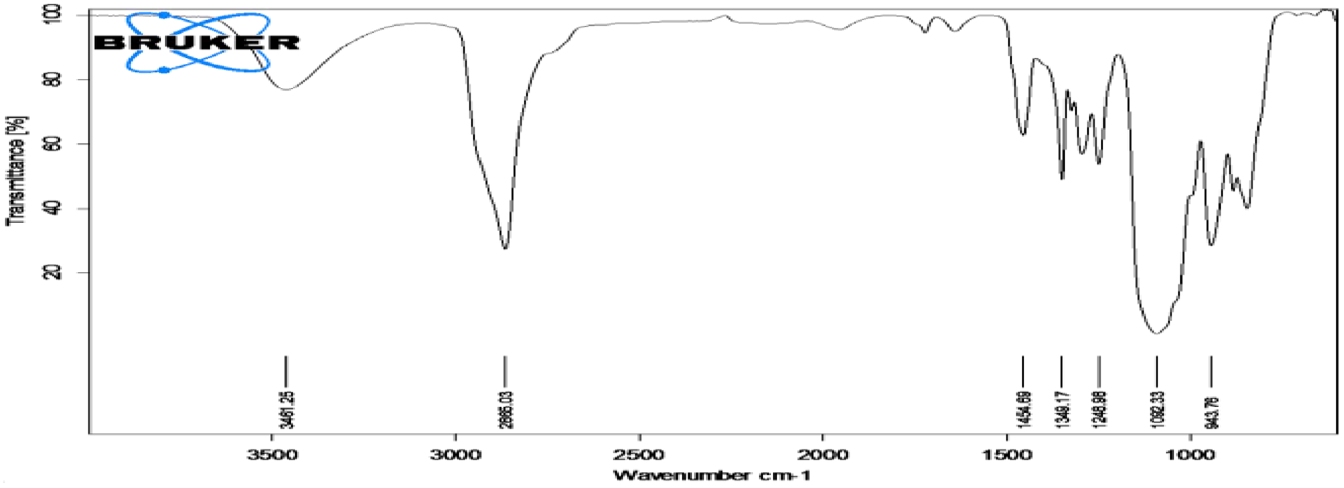


Fig. 4: IR Spectra of PEG-600

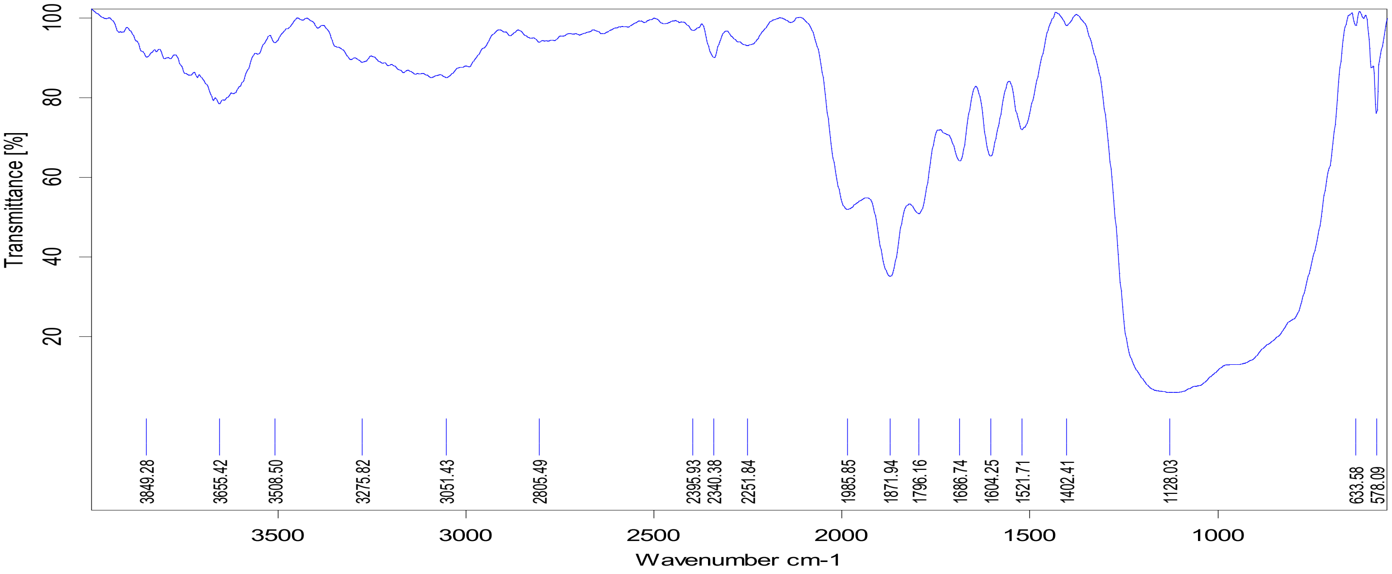


Fig. 5: IR spectra of FA

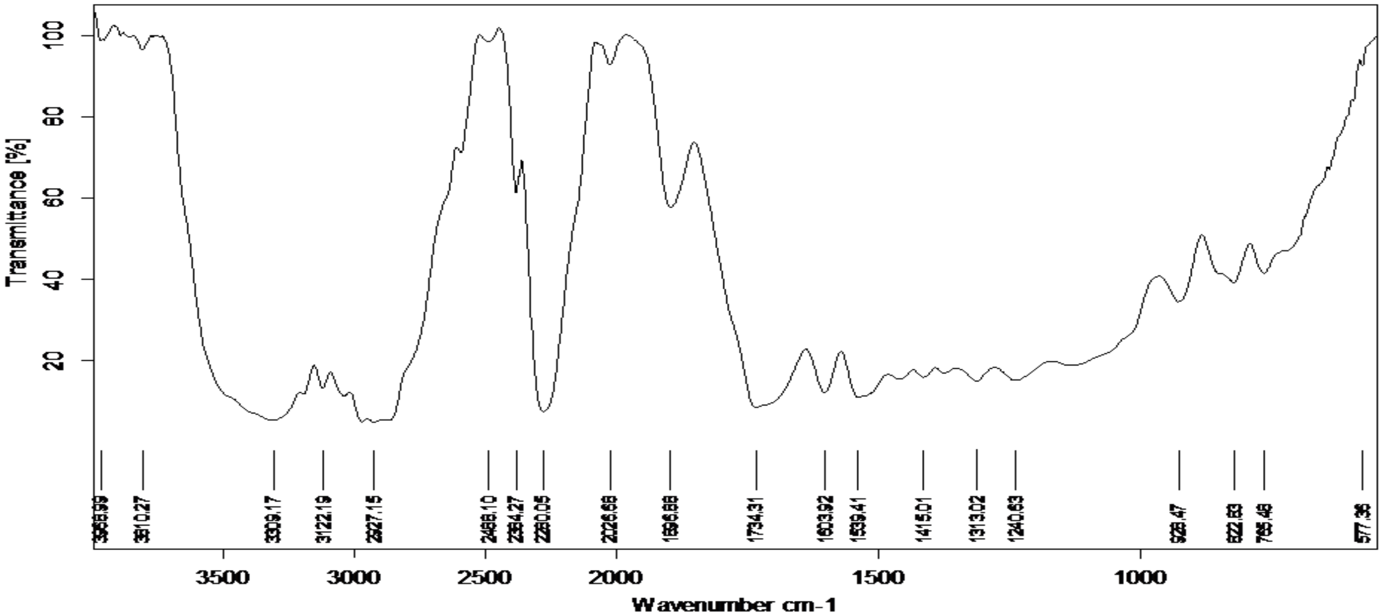


Fig. 6: IR spectra of FA-r-PU composite

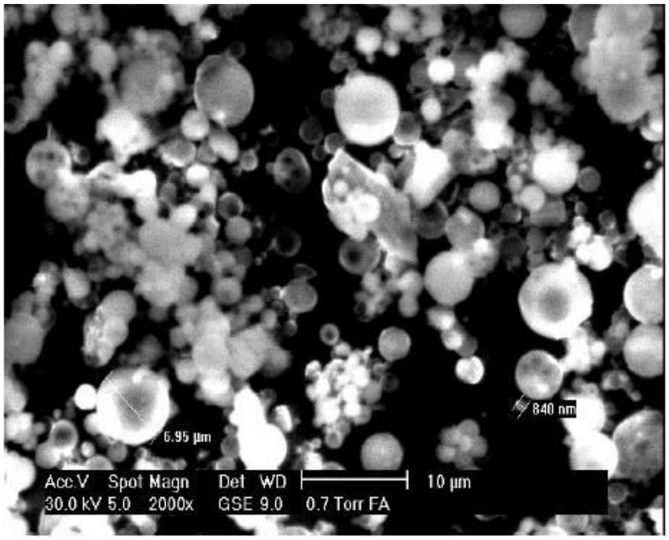


Fig. 7: SEM image of FA

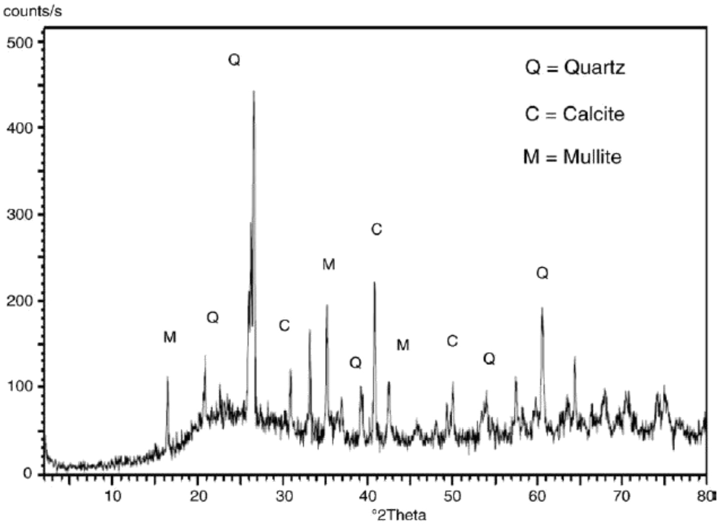


Fig. 8: XRD pattern of FA

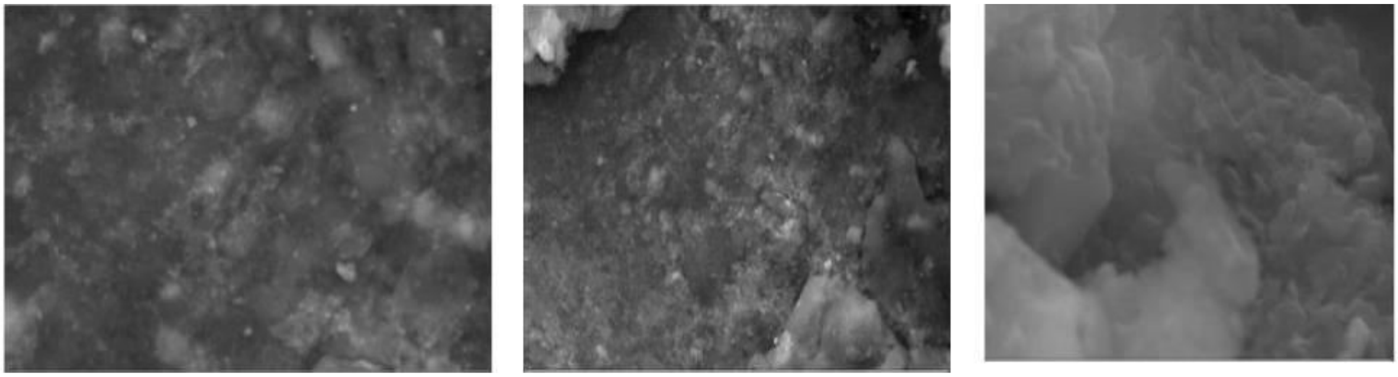

(A) (B) (C)

Fig. 9: SEM images of FA-r- PUC

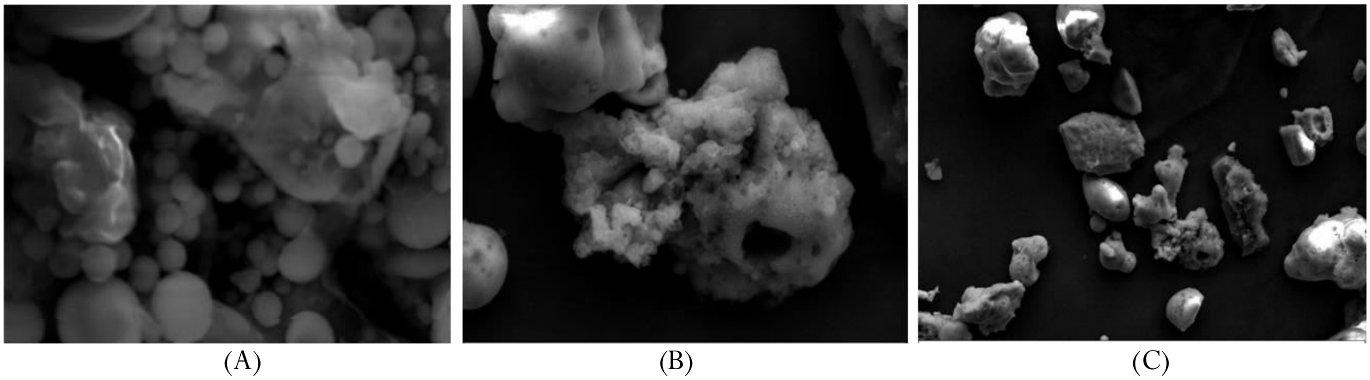


Fig. 10: SEM images showing the non uniform distribution of filler in the PU matrix

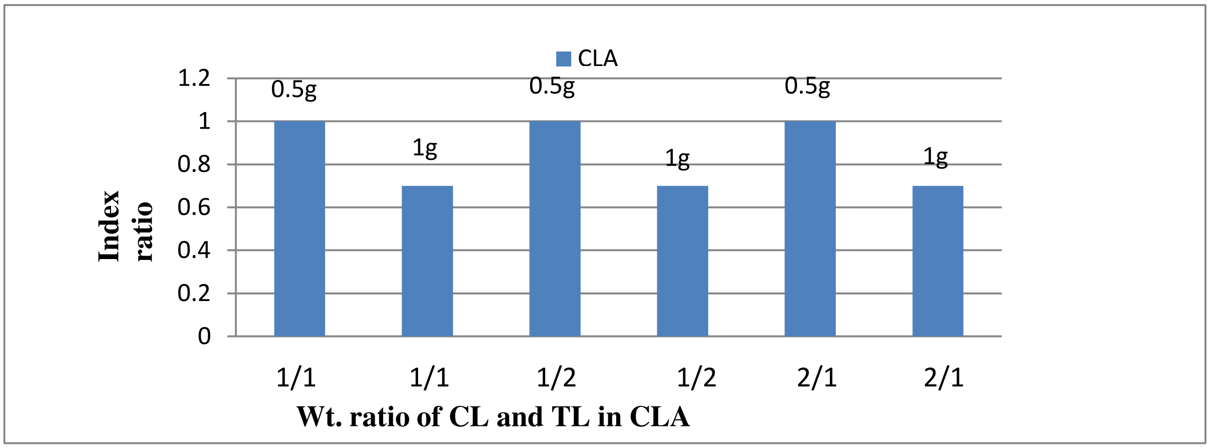


Fig. 11: Showing the effect of wt ratio of CL and TL in CLA on IR

3.3. Effect of component's concentration variation of PU system on its mechanical properties at constant Index Ratio.

Experiments were designed in synthesizing FA-r-PUC by varying the concentration of single component of PU system while keeping other component concentration unchanged in a way to achieve IR 1&1.1 and 0.9, whose mechanical properties in terms of Tensile Strength (TS) and Young Modulus (YM) (Table 1) have been shown by graphs in terms of load/strain (Graph 1-3).

FA-r-PUC designed at IR 1 possess TS; 33MPa, and YM; 16.5GPa while FA-r-PUC designed at IR 1.1 either by increasing CRA concentration or decreasing CLA or binder concentration shows TS; 26MPa, YM;13GPa, TS;11MPa, YM;5.5GPa and TS;13 MPa, YM;6.5GPa respectively, lesser mechanical properties of FA-r-PUC at IR 1.1 at higher concentration of CRA is attributed to the fact that NCO locked up all the OH moieties of polyols by urethane linkages making the filler effectively packed , yet the excess amount of NCO would have reacted with physisorbed water molecules of FA making the composite slightly porous due to release of CO_2 . Lower mechanical properties of FA-r-PUC at IR1.1 with lower concentration of CLA is attributed to the lesser extent of inter molecular Hydrogen bonding between the OH moieties of the CLA, however low concentration of BN at IR1.1 leads to decrease in mechanical properties of FA-r-PUC as lower binder concentration decreases the packing efficiency of the filler (Fig.12) [18-21].

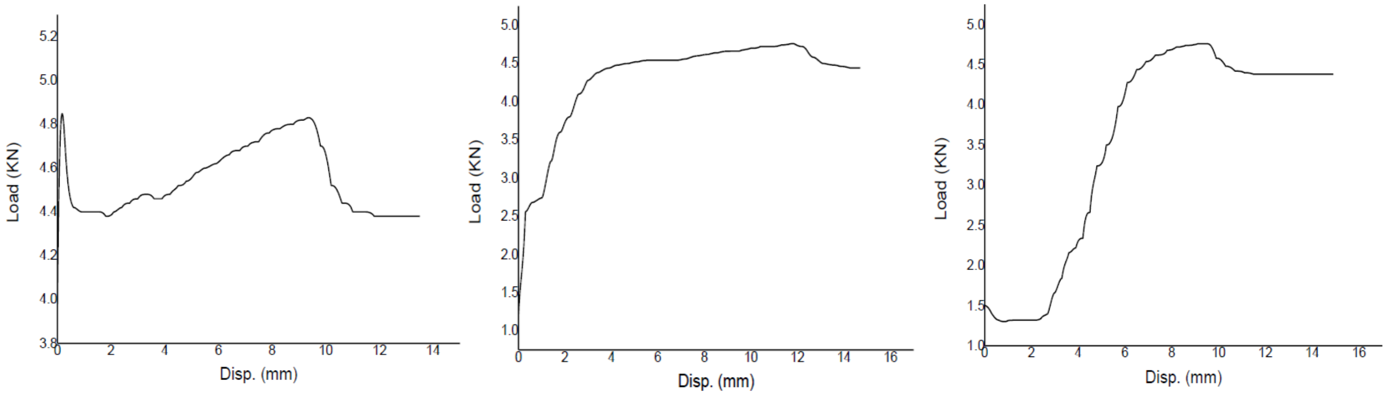
FA-r-PUC designed at IR0.9 by either increasing concentration of CLA or BN or decreasing CRA concentration shows mechanical properties as TS;22MPa, YM;11GPa, and TS;10MPa,YM;5GPa and TS;8MPa, YM;4GPa respectively. Higher values of mechanical properties of FA-r-PUC at IR0.9 with higher concentration of CLA compared to FA-r-PUC at IR1.1 at lower concentration of CLA clearly signifies role of Intermolecular Hydrogen bonding between OH functionalities of CLA making better reinforcement in composites [22-25].

FA-r-PUC designed at IR0.9 with higher concentration of BN shows lower mechanical properties compared with FA-r-PUC at IR1.1 with lower concentration of BN which signifies that at higher concentration of BN there is more probability of SS interaction of polyols with HS segments of urethane links making segregation of HS less pronounced thereby declining the intrinsic reinforcement of the composite. (Fig.12) [26-28].

Composites designed at IR0.9 with lesser concentration of CRA shows lower mechanical properties compared to composites at IR1.1 with higher concentration of CRA is attributed to the lesser extent of urethane locks required to tie all the possible OH moieties, the above explanations are represented graphically [29,30] (Fig.13).

Table 1: Composition of components of PU system at various IR and their Mechanical properties

Experiment No:	BN(g)	CLA(g)	FA(g)	CRA(g)	IR (NCO/OH)	YM (GPa)	TS (MPa)
1	3	2.49	4	2	1.00	16.5	33
2	3	2.49	4	2.20	1.1	13	26
3	3	2.09	4	2	1.1	5.5	11
4	2.37	2.49	4	2	1.1	6.5	13
5	3	2.49	4	1.80	0.9	4	8
6	3	2.99	4	2	0.9	11	22
7	3.76	2.49	4	2	0.9	5	10

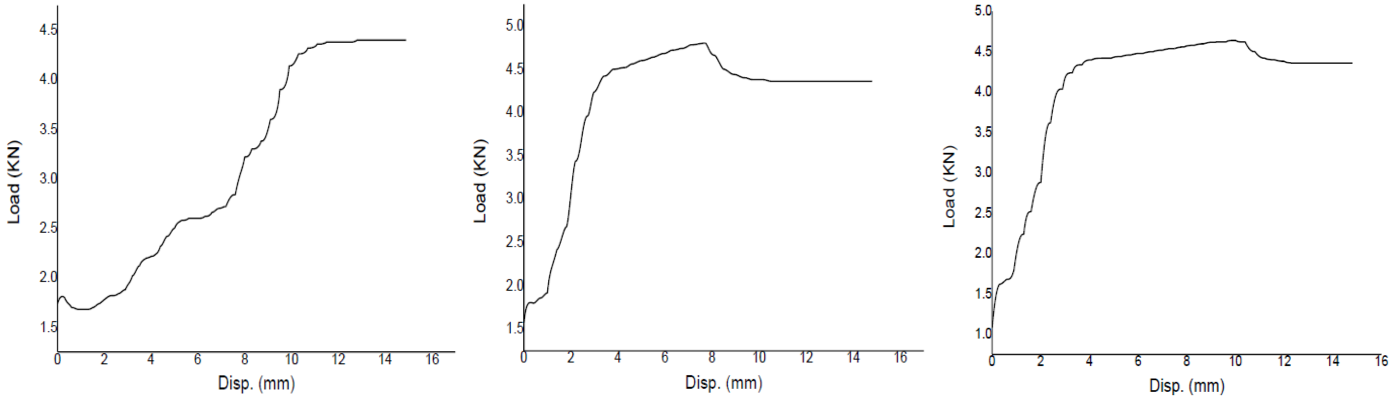


TS; 26 MPa , YM; 13GPa

TS; 11 MPa ,YM; 5.5GPa

TS; 13 MPa, YM; 6.5GPa

Graph 1: Showing load v/s displacement of FA-r-PUC with IR 1.1

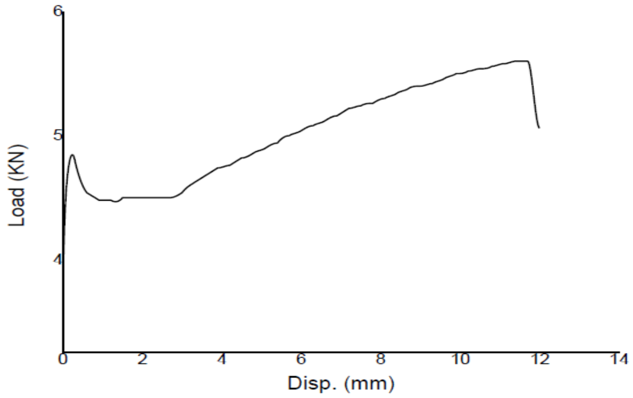


TS; 8 MPa, YM; 4GPa

TS; 22 MPa, YM; 11GPa

TS; 10 MPa, YM; 5 GPa

Graph 2: Showing load v/s displacement of FA-r-PUC with IR 0.9



TS; 33 MPa, YM; 16.5GPa

Graph 3: Showing load v/s displacement of FA-r-PUC with IR 1

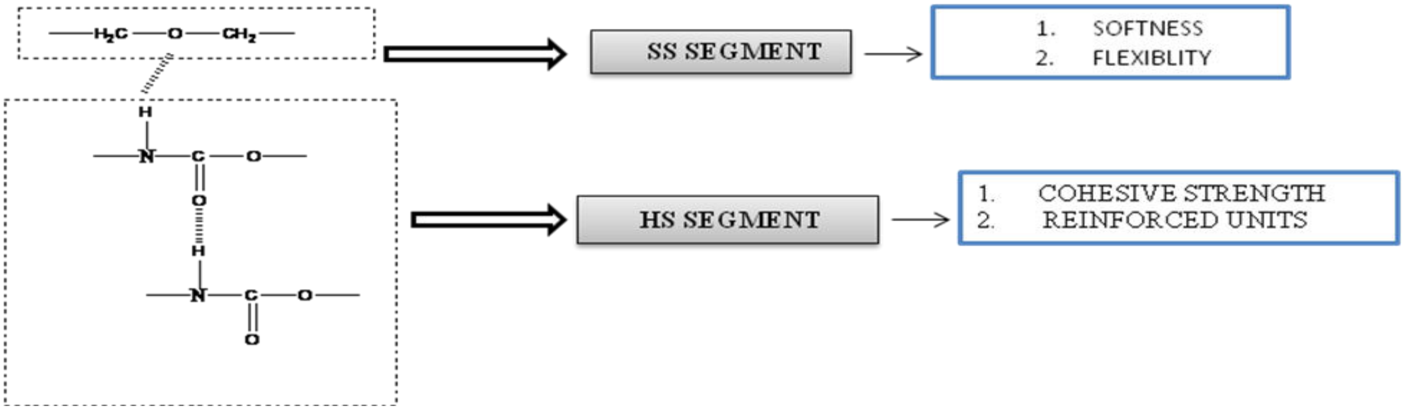


Fig. 12: Showing complete description of the HS and SS domain of Pus

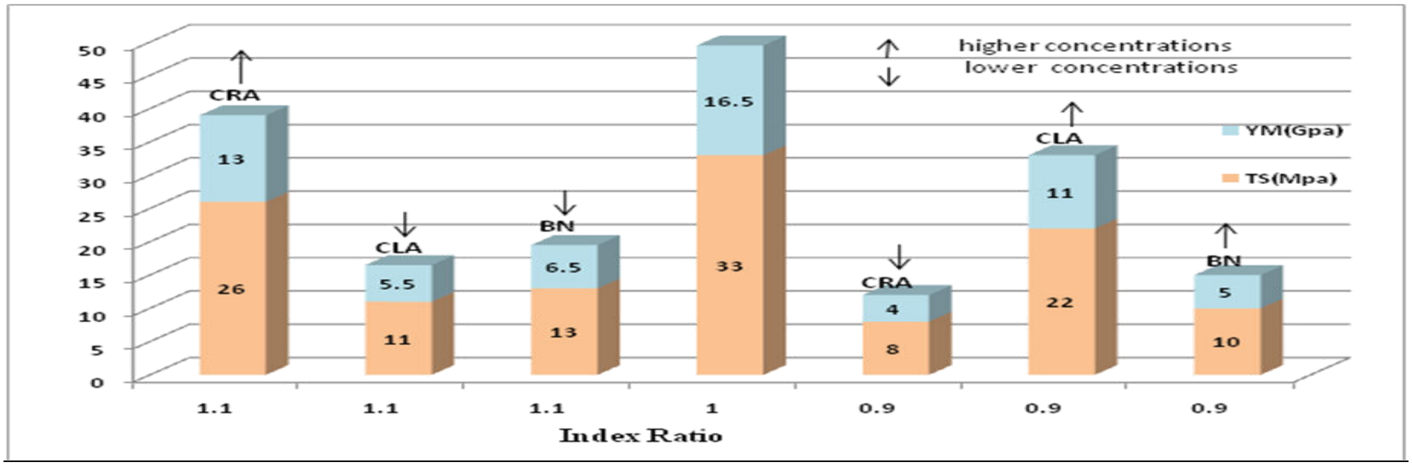


Fig. 13: Showing the comparative mechanical strength of FA-r-PUC at same IR

4. CONCLUSION

The unique property of PU foams/composites is the tailoring of PU system as per the end use by varying the IR values, different IR possessing PU material shows different mechanical properties. The present research work envisaged the variation of mechanical properties at the same IR with different concentration of PU components [31-35] wherein IR 1.1 PU system shows higher TS (26MPa) and YM (13GPa) when concentration of CRA was kept higher than BN and CLA and least TS (11MPa) and YM (5.5 GPa) when concentration of CLA was increased , PU system with 0.9 IR value shows higher TS (11 MPa) and YM (22 GPa) when concentration of CLA was higher than BN and CRA while lower TS and YM were shown when concentration of CRA was kept lower than BN and CLA. Comparing IR 1.1 with IR 0.9 possessing PU system, later shows higher mechanical properties viz. TS (22 MPa) and YM (11 GPa) at high concentration of CLA while the former at the lower concentration of CLA shows lower mechanical properties with TS;11 MPa, YM;5.5 GPa. The significance of monomer molar equivalency was shown by the PU system with IR unity wherein the best mechanical properties were noticed (TS; 33 MPA, YM; 16.5 GPa)

Higher values of mechanical properties (TS &YM) can be achieved at lower IR by keeping higher concentration of cross linking agents.

Conflict of interest

None declared

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