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Preview of Monomer Molar Equivalency in Polyurethane System: A model study

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Abstract

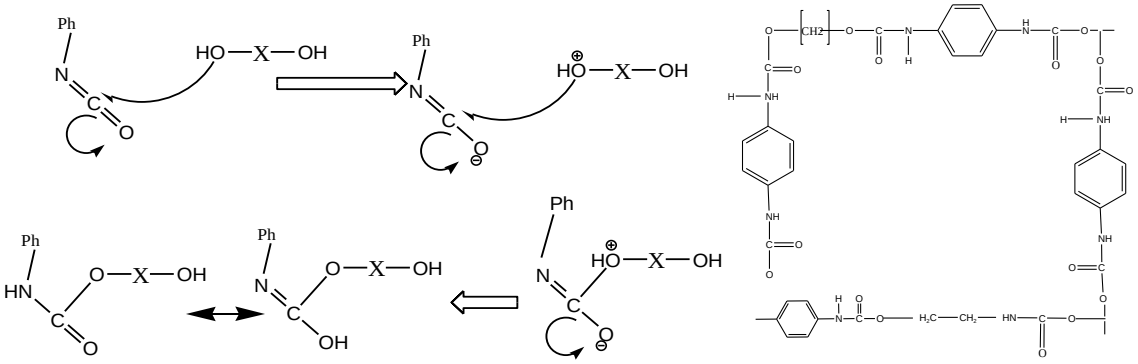
Polyurethane (PU) the organic polymers having monomers as polyols and polyisocyanates, are joined by carbamate (urethane) links. To understand the theoretical preview of PU-Polymerization the concept of monomer mole ratio equivalency have been used in the present research work, monomer units taken are : chain extenders(CE) PEG-600 (polyethylene glycol) , cross linkagers (CLA)homogenous mixture of 1,4-butanediol(BD) and 1,1,1-trimethylol propane (TMP) , curing agents(CRA) 2,4-toluene diisocyanates. For evaluating the extent of polymerization, NCO/OH (IR= index ratio) have been evaluated by using mole concept and is compared by using experimentally verified proposed models $[7n_{TDI}-0.1]/2n_{CE}+13nCLA$ while other models viz. $2n_{CE}$ X 10^{21}, $13n_{BD}$ X 10^{21}, $13n_{TP}$ X 10^{21}, for determining the number of OH functionalities, for CE, BD, TMP respectively. While for number of NCO functionalities of curing agent TDI , by $[7n_{TD}-0.1]$ X 10^{21}, the extent of polymerization has been studied through SEM images of PUC. The models for this PU system is time effective , for evaluating the weight of CRA, a model $n_{TDI} = [2n_{CE}+13nCLA+0.1]/7$is proposed with least variability , the research work also envisages on the extent of polymerization independency on the ratio of binary components of CLA but depends on the weight of CLA taken in the mixture, evaluated by the proposed model $\sum_n^{TMP}$OH + $\sum_n^{BD}$OH = [W]CLA $_{mix}$ X 13 X 10^{21} . Total OH functionalities given by CLA & CE by proposed model is given by $2n_{CE}+13n_{CLA}$ +0.1.Effect of w/w ratio variation of binary components TMP and BD of CLA on the mechanical properties of composite has been studied by evaluating Tensile strength(TS) Young Modulus(YM) by Universal testing machine(UTM) and hardness was evaluated by durometer.

IR values less than unity incomplete polymerization, while for IR values unity effective/complete polymerization was noticed.

Keywords: chain extenders, cross linking agents, curing agents, index ratio.

INTRODUCTION

Polyurethanes (PU)[1,2,15] are polymers made of organic units joined by carbamates[29,32] (urethane) links , and are formed when polyols (chain extenders: CE) [3,4,28] containing two or more hydroxyl groups per molecule reacts with molecules having two or more isocyanate group called as the curing agent(CRA). The reaction between CRA [7, 18] and CE is exothermic in nature; mixture becomes viscous and eventually forms solid mass.



Mechanism of PU synthesis

The properties of polyurethane [24, 25, 26, 30] is decided by the nature of polyols and isocyantes being used, like soft and elastic PU are formed by using polyols which render long flexible segments while rigid PU having three dimensional structure with high molecular weight can be synthesized by using cross linking agents (CLA) [5, 6,16, 17,23], CLA[19,27,31] are monomers having two or more functionalities with two, three or four crosslinking sites.

Amount of CRA required for complete linkage of NCO functionalities with OH not only depends on the concentration of CE [20,21,22] solely, but also on the concentration of the additives added to the mixture having OH functionalities too.

The general formula for evaluating the concentration of the curing agent for PU synthesis is $W_{cur} = IR[EW_{cur}][\Sigma W_n/EW_n]$. where W_{cur} is weight of curing agent, EW_{cur} is NCO Eq. Wt of curing agent, W_n is weight of each liquid components, EW_n is OH Eq.Wt for each liquid, IR is index ratio for NCO to OH[8,9,10,11,12], Eq.Wt for hydroxyl compound is 56100/hydroxyl number, and for isocyantes Eq.Wt. is 4200/%NCO. The formula incorporates NCO and OH values, whose determination is through volumetrically or potentiometrically. The same evaluation can be achieved by understanding the polymerization fundamentals through mole concept with least variations. The present research work focus on the monomer mole ratio equivalency concept, for understanding the theoretical preview of polymerization by using chain extenders(CE) PEG-600(polyethylene glycol) , cross linkagers , (CLA):homogenous mixture of 1,4-butanediol(BD) and 1,1,1-trimethylol propane (TMP) , curing agents(CRA) 2,4-toluene diisocyanates .

Number of moles for each monomer unit is based on the general formula $[w/M]fN_0$ wherein w=wt.(g) , M(mol.wt), f=functionality, N_0 =Avagadro number, for ideal case of polymerization, number of moles for all the monomer units having OH functionalities should be equal to the number of moles of curing agent with NCO functionality i.e $[(w/M)fN_0]_{OH} = [(w/M)fN_0]_{NCO}$ which is the IR(index ratio) 1 in ideal case, based on this fundamental, models were proposed like $2n_{CE}$ X 10^{21} , $13n_{BD}$ X 10^{21}, $13n_{TP}$ X 10^{21}, for determining the number of OH functionalities, for CE, BD, TMP respectively n is weight in grams, while for number of NCO functionalities of CRA(TDI) , by $[7n_{TD}-0.1]$ X 10^{21}, the models for this PU system is time effective , for evaluating the weight of CRA needed for linking all the OH functionalities by carbamate links, a model[13,14] $n_{TDI} = [2n_{CE} + 13n_{CLA} +0.1] / 7$ is proposed with least variability , the research work also envisages on the extent of polymerization independency for the ratio of components of CLA but is the function of the weight of CLA taken in the mixture, evaluated by the proposed model $\sum_n^{TMP} OH + \sum_n^{BD} OH = [W] CLA_{mix}$ X 13 X 10^{21} , total OH functionalities given by CLA & CE by proposed model is given through$[2n_{CE}+13n_{CLA} +0.1]$

For IR values less than unity incomplete polymerization, while for IR values unity effective/complete polymerization was noticed.

EXPERIMENTAL

Materials

PEG-600 as CE (sigma aldrisch), TDI (2, 4 isomer, Sigma Aldrisch) as CRA and homogenous mixture of BD (AR grade Sigma Aldrisch) and TMP (AR grade Sigma Aldrisch) was used as CLA .in order to remove any water content from iisocyanate drying process was carried at 105^0C to avoid reaction between isocyantes and water forming CO_2 bubbles, which may deform the PU system. For casting wooden mold was used, pre treated with silicon spray as mold release (ALFA-40, JIVIKA company New Delhi). The cured PUC was prepared as per the ASTMD638 Type I standards (Fig.1) for evaluating mechanical properties by Universal Test Machine UTE-40(FiE make, NEI limited, Gujrat. The Filler used was fly ash(FA) for making FA-reinforced PUC, for which FA was dried a at 110 ºC for 2.5 hours to remove any moisture content which may further react with isocyanates forming CO_2 bubble which degrade PUC properties.

Fig1. FA-reinforced PU composite sample as per ASTM D638 type I standard

Spectroscopic characterization of, CLA, CRA, PU-foam.

1,1,1-trimethylol propane (Fig.2) shows two bands of methyl along with methylene around 2925cm-^{1} , 1,4-butanediol (Fig.3) shows two peaks (symmetric and asymmetric stretching bands) of methylene only around 2925cm^{-1}, The binary component TMP &BD of CLA both shows a common characterizing peak for OH group around 3200-3600cm^{-1} (Fig.4)

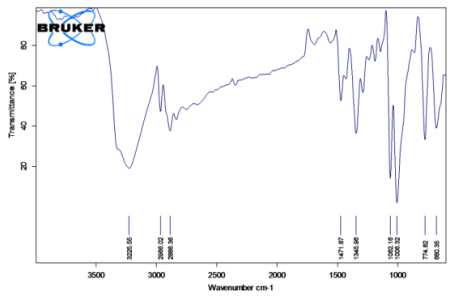


Fig2. IR spectra of TMP

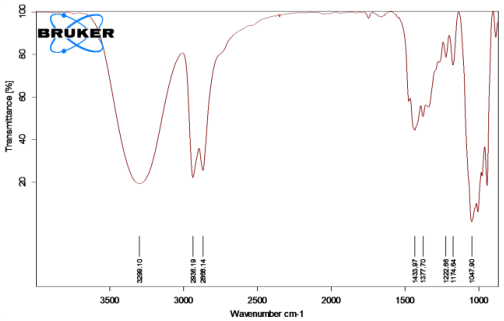


Fig.3 IR spectra of BD

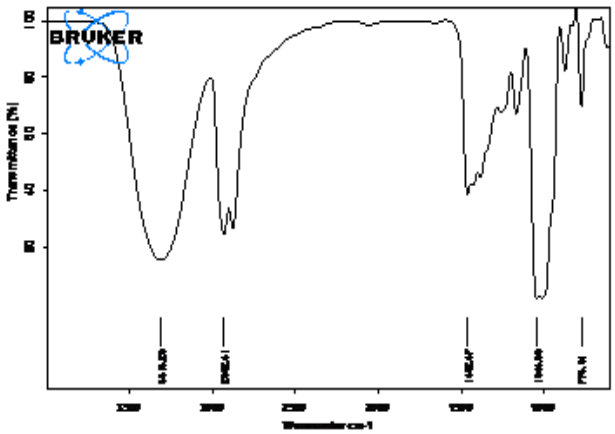


Fig4. IR spectra of mixture of BD &TMP

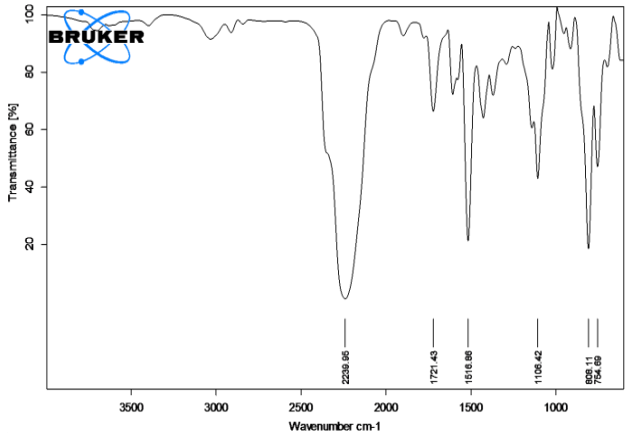


Fig.5 IR spectra of TDI

CRA (Fig.5) characterized by band around 2249cm[1] of –N=C=O functional group and aromatic ring characteristic bands around 1522cm^{-1}, 1578cm^{-1}, and 1611cm^{-1}.The CE, PEG-600 (Fig.6), shows broad and less intense peak around 3200- 3600cm-1 indicating the presence of hydroxyl group, while strong and intense peak around 2925cm-1 signifies the presence of methylene group as a part of polymeric system. The PUC formed is characterized by the formation of urethane links –NHCOO- , shown by by the IR peaks of C=O around 1711 cm-1 and around 3309cm-1 for N-H stretching (Fig 7).

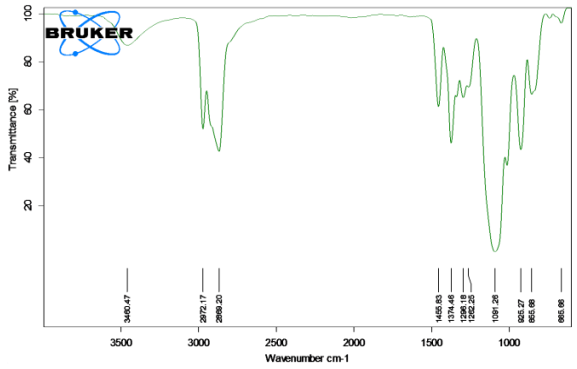


Fig.6 IR spectra of PEG-600

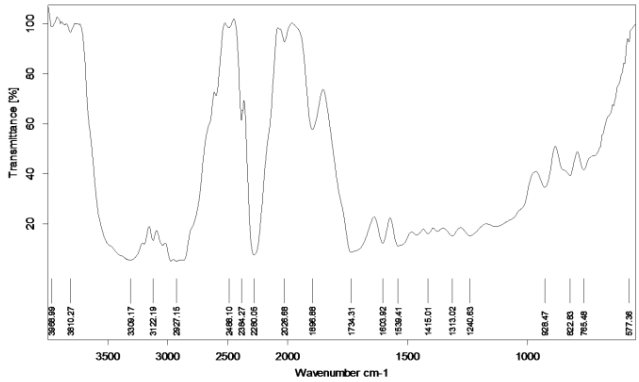


Fig.7 IR spectra PU-Composite

RESULTS AND DISCUSSION

Proposed models for CE, CLA and CRA.

The number of OH functionalities given by CE, CLA, and NCO functionalities by CRA, IR and weight of curing agents has been evaluated by the model proposed.

Monomers	***Proposed Models***
PEG-600 ,f=2	Σ OH $=2n_{CE}$ X 10^{21}
TDI, f=2	Σ NCO $=[7n_{TD}-0.1]$ X 10^{21}
BD, f=2	Σ OH $=13n_{BD}$ X 10^{21}
TMP, f=3	Σ OH $=13n_{TP}$ X 10^{21}
IR(Index ratio)	NCO/OH = $[7n_{TD}-0.1]/2n_{CE}+13\,n_{CLA}$
Wt. of Curing Agents	Wt = $[2n_{CE}+13\,n_{CLA}+0.1]$ /7 g
	Σ OH [CLA&CE] = $2n_{CE}+13nCLA+0.1$

.* n=wt in gm , f=functionality

The present research work focuses on the preparation of PU matrix at constant weight ratio 3:2 of CE and CRA, while the binary components (BD&TMP) of CLA were in 1:1, 1:2 &2:1weight ratios. Weight of CLA taken was either 0.5 or 1g for the various weight ratios of binary components of CLA. Using the proposed models Σ OH $=2n_{CE}$ X 10^{21} for evaluating the number of OH functionalities of CE(3g)it is $6X10^{21}$ and number of NCO functionalities by proposed model Σ NCO $=[7n_{TD}-0.1]$ X 10^{21} of CRA(2g) is 13.9 X 10^{21} were kept constant. In all the experiments wherein the sum total of OH functionalities of CE and CLA(with all the weight ratios of binary components & wt of CLA as either 0.5 or 1 g) were equal to number of NCO[28] functionalities i.e 13.9 X 10^{21} complete polymerization was noticed. The values evaluated by the proposed models for evaluating number of OH &NCO functionalities, and Index ratio all were in good agreement with those evaluated by mole concept$[w/M]fN_0$ with least variability. The experiments are explained in the tabulated form through proposed models.

Evaluation of extent of complete Polymerization in PUC by proposed model

[NCO/OH] IR=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}

The extent of polymerization evaluated by the IR of the PU system calculated through proposed models were explained by the SEM image showing the FA distribution in PUC. In the experiments 1,3 &5 wherein 0.5 g of CLA was taken at all wt/wt ratio of BD and TMP (1:1,1:2 and 2:1) the Σ NCO functionalities ≥ Σ OH [CLA&CE] functionalities i.e [7n_{TD}-0.1] 10^{21} ≥ [2n_{CE}+13nCLA+0.1] 10^{21} for various ratios of BD and TMP of CLA. Complete polymerization with IR 1.1 evaluated by the proposed model for IR NCO/OH = [7n_{TD} -0.1]/2n_{CE}+13 n_{CLA} was supported by the SEM images(Fig8,Fig10, and Fig12) wherein uniform distribution of FA was seen in PU matrix.

Experiment 1	n = wt in gm
BD:TMP(ratio)	**1:1**
CLA (wt)	**0.5g**
Σ OH=13n_{BD} X 10^{21}	3.25X10^{21} n=0.25
Σ OH=13n_{TP} X 10^{21}	3.25X10^{21} n=0.25
Σ OH =2n_{CE} X 10^{21}	6X10^{21} n=3
Σ OH(CLA& CE)	13.9X10^{21} n=2
Σ NCO=[7n_{TD}-0.1] X 10^{21}	13.9X10^{21} n=2
NCO/OH=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}	**1.1**
[7n_{TD}.0.1]≥2n_{CE}+13nCLA+0.1	**Complete polymerization**

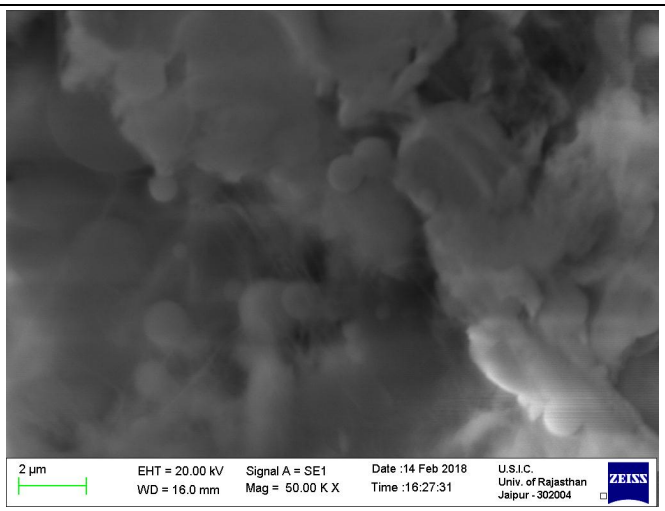


Fig.8. SEM image showing the formation of the FA reinforced PUC (uniform distribution of FA in PU matrix)

Evaluation of extent of incomplete Polymerization by proposed model.

[NCO/OH] IR=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}

The extent of polymerization was evaluated by the IR for the PU system which was calculated through proposed models and was explained by the SEM image showing FA agglomeration over the small domain in PUC in the experiments 2,4 &6 wherein 1 g of CLA was taken at all wt/wt ratio of BD and TMP (1:1,1:2 and 2:1) the OH [CLA&CE] functionalities ≥ Σ NCO functionalities i.e [2n_{CE}+13nCLA+0.1] 10^{21} ≥ [7n_{TD}-0.1] 10^{21} for various ratios of BD and TMP of CLA. Incomplete polymerization with IR 0.7 evaluated by the proposed model for IR NCO/OH = [7n_{TD} -0.1]/2n_{CE}+13 n_{CLA} was supported by the SEM images(Fig9,Fig11, and Fig13) wherein non uniform distribution/clumping of FA was seen in PU matrix.

Experiment 2	n = wt in gm
BD:TMP(ratio)	**1:1**
CLA (wt)	**1g**
Σ OH=13n_{BD} X 10^{21}	6.5X10^{21} n=0.5
Σ OH=13n_{TP} X 10^{21}	6.5 X10^{21} n=0.5
Σ OH =2n_{CE} X 10^{21}	6X10^{21} n=3
Σ OH(CLA& CE)	19 X10^{21}
Σ NCO=[7n_{TD}-0.1] X 10^{21}	13.9X10^{21} n=2
NCO/OH=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}	**0.7**
2n_{CE}+13nCLA+0.1≥[7n_{TD}. 0.1]	**Incomplete polymerization**

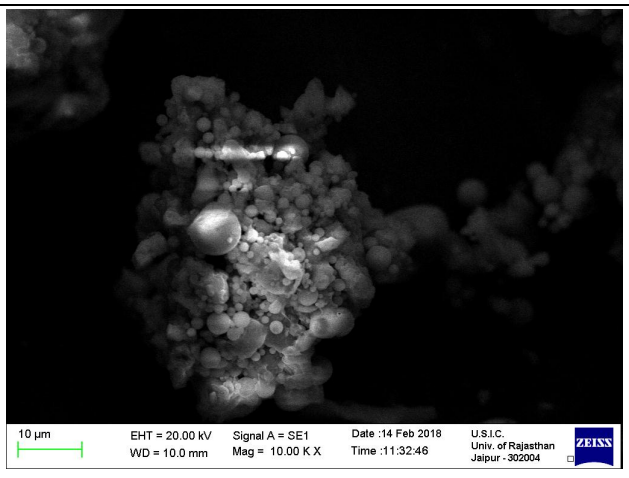


Fig.9 SEM image showing the incomplete formation of the FA reinforced PUC(FA clumping in PU matrix)

Experiment 3	n = wt in gm
BD:TMP(ratio)	**1:2**
CLA (wt)	**0.5g**
Σ OH=13n_{BD} X 10^{21}	2.0X10^{21} n=0.16
Σ OH=13n_{TP} X 10^{21}	4.2X10^{21} n=0.33
Σ OH =2n_{CE} X 10^{21}	6X10^{21} n=3
Σ OH(CLA& CE)	12.2X10^{21}
Σ NCO=[7n_{TD}-0.1] X 10^{21}	13.9X10^{21} n=2
NCO/OH=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}	**1.1**
[7n_{T}- .0.1] ≥2n_{CE}+13nCLA+0.1	**Complete polymerization**

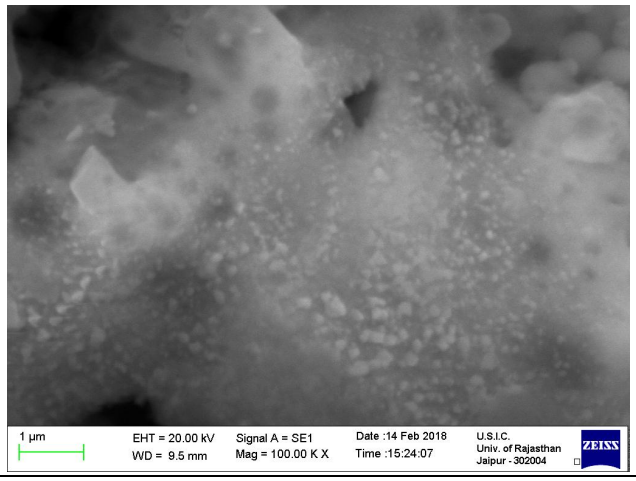


Fig.10. SEM image Showing the formation of the FA reinforced PUC.(uniform distribution of FA in PU matrix

Experiment 4	n = wt in gm
BD:TMP(ratio)	**1:2**
CLA (wt)	**1g**
Σ OH=13n_{BD} X 10^{21}	4.2X10^{21} n=0.33
Σ OH=13n_{TP} X 10^{21}	8.5X10^{21} n=0.66
Σ OH =2n_{CE} X 10^{21}	6X10^{21} n=3
Σ OH(CLA& CE)	18.7X10^{21}
Σ NCO=[7n_{TD}-0.1] X 10^{21}	13.9X10^{21} n=2
NCO/OH=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}	**0.7**
2n_{CE}+13nCLA+0.1≥[7n_{TD}- 0.1]	**Incomplete polymerization**

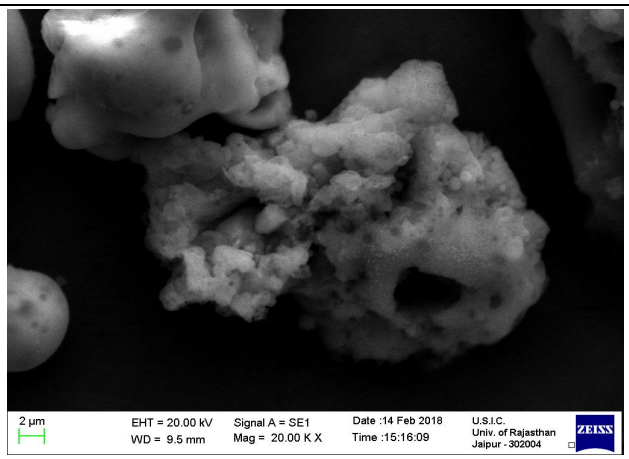


Fig.11 SEM image showing the incomplete formation of the FA reinforced PUC.(FA clustering in PU matrix)

Experiment 5	n = wt in gm
BD:TMP(ratio)	**2:1**
CLA (wt)	**0.5g**
Σ OH=13n_{BD} X 10^{21}	4.2X10^{21} n=0.33
Σ OH=13n_{TP} X 10^{21}	2.0X10^{21} n=0.16
Σ OH =2n_{CE} X 10^{21}	6X10^{21} n=3
Σ OH(CLA& CE)	12.2X10^{21}
Σ NCO=[7n_{TD}-0.1] X 10^{21}	13.9X10^{21} n=2
NCO/OH=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}	**1.1**
[7n_{TD}- 0.1] ≥2n_{CE}+13nCLA+0.1	**Complete polymerization**

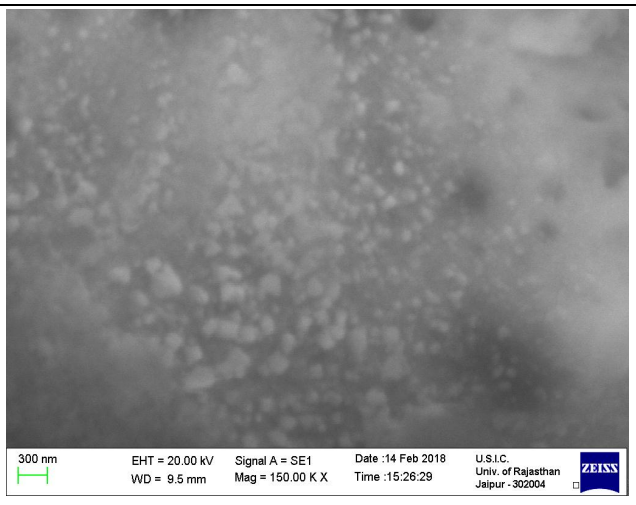


Fig.12 SEM image Showing the formation of the FA reinforced PUC (uniform distribution of FA in PU matrix)

Experiment 6	n = wt in gm
BD:TMP(ratio)	2:1
CLA (wt)	1g
Σ OH=13n_{BD} X 10 ^{21}	8.5X10^{21} n=0.66
Σ OH=13n_{TP} X 10 ^{21}	4.2X10^{21} n=0.33
Σ OH =2n_{CE} X 10 ^{21}	6X10^{21} n=3
Σ OH(CLA& CE)	18.7X10^{21}
Σ NCO=[7n_{TD}-0.1] X 10 ^{21}	13.9X10^{21} n=2
NCO/OH=[7n_{TD}-0.1]/2n_{CE}+13 n_{CLA}	0.7
2n_{CE}+13nCLA+0.1≥[7n_{TD}- 0.1]	**Incomplete polymerization**

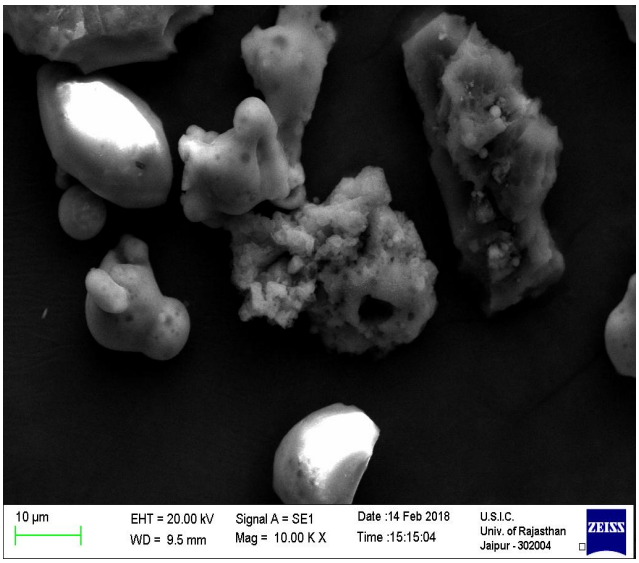


Fig.13. SEM image showing the incomplete formation of the FA reinforced PUC.(agglomeration of FA in PU matrix)

Graphical representation for model validation

Evaluating IR, number of OH functionalities of CE, BD, TMP and number of NCO functionalities of CRA simultaneously by models and mole concept and validations of the values by both the methods is shown in 3D Fig 14,15,16,17,18,19,20 and 21.

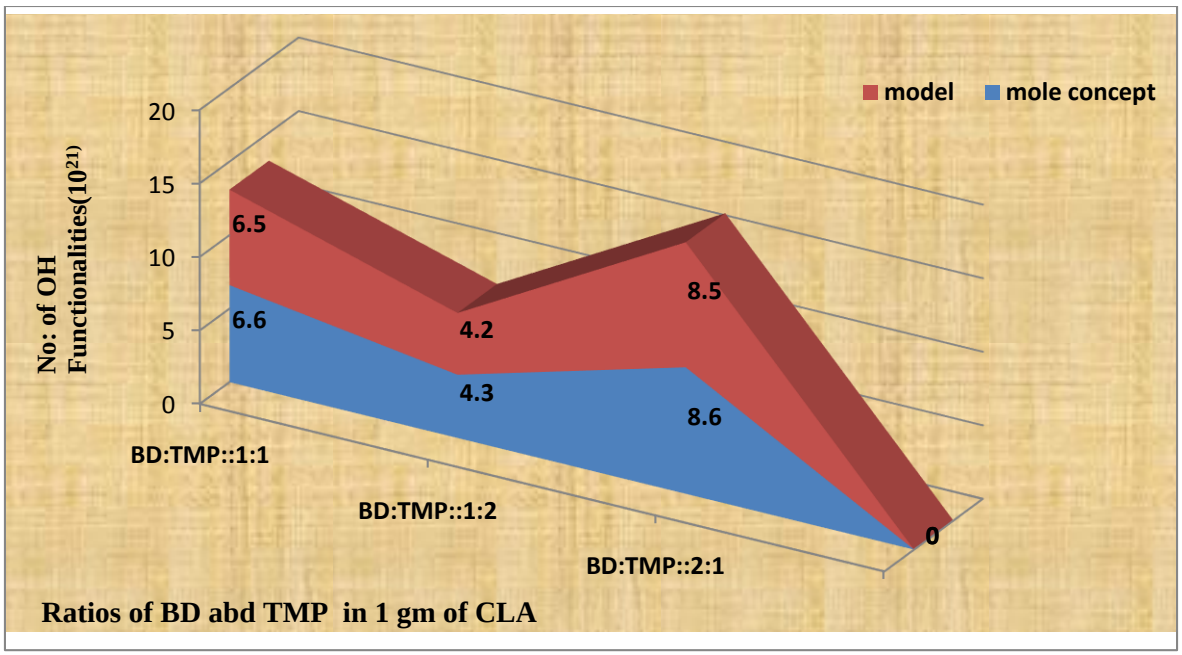


Fig.14 comparison of number of OH functionalities of BD in CLA (1gm) by mole concept and by model

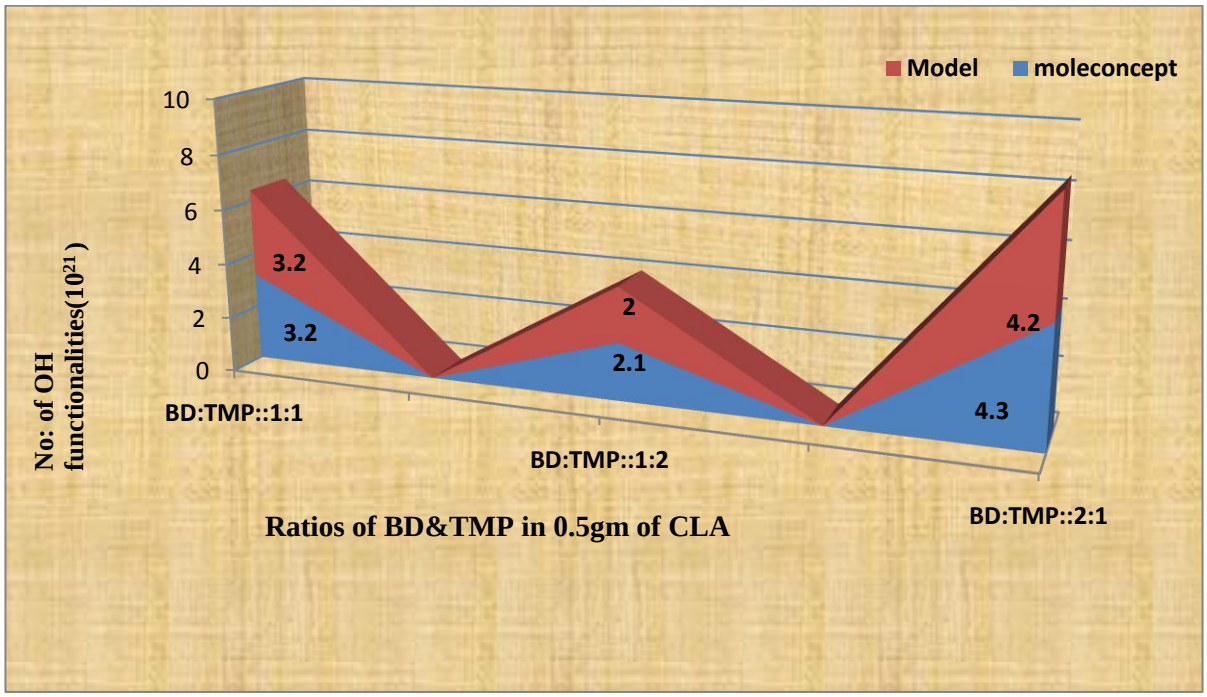


Fig.15 comparison of number of OH functionalities of BD in CLA (0.5gm) by mole concept and by model

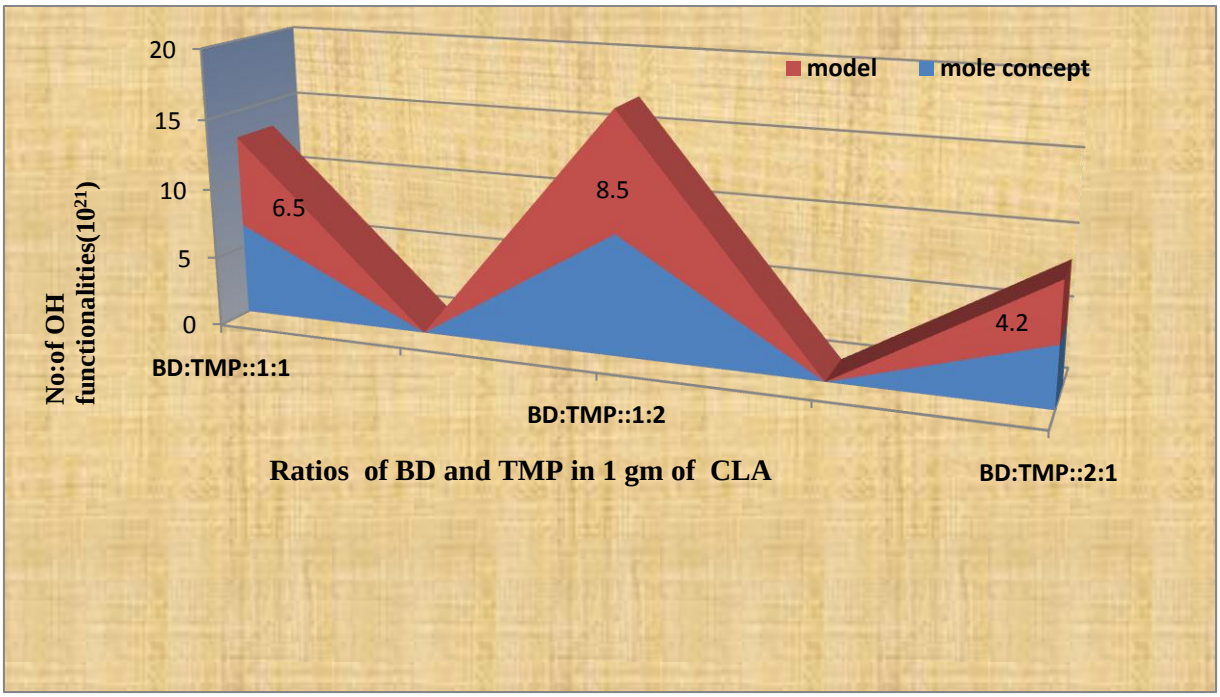


Fig.16 comparison of number of OH functionalities of TMP in CLA (1gm) by mole concept and by model

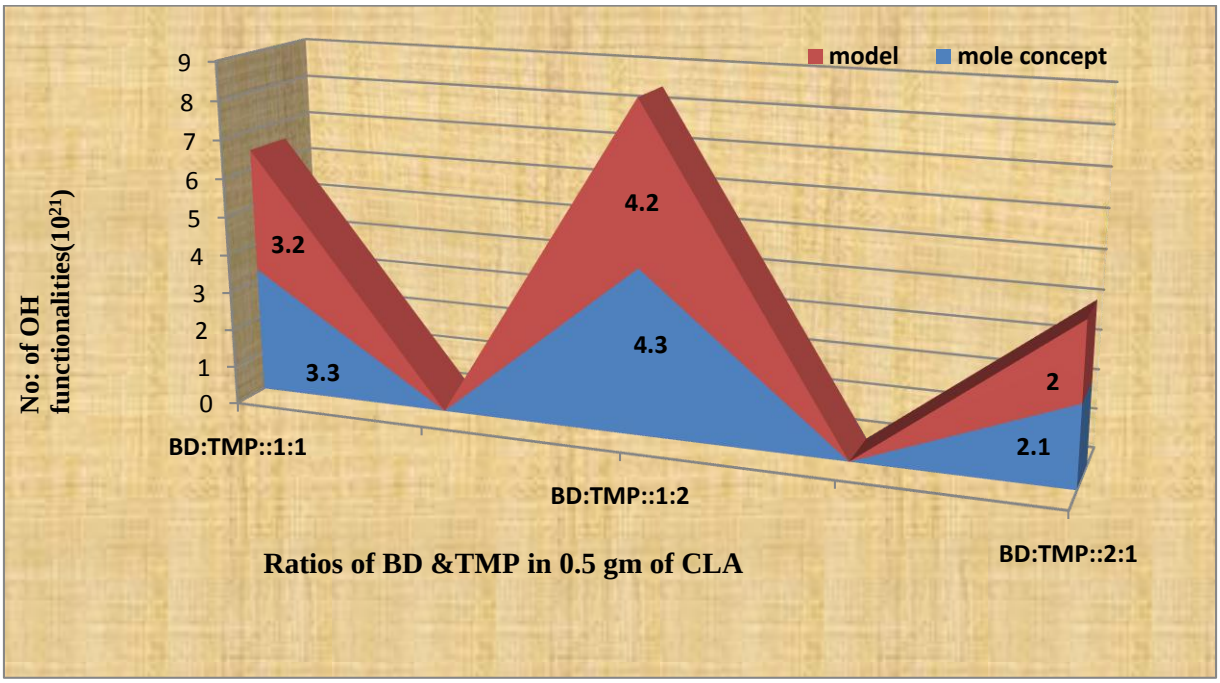


Fig.17 comparison of number of OH functionalities of TMP in CLA (0.5gm) by mole concept and by model

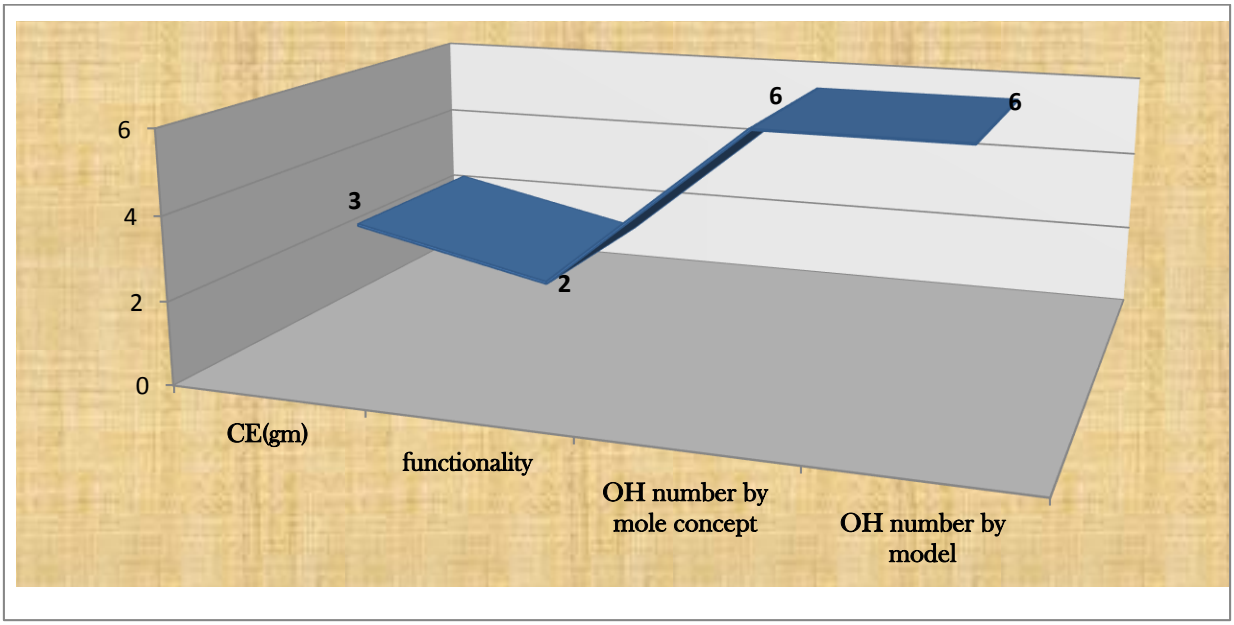


Fig.18 Number of OH (10^{21}) functionalities of CE by mole concept and by model

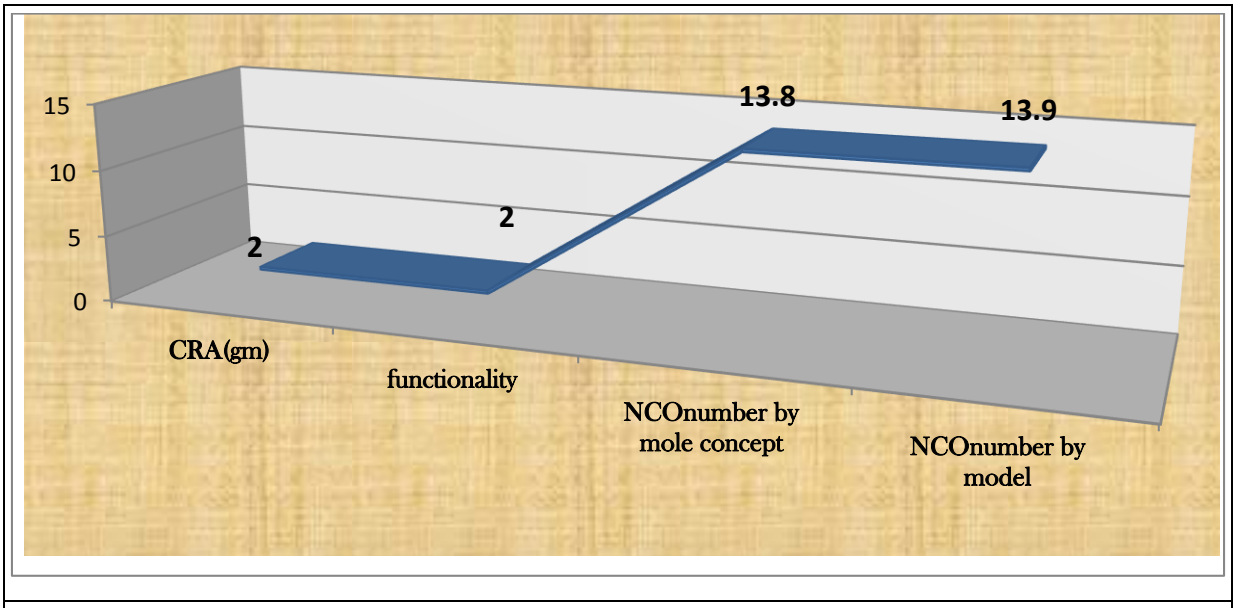


Fig.19 Number of NCO (10^{21}) functionalities of TDI by mole concept and by model

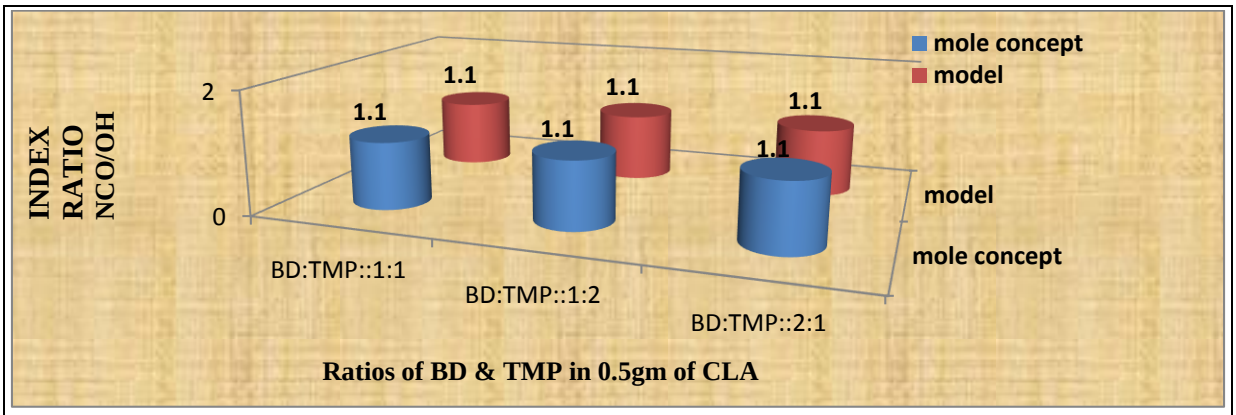


Fig.20. Comparison of Index Ratio (NCO/OH) for PUC when 0.5 gm of CLA taken at constant wt/wt ratio of CE&CRA3:2 by model & mole concept.

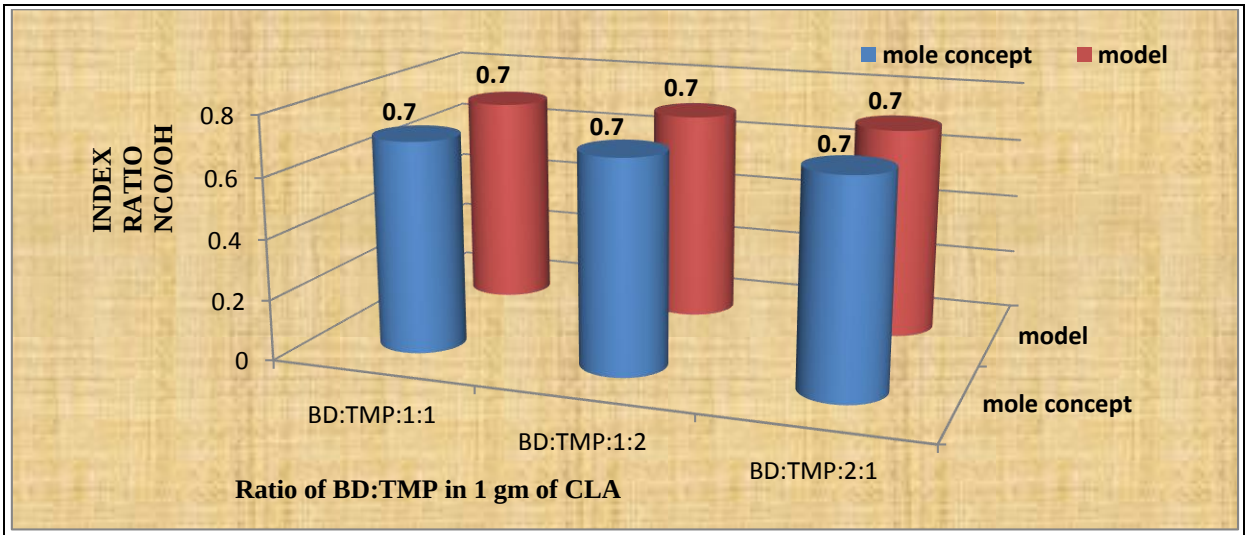


Fig.21. Comparison of Index Ratio (NCO/OH) for PUC when 1 gm of CLA taken at constant wt/wt ratio of CE&CRA3:2 by model & mole concept.

Extent of polymerization is not the function of ratio of binary components of CLA

In experiments for IR values 0.7 incomplete polymerization was seen while for IR value as 1.1, complete polymerization was noticed. PU synthesis having OH contribution from CE , CLA and NCO contribution from CRA evaluated by proposed models were in good agreement with the mole concept method. IR values evaluated by the mole concept and the models were in great approximation. The present research work also envisages on the independency of the ratio of components of CLA on the extent of polymerization but solely shows dependency on the weight of CLA taken in the mixture: $\sum_n^{TMP} OH + \sum_n^{BD} OH = [W]_{mix} X 13 X 10^{21}$, general form for any ratio of BD and TMP when taken as homogenous mixture

$$\sum_n^{TMP} OH + \sum_n^{BD} OH = [(B/B+T) + (T/B+T)] W X 13 X 10^{21}$$

$$\sum_n^{TMP} OH + \sum_n^{BD} OH = [W]_{mix} X 13 X 10^{21}$$

B=BD and T=TMP

Determination of mechanical properties of PUC

Mechanical properties viz. Tensile strength (TS), Young modulus (YM) and hardness were evaluated for FA reinforced PUC and were found to depend on the wt/wt ratio of binary components of CLA which is shown by the UTM graphes plotted between load v/s displacement(Fig.22,23,24). Graphical representation of TS, YM and Hardness of FA reinforced polyurethane composites with various ratios of BD and TMP in CLA as 1:1(A), B (1:2) and C (2:1) is shown in Fig.25.

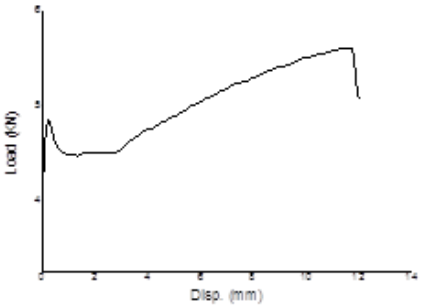


Fig.22. load v/s displacement for PUC at 1:1 w/w ratio of BD& TMP

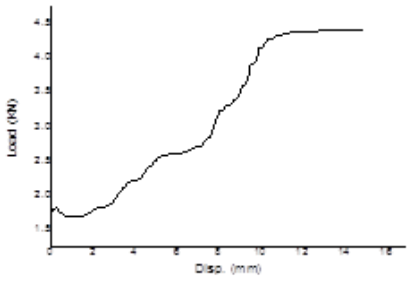


Fig23. load v/s displacement for PUC at 1:2 w/w ratio of BD&TMP

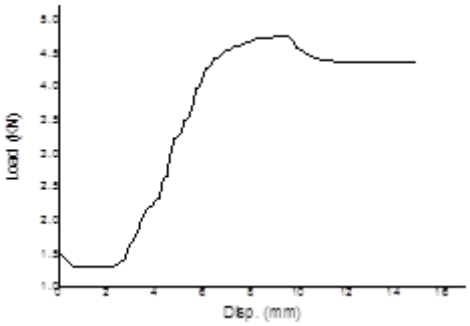


Fig.24. load v/s displacement for PUC at 2:1 w/w ratio of BD& TMP

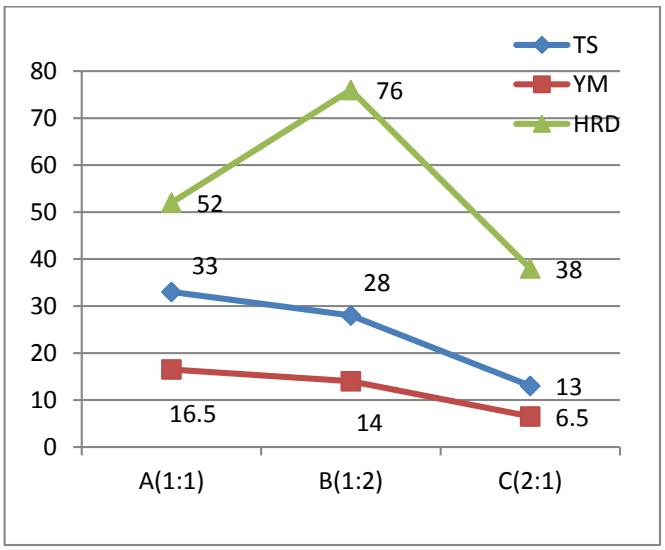


Fig.25. Graph representing TS, YM and Hardness of FA reinforced polyurethane composites with various ratios of BD and TMP in CLA as 1:1(A), B (1:2) and C (2:1).

CONCLUSION

For PU synthesis using BD and TMP homogenous mixture as CLA, the extent of polymerization is independent of the ratio of components of the CLA but depends on the amount of CLA added to CE, however the mechanical property of polymer [19,20,22] depends on the weight ratio of binary components of CLA. The OH and NCO value calculated by using the mole concept is in match with the one evaluated by using the proposed models. The IR values evaluated for deciding the extent of polymerization were in great agreement with values through mole concept and by the proposed models. The models proposed for this PU system is time effective and a good mathematical tool for predicting the extent of polymerization. When 0.5 g of CLA was added to 3g of CE, the requisite amount of CRA for polymerization by the proposed model Wt = $[2n_{CE}+13\,n_{CLA}+0.1]$ /7 g was 1.8g, for which in experiment 2g was added which gave IR 1.1, however for 1g of CLA with the same weight ratio of CE (3g) requisite amount of CRA by the proposed model was 2.7g for which only 2g was added in experiment giving IR only 0.7

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