



Synthesis and Characterization of Phenolic Modified Castor Oil Based UV Resistant Coatings

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Abstract: Castor (*Ricinus Communis*) is typically farmed for its oil-producing seeds, which contain ricinoleic acid. Castor oil can only be used as modified polyol since it only includes castor oil with hydroxyl groups in its chemical structure. To create the polyol in the current work, castor oil was changed by combining phenolic resin with diethyleneglycol (DEG). Measurements have been made of the physico-chemical characteristics of synthetic coatings, including its mixing time, surface dry time, hard time and gel time. Spectroscopic experiments of the synthetic polyol based on castor oil are conducted using FTIR, NMR and XRD. FTIR studies show the information of changes in the functional group with changing concentration of diethyleneglycol (DEG) and phenolic resin (Ph. resin). Infrared spectroscopy (IR) is used to understand the characterization worth with suitable standards in view of chemical and structural characterization of synthesized polyol.

Key words: Phenolic resin, Castor Oil, diethyleneglycol (DEG) and Physico- chemical properties.

1. INTRODUCTION:

Research that focus on the spectroscopic and analytical characterization of polymeric materials may yield the relevant data necessary for a wide range of engineering applications. Just a few studies have been published on the creation of agriculturally based products and their spectroscopic characterization, despite the fact that many research projects have been focused on polyurethanes (PUs) based on petrochemicals. Products made of polyurethane are rapidly evolving, particularly in the coatings industry. Exploring the possible application of renewable and unconventional raw materials for the synthesis of resins is thus a significant topic of current study in surface coating materials [1]. Starch, cellulose, and different oils, including castor oil, soya bean oil, etc., are the most prevalent of these substances. Due to their excellent temperature and electrical resistance qualities, phenolic resins are among the most significant thermosetting polymers. Traditional phenolic resins provide a number of benefits, including heat resistance, high electrical characteristics, and flame retardance. Phenolic resins are employed as cross-linkers in a variety of coating types to improve interfacial bonding and modify flexibility [2,3]. Phenolic resins nonetheless serve important purposes despite their declining relevance.

As the utilized raw materials can be obtained at a fair price, their significance is expected to stay substantial. Despite their extensive history, phenolic resins are constantly being developed individually [4]. Current coating business is becoming more and more dependent on the ability to synthesize polymers with moieties that can participate in polymerization processes. In the paint and coatings sectors, alkyd resins, which are complicated network polyesters, are frequently employed [5]. Polyols are alkyd resins with a defined high hydroxyl content that can combine with substances containing epoxy, isocyanate groups to create hybrid coatings with better performance. According to a review of the literature, polyurethanes based primarily on petrochemicals, which are more expensive as raw materials than PUs based on veggie oil, have dominated the polymer industry [6-8].

In the current study, an effort has been made to create polyols for polyurethane systems using castor oil, an oil-based polyol amended with diethanoglycol (DEG), and phenolic resin. For the purpose of characterizing the produced phenolic modified coatings, physicochemical characteristics like gel time, mixing time, hard dry time, and surface dry time as well as spectroscopy methods like FTIR, and NMR have been employed.

2. EXPERIMENTAL

2.1 Raw Materials

Castor oil (Krishna Chemicals pvt. Limited, Delhi), Phenolic Resin (Ashoka Scientific pvt. Limited, Haryana), diethyleneglycol(DEG) (S.D Fine chem. Mumbai), Acetone (Sisco Reasearch laboratory, AR grade), Glycerol, Isophorone diisocyanate (IPDI), Hexamethylene diisocayante (HMDI), Nitric acid, Sulphuric acid (Garg pvt. Limited, Delhi), KOH as reagent (Himedia Laborateries Pvt. Ltd. Mumbai) and ethanol (Ashoka scientific pvt. Ltd. Haryana).

2.2 Preparation of Two Component Polyurethane Coating

Preparation of two component polyurethane coatings is two step process.

1. Synthesis of Polyol

The reaction for the preparation of modified polyol from castor oil was takes place in three mouths round bottom flask. In first mouth nitrogen inlet was fitted, in second mouth a thermometer and stirrer is fitted and in third mouth a reflux condenser is fitted. Three set of polyols are formed with variation in concentration of diethyleneglycol(DEG)and phenolic resin under same condition. The reaction was carried out at 140°C temperature for around 5 – 6 hours.

2. Synthesis of PU coatings

All the prepared polyols are then reacted with IPDI and HMDI at room temperature 25°C and 80% humidity to form coatings after the reaction blended PU are coated on glass slides for the observation of their curing times, gel times, mixing time, surface dry time and hard dry time. These coated panels were then kept for post- curing in oven at 60°C for 72 hours. After that these coated panels are studied for chemical and water resistance. For chemical resistance coated panels are immersed in different chemical solutions like nitric acid, hydrochloric acid, ethanol and acetic acid.

3. RESULTS AND DISCUSSION

The prepared coatings are characterized using spectroscopic techniques such as FTIR, XRD and NMR. Chemical and water resistance of glass coated panels were also investigated. Performance properties like gel time, mixing time, surface dry time, surface hard time were also checked.

3.1 Spectroscopic Characterization

FTIR study for IPDI polyurethane coatings

Figure 1 depicts the FTIR spectra of produced coatings. Peaks at 3364, 1602, and 1539 Cm^{-1} corresponding to -NH (stretching), -C=O (stretching), and -NH (bending), respectively, were found, showing the formation of the chemical structure for polyurethane. In addition, the peaks at 2934 and 2856 Cm^{-1} are due to C-H stretching of CH_2 and CH_3 groups of IPDI were also observed. The methyl group (CH_3) stretching is attributed to the peak at 3009 Cm^{-1} in the polyurethane coatings spectra. The stretching of free urethane carbonyl groups was the indicated by the peak at 1733 Cm^{-1} . The unreacted isocyanate group $\text{O}=\text{C}=\text{N}$ is accountable for the peak at 2276 Cm^{-1} . Peak at 725 Cm^{-1} is due to aromatic ring. The peak at 1457 Cm^{-1} gives strong evidence for ester formation [9].

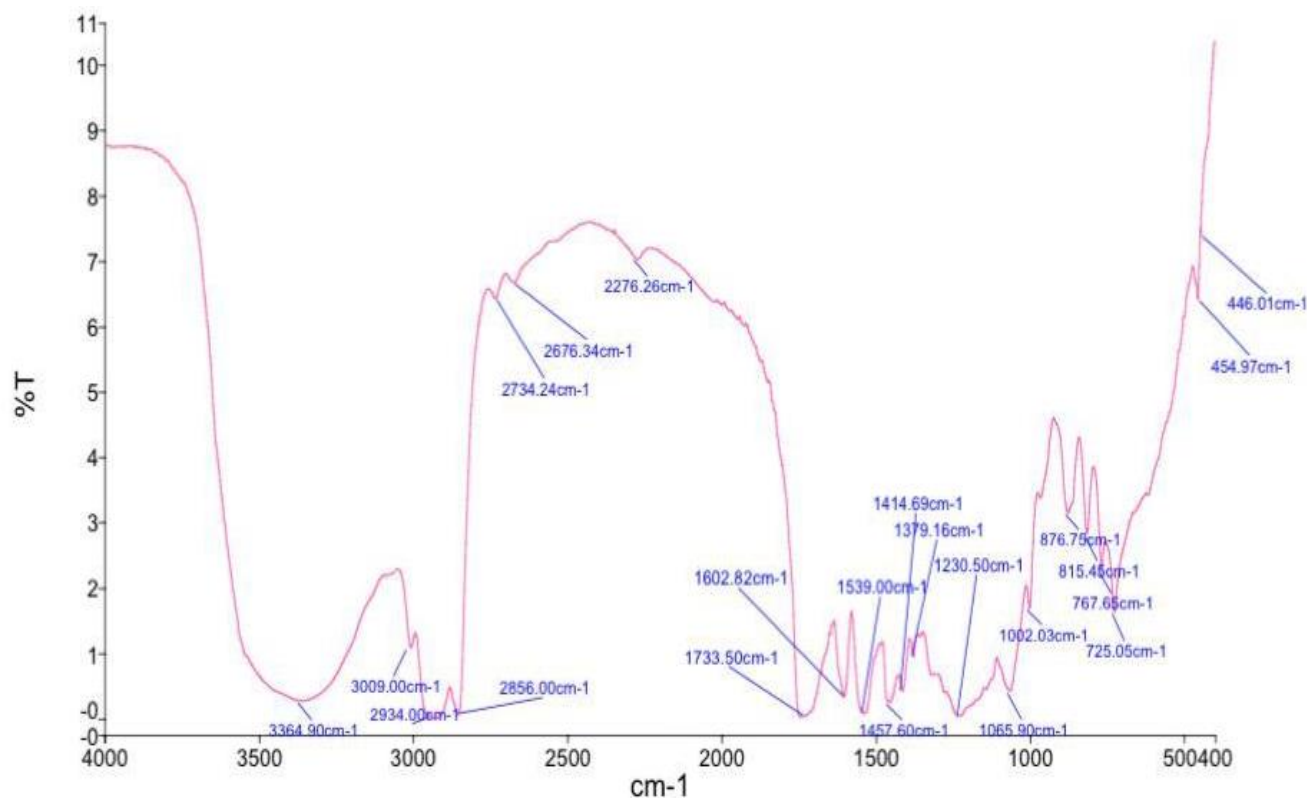


Figure 1: FTIR spectra of synthesized DEG polyurethane coating from IPDI

FTIR study for HMDI polyurethane coatings

The presence of urethane bond between HMDI and castor was confirmed by Fourier Transform Infrared (FTIR) spectroscopy. The IR spectrum of formed coating is shown in figure 2. The presence of peak at 1534 Cm^{-1} in PU coatings prepared with HMDI is evidence of the establishment of urethane linkage. The vibration peak at 3387 Cm^{-1} corresponds to the amide N-

H stretching in urethane. There is a distinctive peak at 2286–2383 cm^{-1} , which has been ascribed to the unreacted isocyanate group $\text{O}=\text{C}=\text{N}$. The peak at 1727 cm^{-1} which is attributed to the ester carbonyl ($\text{C}=\text{O}$) stretching of castor oil and urethane carbonyl. The bands between 2862 and 2933 cm^{-1} indicates to the methylene (CH_2) asymmetric and symmetric stretching vibration of the hydrocarbon chain of castor oil and HMDI. The spectrum shows a broad peak at 3387 cm^{-1} indicating the hydroxyl group of polyols [10]. The peak at 1727 cm^{-1} which is attributed to the ester carbonyl ($\text{C}=\text{O}$) stretching of castor oil and urethane carbonyl. The spectrum shows a broad peak at 3387 cm^{-1} indicating the hydroxyl group of polyols.

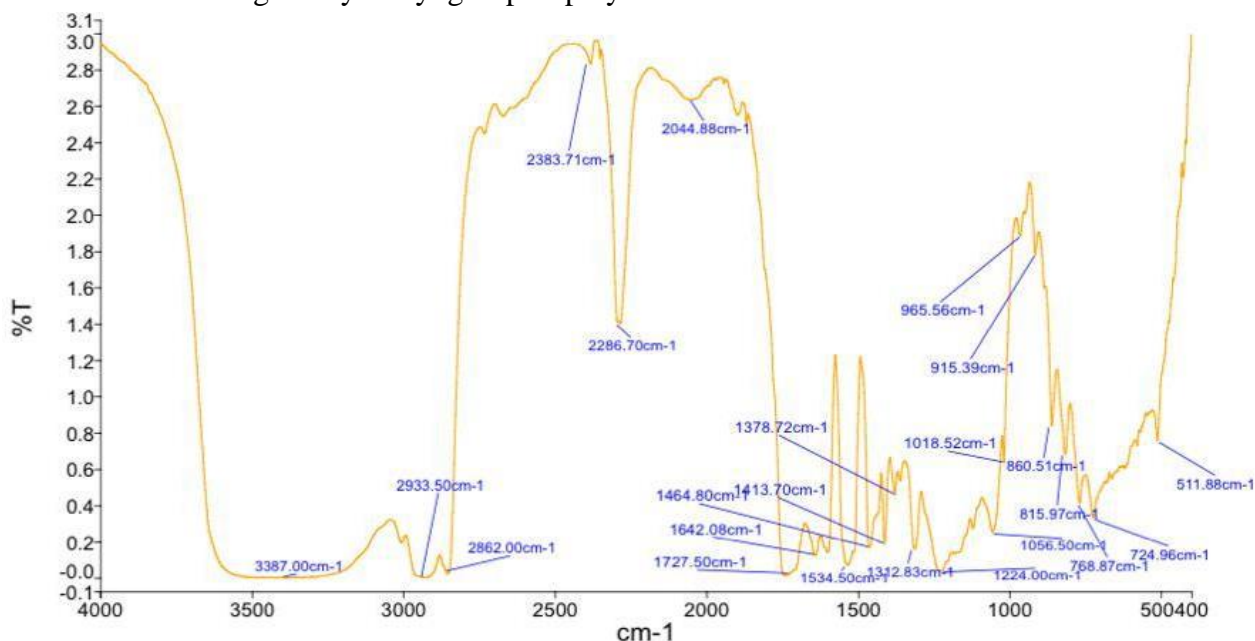


Figure 2: FTIR spectra of synthesized DEG polyurethane coating from HMDI

NMR Spectroscopy

With the help of a Bruker Spectrospin DPX-300, a ^1H - NMR spectroscopic analysis of the chemically changed polyols was performed. . Peak attributed at 3.6 ppm is for CH_2OH . Peak obtained at 5.2 ppm determine existence of $\text{C}=\text{CH}$ group. Peak obtained at 4.2 ppm indicate existence of acetate protons. The peak of aromatic protons has been shown to boost as the quantity of phenolic resin increases, indicating that the maximum amount of phenolic resin and diethylene glycol interacted with castor oil to favour the synthesis of modified polyols [11].

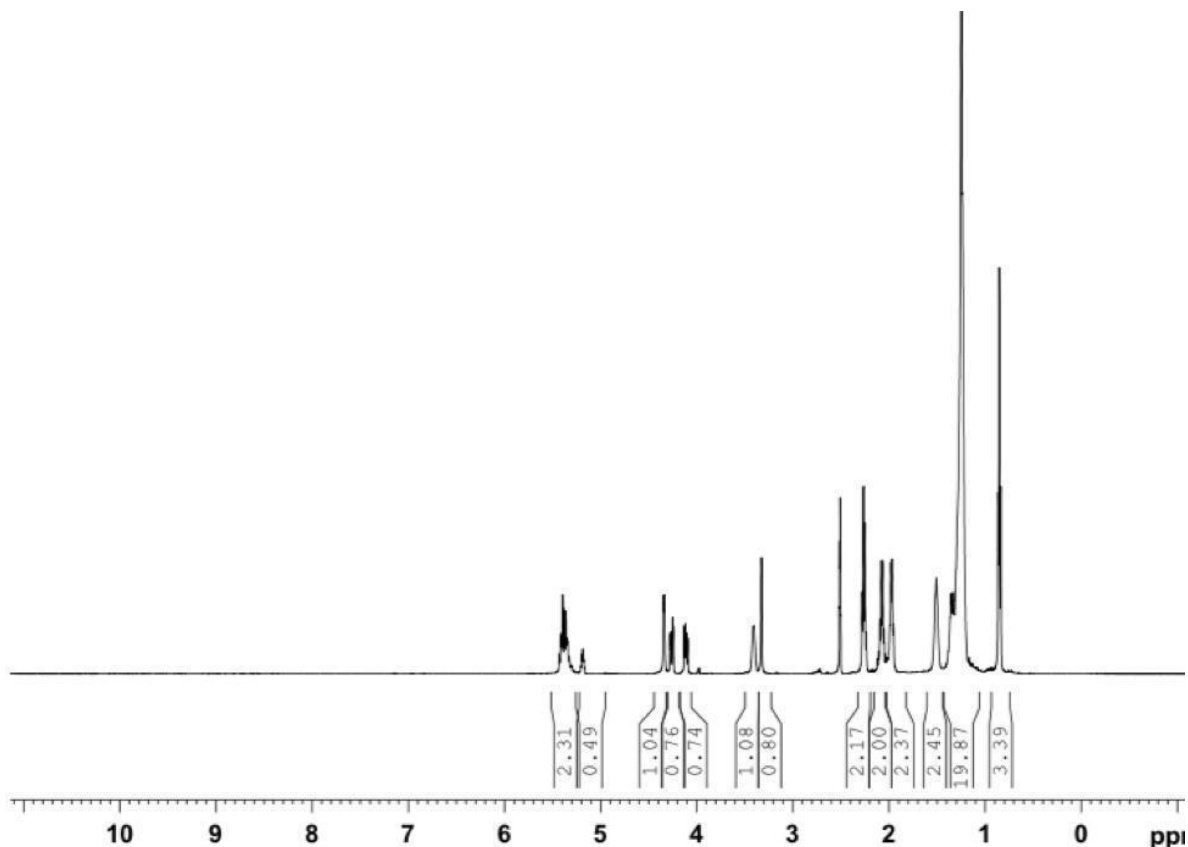


Figure 3: NMR spectra of PU coatings with phenolic resin

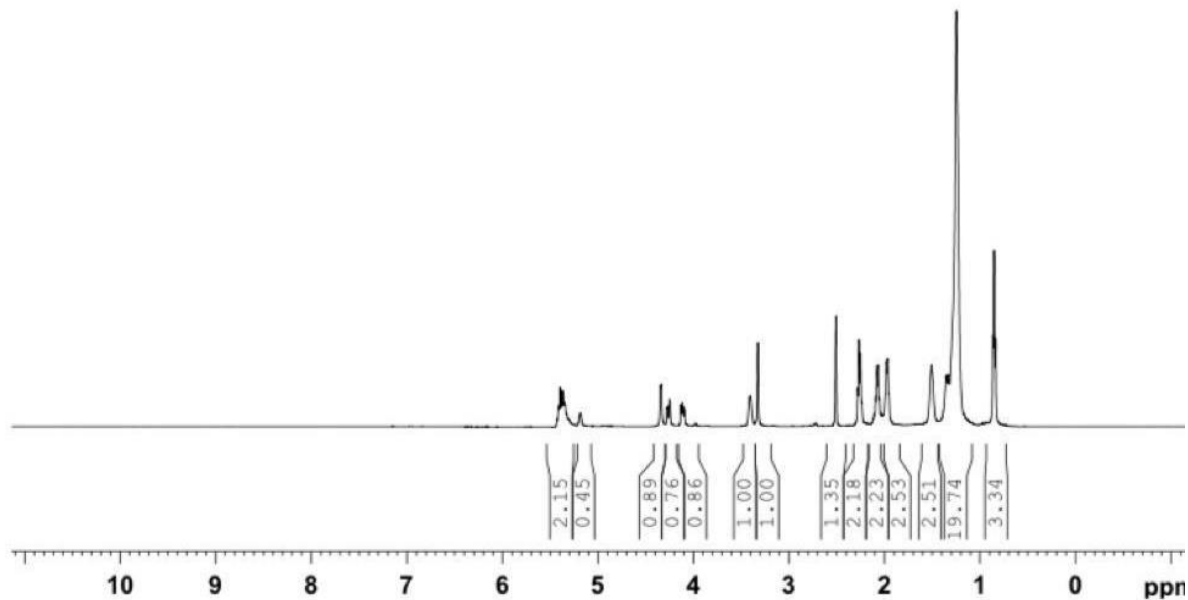


Figure 4: NMR spectra of PU coatings with DEG formed from IPDI

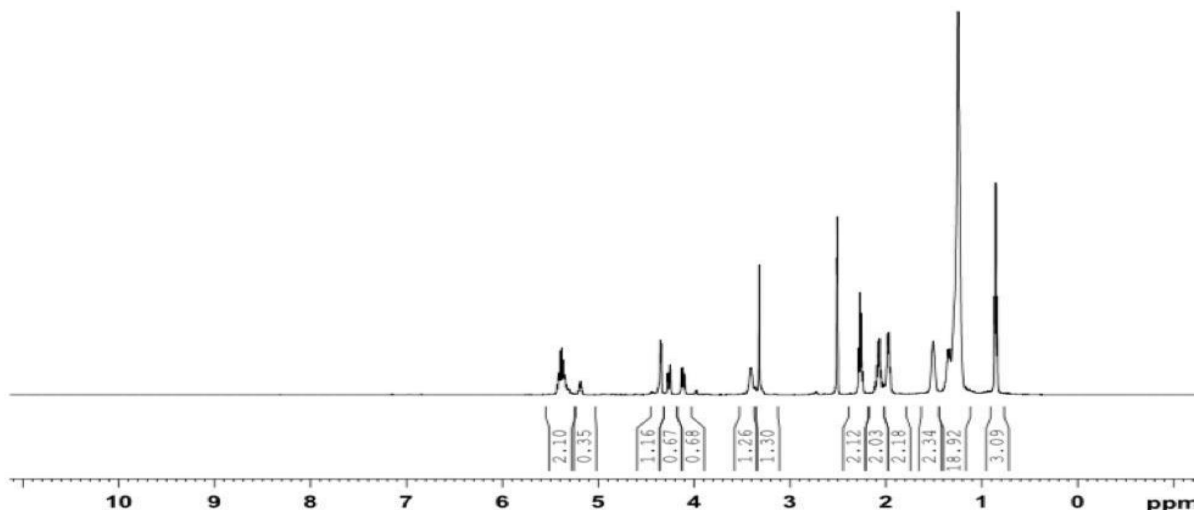


Figure 5: NMR spectra of PU coatings with DEG formed from HMDI

XRD study

The XRD patterns of blended coatings are presented in figure 6-8. The concentration DEG and phenolic resin vary in sample as 70+15, 70+10, and 70+5. XRD studies tell about the structural characteristics of material. One broad peak is observed from the data made from IPDI and HMDI. This broad curve tells about the amorphous nature of materials. In case of pure phenolic resin peak obtained at 20.6 degree but in these synthesized sample the peak observed at angle 18.6 degree is due to the difference in chemical structure of soft segment condition and these condition occur due to addition of diisocyanates in the castor oil [12,13].

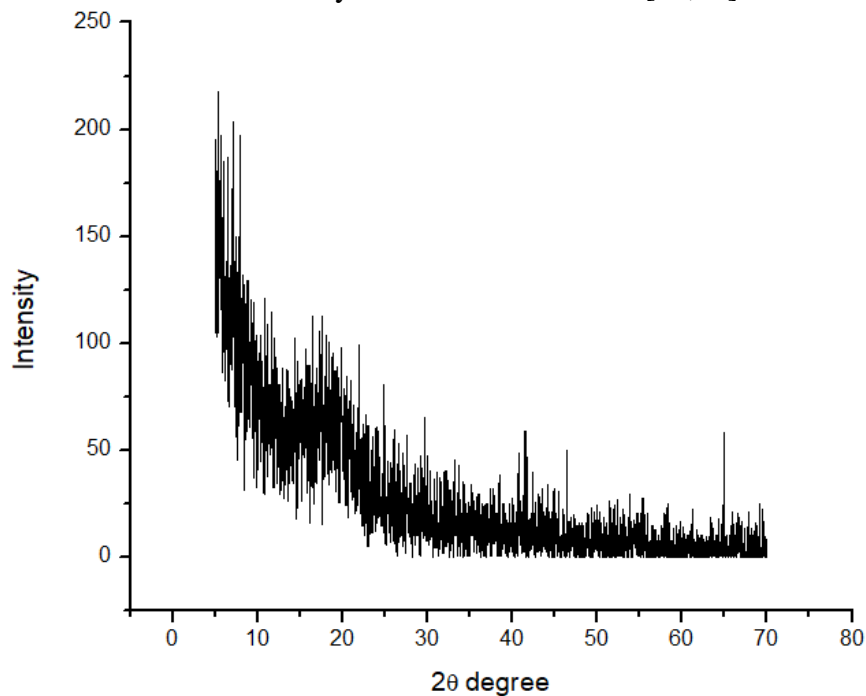


Figure 6: XRD spectra of PU coatings formed with phenolic resin

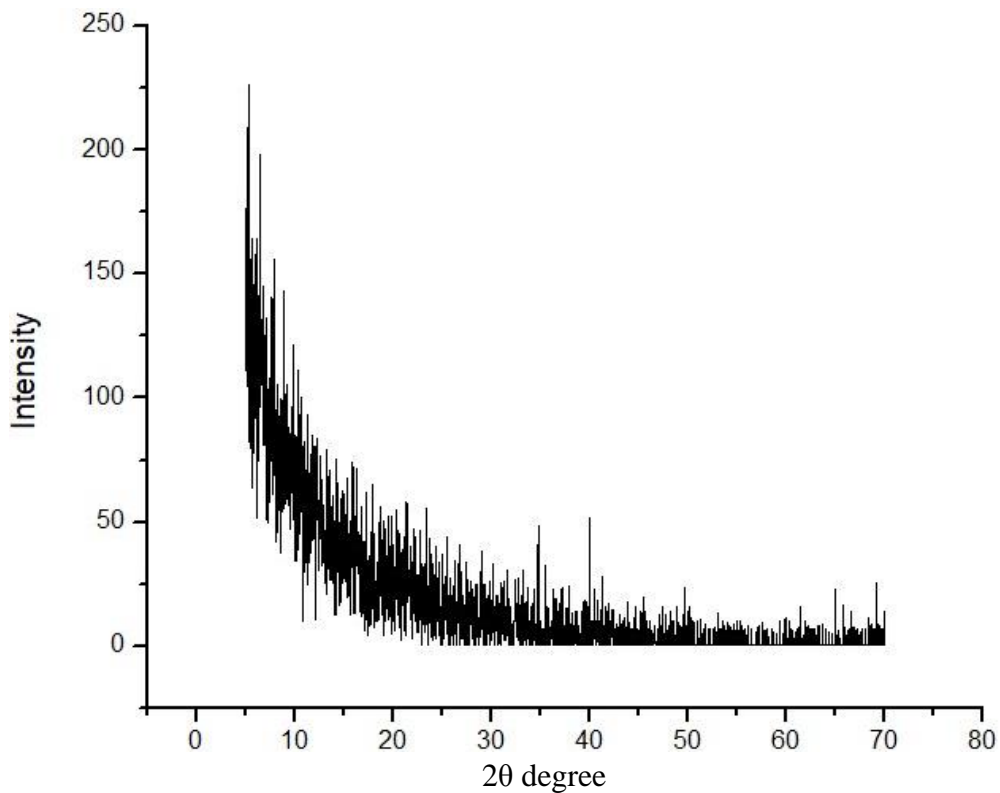


Figure 7: XRD spectra of DEG PU coatings formed with IPDI

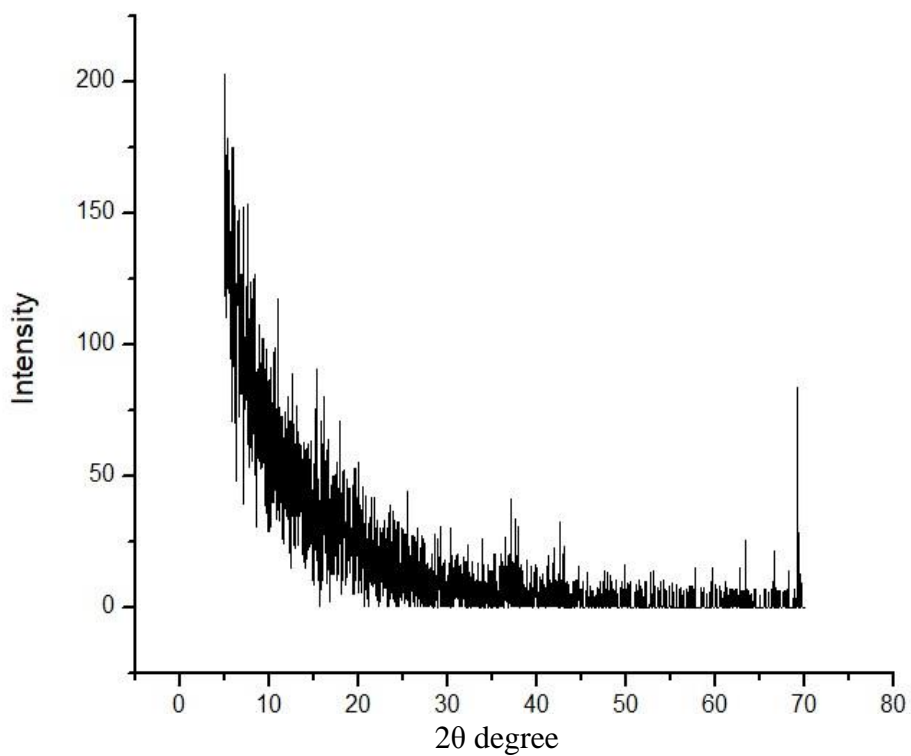


Figure 8: XRD spectra of PU coatings formed with HMDI

3.2 Performance Properties

All of the synthesized polyurethane coatings had their performance characteristics assessed using Indian Standard procedures, and the results of these evaluations were compared. The produced coated panels underwent testing for their chemical and solvent resistance, surface dry time, hard dry time, mixing time, tack-free time, and gel times.

3.2.1 Physico-Chemical Characteristics

For verification of the successful completion of the reaction, two different types of polyols modified with phenolic resin and phenolic resin combined with diethyleneglycol (DEG) in varying concentrations as shown in Table 1 for their composition were tested by measuring their acid and hydroxyl values. In order to ensure that there are no water molecules in the synthesised polyols, which may otherwise result in coating development, the moisture content was also evaluated. Following the steps outlined in Tables 1- 4 of the coatings formulation, polyol, a UV-resistant compound, and an aliphatic isocyanate were used to create the polyurethane coatings. It was discovered that the polyurethane coatings made with diethylene glycol and phenolic resin modified polyols had somewhat shorter drying and gel times than those made with phenolic resin modified polyols. Also, it was noted that the drying periods for the coatings with various phenolic resin concentrations did not significantly differ. In the case of diethyleneglycol (DEG) modified polyols, polyurethane coatings created with the highest concentration of DEG, or c set, dried a little quicker than A and B set.

Table1: Physico-chemical characteristics of two-component PU coatings prepared using IPDI-modified phenolic resin polyol

Coating system	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1 st set					
2% BHT	10 sec	4 hr 25 min.	15 hr 45 min.	21 hr 10 min.	25 hr 05 min.
8% BHT	10 sec	4 hr 15 min.	15 hr 55 min.	21 hr 05 min.	25 hr 30 min.
2 nd set					
2% BHT	10 sec	3 hr 30 min.	14 hr 40 min.	20 hr 45 min.	24 hr 15 min.
8% BHT	10 sec	3 hr 30 min.	16 hr 05 min.	21 hr	24 hr 40 min.
3 rd set					
2% BHT	10 sec	3 hr 50 min.	14 hr 55 min.	20 hr 35 min.	23 hr 50 min.
8% BHT	10 sec	3 hr 45 min.	14 hr 45 min.	20 hr 45 min.	24 hr 55 min.

Table 2: Physico-chemical characteristics of two-component PU coatings produced with IPDI and DEG modified polyol

Coating system	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1 st set					
2% BHT	10 sec	4 hr 10 min.	15 hr 30 min.	20 hr 45 min.	24 hr 50 min.
8% BHT	10 sec	4 hr	15 hr 50 min.	21 hr 10 min.	25 hr 10 min.
2 nd set					
2% BHT	10 sec	3 hr 50 min.	14 hr 55 min.	20 hr 30 min.	24 hr 10 min.
8% BHT	10 sec	3 hr 55 min.	15 hr	21 hr	24 hr 45 min.
3 rd set					
2% BHT	10 sec	3 hr 35 min.	14 hr 25 min.	20 hr 40 min.	25 hr
8% BHT	10 sec	3 hr 45 min.	14 hr 35 min.	20 hr 55 min.	24 hr 35 min.

Table 3: Physico-chemical characteristics of two-component PU coatings prepared using HMMDI-modified phenolic resin polyol

Coating system	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1 st set					
2% BHT	10 sec	3 hr 50 min.	15 hr 35 min.	21 hr 15 min.	25 hr 10 min.
8% BHT	10 sec	4 hr 15 min.	15 hr 50 min.	21 hr 10 min.	25 hr 25 min.
2 nd set					
2% BHT	10 sec	3 hr 35 min.	14 hr 20 min.	20 hr 25 min.	24 hr 35 min.
8% BHT	10 sec	3 hr 45 min.	16 hr 10 min.	21 hr 05 min.	24 hr 45 min.
3 rd set					
2% BHT	10 sec	3 hr 35 min.	14 hr 50 min.	20 hr 45 min.	23 hr 50 min.
8% BHT	10 sec	3 hr 45 min.	14 hr 55 min.	20 hr 45 min.	24 hr 55 min.

Table 4: Physico-chemical characteristics of two-component PU coatings produced with IPDI and DEG modified polyol

Coating system	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1 st set					
2% BHT	10 sec	4 hr 15 min.	15 hr 35 min.	20 hr 40 min.	24 hr 55 min.
8% BHT	10 sec	4 hr 10 min.	15 hr 45 min.	21 hr 15 min.	25 hr 15 min.
2 nd set					
2% BHT	10 sec	3 hr 45 min.	14 hr 35 min.	20 hr 35 min.	24 hr 15 min.
8% BHT	10 sec	3 hr 35 min.	15 hr	21 hr	24 hr 45 min.
3 rd set					
2% BHT	10 sec	3 hr 55 min.	14 hr 35 min.	20 hr 30 min.	23 hr 55 min.
8% BHT	10 sec	3 hr 45 min.	14 hr 45 min.	20 hr 45 min.	24 hr 55 min.

3.2.2 Chemical and Solvent Resistance

The different polyurethane coatings resistance to acids, water, and toluene was investigated using the immersion technique for a predetermined amount of time. For coatings A and B designed for acid resistance, the results are good. All of the coating sets responded well when tested with water and a solvent (toluene). Also, during the research, the coatings' gloss was maintained. In Table 5.5, the results for chemical and solvent resistance are shown.

Table 5: Chemical resistance of the developed two-component aliphatic polyurethane coatings manufactured using DEG modified polyols and IPDI

Coating system	% BHT	2% Acetic Acid	2% Sulphuric Acid	Toluene	Water
A	2%	a	a	b	a
	8%	a	b	a	a
B	2%	c	a	a	a
	8%	a	a	a	a
c	2%	a	a	c	a
	8%	a	b	c	a

a= no change; b= dullness in colour; c= loss in gloss

Table 6: Chemical resistance of the developed two-component aliphatic polyurethane coatings manufactured using DEG modified polyols and HMDI

Coating system	% BHT	2% Acetic Acid	2% Sulphuric Acid	Toluene	Water
A	2%	a	C	a	a
	8%	b	a	b	a
B	2%	c	a	a	a
	8%	a	b	b	a
c	2%	a	a	c	a
	8%	c	a	a	a

a= no change; b= dullness in colour; c= loss in gloss

4. CONCLUSION

Castor oil was modified in the current study to create two component polyurethane coatings using phenolic resin, DEG, and aliphatic diisocyanates. FTIR data showed that the modified polyols were effectively produced, and they were then reacted with aliphatic diisocyanates to create PU coatings. The structural changes that take place during the response of PU coatings are understood using IR spectroscopy. The PU coatings of aliphatic diisocyanates shows very high transmittance spectra hence they can easily used as transparent coatings. The UV absorbance spectra proves that coatings made with phenolic resin along with DEG modified polyols performed better in comparison to coatings made only with phenolic resin modified polyols, due to better cross linking among the polymer. Hence shows better performance against UV radiations. NMR study shows that increasing amount of modifiers favours the modified polyol formation.

Physico-chemical properties observed for PU coatings prepared with phenolic modified polyols and DEG modified polyols similar curing times of coatings with varying amount of modifiers. While on comparing the curing times of PU coatings made with IPDI and HMDI a significant difference has been observed. Chemical resistance was also checked for all the prepared PU coatings that are in good concurrence without harming the coatings.

5. REFERANCES

1. S. ATTAJARIYAKUL, S. VANICHSENI: Development of a kinetic model for resole type phenolic resin formation, *Thammasat Int. J. Sc. Tech*, (6) (2001) 3, pp. 13–18
2. A. M. MOTAWIE, E. M. SADEK: Adhesives and coatings based on poly(vinyl acetal)s, *Journal of Applied Polymer Science*, (70) (1998) pp. 1769– 1777
3. S. A. OSEMEAHON, J. T. BARMINAS: Development of amino resin for paint formulation: Copolymerization of methylol urea with polyester, *African Journal of Biotechnology*, (6) (2007) 12, pp. 1432–1440
4. A. SPYROS: Quantitative determination of distribution of free hydroxyl and carboxylic groups in unstaturated polyester and alkyd resins by ³¹P- NMR spectroscopy, *Journal of Applied Polymer Science*, (83) (2002) pp. 1635–1642
5. T. P. SHARMA, D. PATIDAR, N. S. SAXENA, K. SHARMA: Measurement of structural and optical band gaps of Cd_{1-x}Zn_xS(x = 4 and 6) nanomaterials, *Indian J Pure & Appl Physics*, (44) (2006) pp. 125–128
6. V. ALI, Z. HAQUE NEELKAMAL, M. ZULFEQ-UAR, M. HUSAIN: Preparation and characterization of polyether based polyurethane dolomite composite, *Journal of Applied Polymer Science*, (103) (2006) pp. 2337–2342
7. H. S. PARK, J. P. WU, H. K. KIM: Synthesis and physical properties of two component polyurethane coatings using bromine-containing aromatic modified polyesters, *Journal of Ind. & Eng. Chemistry*, (3) (1997) 4, pp. 282–287
8. J. V. PATEL, S. D. DESAI, V. K. SINHA: Bioacrylic polyols for two pack polyurethane coating, *Journal of Scientific & Industrial Research*, (63) (2004) pp. 259–264
9. M. A. ESPINOSA, M. GALIA, V. CA'DIZ: Novel phosphorilated flame-retardant thermosets: Epoxybenzoxazine-novolac systems, *Polymer*, (45) (2004) pp. 6103–6109
10. A. M. MOTWIE, M. M. BADR, M. S. AMER, H. Y. MOUSTAFA, I. M. ALI: Some coating studies on phenolic epoxy/poly(vinyl acetal) resins, *Journal of Applied Sciences Research*, (4) (2008) 9, pp. 1043– 1051
11. V. ISABELLE, L. TIGHZERT: Biodegradable Polymers, *Materials*, (2) (2009) 2, pp. 307–344
12. S. N. SURESH, Y. JIN, K. XIAOHUA: Production of polyols from canola oil and their chemical identification and physical properties, *J Amer Oil Chem Soc*, (84) (2007) pp. 173–179