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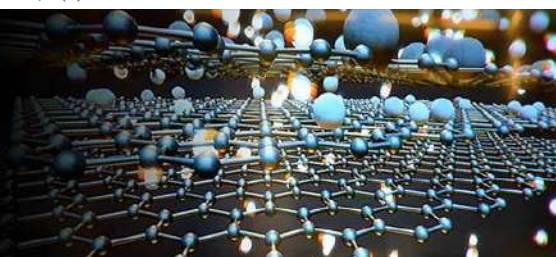
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Synthesis and characterisation of two component polyurethane coatings blended with phthalic anhydride formed with TDI

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Abstract
In the present study, castor oil has been modified with blending of phenolic resin and phthalic anhydride to synthesize polyol. Then these modified polyol are reacted with toluene diisocyanate (TDI) in presence of a suitable catalyst to synthesize the PU coatings. The copolymer structure was confirmed by Fourier transform infrared spectroscopy (FTIR); whereas thermal characteristics of the materials were characterized using dynamic mechanical analysis (DMA) and its ultraviolet resistivity is confirmed with the help of Ultra violet (UV-VIS) spectroscopy. XRD helps in determining the nature of PU. The gel time, hard time, mixing time and chemical or water resistance characteristics were also examined to confirm the performance properties.

Keywords: Castor oil, Phenolic resin, Phthalic anhydride, toluene diisocyanate

1. Introduction

In the field of polymers polyurethane are known as versatile materials as it is widely used in commercial industries as well as in day to day life such as footwear, medical instrumentation, coatings, paints, tubings, elastic fibres and many more [1-3]. The amount of PU research and development rising year after year demonstrates the industry's explosive expansion. Diisocyanate (NCO) isocyanated with polydiols (OH) of various molecular weights to generate the polymers, which are the major product of this process [4]. PUs serve humanity in a variety of capacities, such as flexible, stiff, semi-rigid, elastomers, surface coatings, and adhesives. Previously petroleum based polyols are formed but these hazardous for our environment. To make PU's environment friendly vegetable oil like castor oil, palm oil, sunflower oil, linseed oil, canola oil, corn oil, soyabean oil etc. are introduced [5-9] The synthesis of polmers from vegetable oils is currently due to worries about the economy and ecology, the production of polymers from vegetable oils is increasingly gaining more attention. Vegetable oil-based raw materials are good sources of PU, alkyd, polyester, amide, and epoxy resins, among other useful polymers. Triglycerides of fatty acids constitute vegetable oils [10-13]. These chemicals need to be functionalized to create polyols in order to be used as starting ingredients for the PU synthesis. Because to its low toxicity and accessibility as a sustainable agricultural resource, castor oil (*Ricinus communis*), from the Euphorbiaceae family, is a viable beginning raw material for PU [14].

Among the natural raw ingredients that may be utilised to make PU is castor oil. It is one of the most beneficial and significant non-edible natural vegetable oils in terms of economic importance [15]. Because it contains a significant amount of ricinoleic acid-containing triglycerides, it is also distinctive industrial oil. Around 87%–90% of a substance's composition is ricinoleic acid, which has double bonds at the 9th and 10th carbons and one hydroxyl group on the 12th carbon. It possesses appropriate hydroxyl functionality for the isocyanate reaction to produce polyurethane elastomers. Castor oil is beneficial for various polyurethane industries due to its distinct features [16].

In the present analysis, efforts have been made to construct PU coatings using phthalic anhydride blended polyol with toluene diisocyanate in presence of catalyst. Synthesized coatings are characterized using various techniques like FTIR, UV-VIS, XRD and DMA. Performance properties of prepared coatings are also measured.

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2. Experimental
2.1 Raw Materials
Castor oil (Krishna Chemicals pvt. Limited, Delhi), Phenolic Resin (Haryana Scientific pvt. Limited, Haryana), Phthalic anhydride (S.D Fine chem. Mumbai), Acetone (Sisco Reasearch laboratory, AR grade), Glycerol, 2, 4' Toulene diisocyanate (TDI), 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 phthalic anhydride and phenolic resin under same condition. The reaction was carried out at 160°C temperature for around 6 – 7 hours.

2. Synthesis of PU coatings
All the prepared polyols are then reacted with TDI 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, UV-VIS, XRD and TGA. Chemical and water resistance of glass coated panels were also investigated. Performance properties like gel time, mixing time, surface dry time, and surface hard time were also checked.

3.1 Spectroscopic Characterization
FTIR Spectra
Fourier Transform Infrared (FTIR) Spectroscopy was used to identify the presence of a urethane link between TDI and castor. Figure depicts the blended PU coatings' IR spectrum. The peaks at the 1534 Cm^{-1} is inductive of urethane linkage (C-N-H) development. The spectra show a broad peak at 3400 and 3418 Cm^{-1} indicating the hydroxyl group of polyols. Peak at 2922, 2926 and 2918 Cm^{-1} attributes C-H stretching of CH_2 group present in the entire compound. The stretching peak at 1731 Cm^{-1} indicating the existence of ester linkage [17]. O-H stretching vibrations from water- or hydroxyl-terminated compounds and N-H stretching vibrations from either urea or the amine group have been observed in the sample as a modest wide band in the range of 4000-3500 Cm^{-1}. The peak at 2261 and 2380 Cm^{-1} attributes the unreacted isocyanate group O=C=N [18]. While the peak at 732 to 751 Cm^{-1} is due to aromatic ring. The peak at 1040 Cm^{-1} shows the existence of C-O bonds. Peak at 1464 Cm^{-1} indicate the existance of C-H bending.
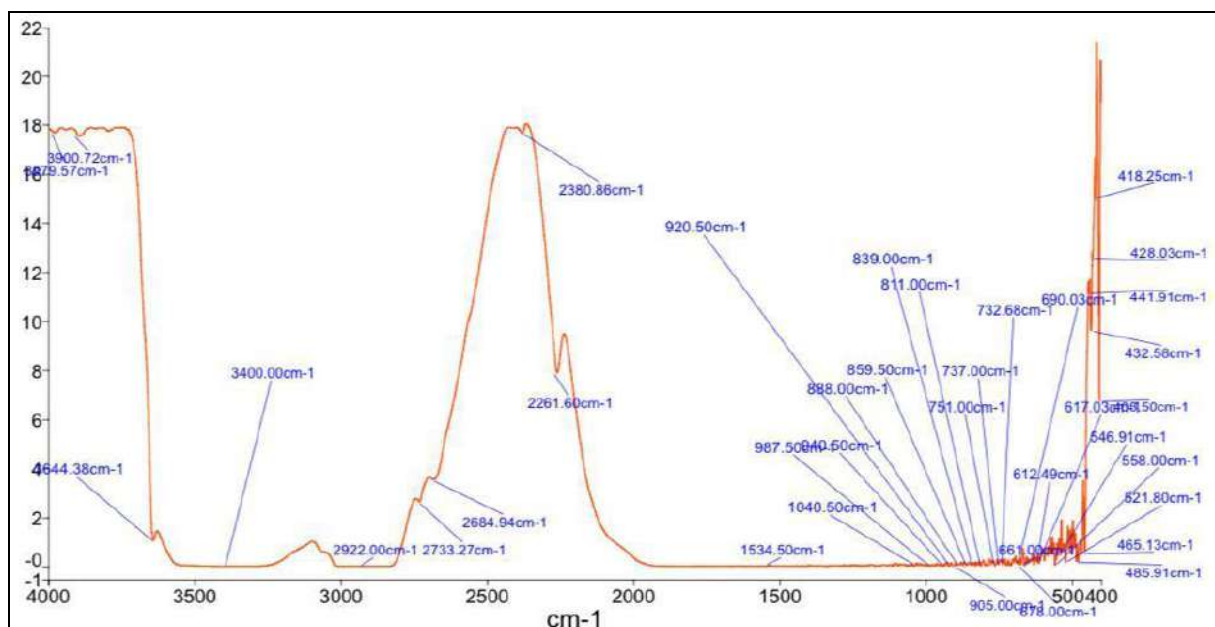

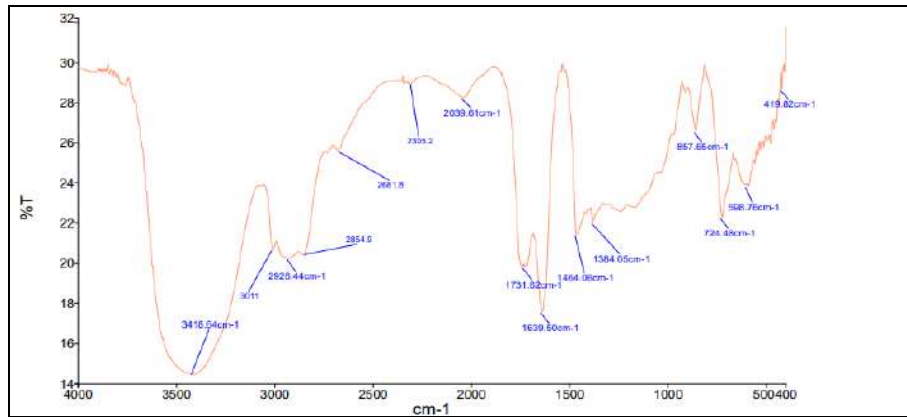**Fig 1:** FTIR spectra of PU coatings made with phenolic resin formed from TDI

Fig 2: FTIR spectra of PU coatings made with phthalic anhydride formed from TDI

UV-VIS spectra

The UV-VIS absorption spectra in figure show that the polyurethane coating formed from TDI has a conjugated structure due to the presence of aromatic rings. where a 395 nm absorption peak is seen on the TDI-PU spectrum is due to the conjugative effect between carbamate and benzene ring, which can lower the energy level of $\pi*$ excited state [19]. The UV-Visible absorption for lone benzene ring resulting from π-$\pi*$ electronic transition is around 390 nm, so as a red-shift of about 4 nm here was observed for TDI-PU.
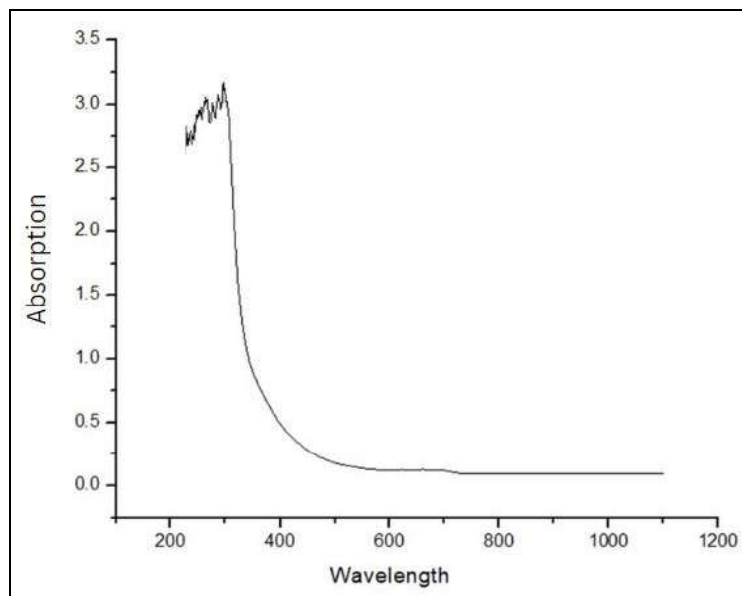

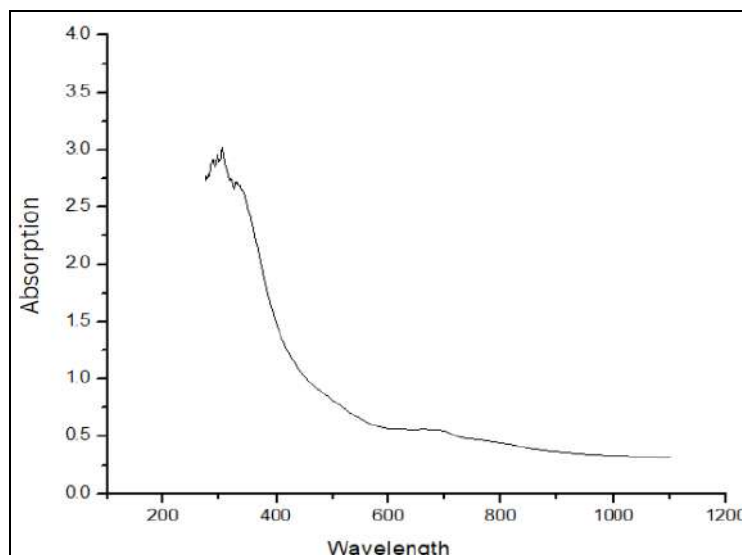**Fig 3:** UV spectra of blended phenolic resin PU coatings made from TDI

Fig 4: UV spectra of phthalic anhydride PU coatings made from TDI

Xrd Study

The XRD patterns of blended coatings are presented in figure 16. These concentration DEG and phenolic resin vary in sample as 80+12, 80+7, and 80+5. XRD studies tell about the structural characteristics of material. One broad peak is observed from the data. This broad curve tells about the amorphous nature of materials. The value $2\theta = 19.8$ and 21.4 due to the difference in chemical structure of soft segment and these condition occur due to addition of diisocyanates in the castor oil [20].
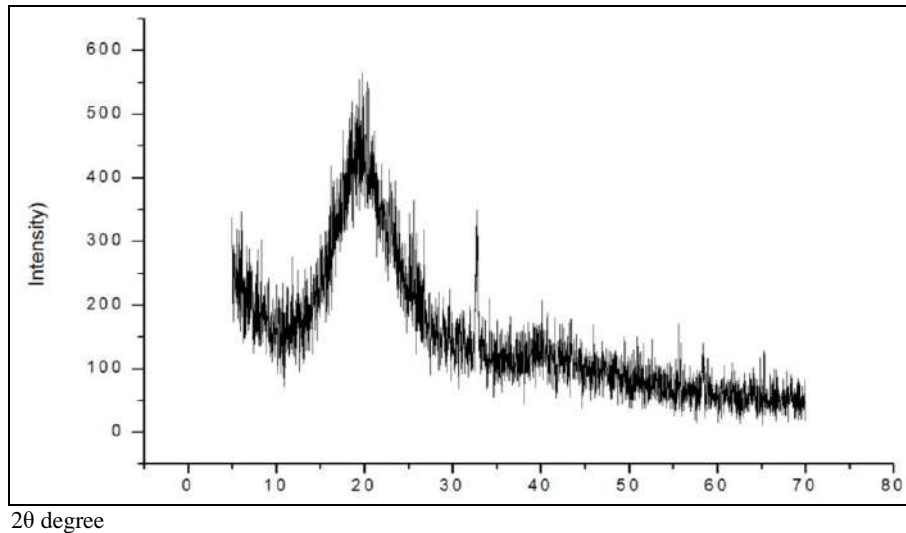

2θ degree

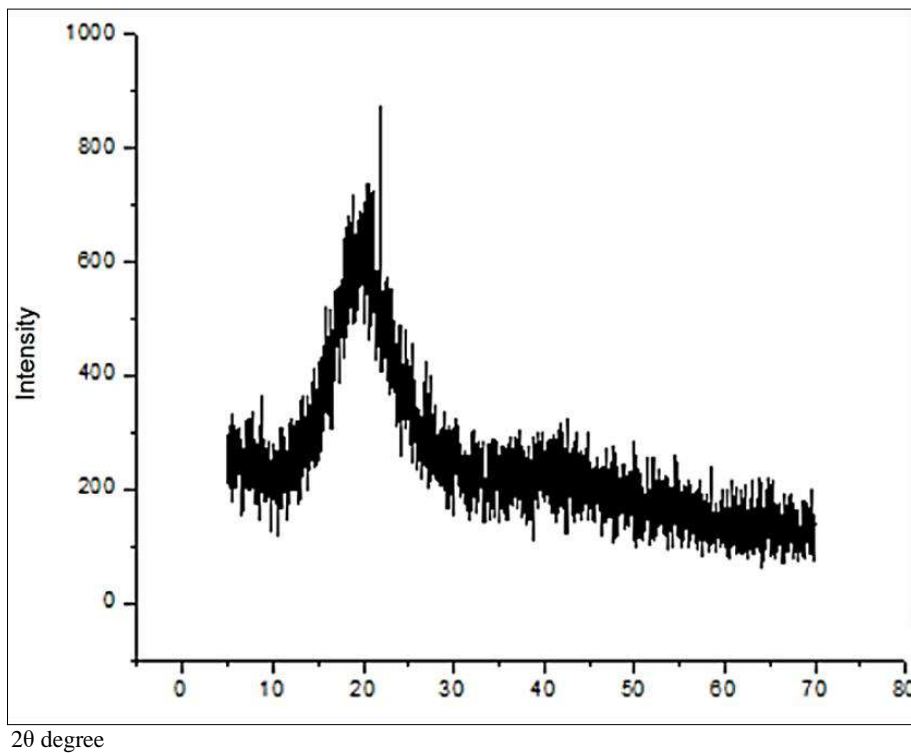**Fig 5:** XRD spectra of Phenolic resin PU coatings formed with TDI

2θ degree

Fig 6: XRD spectra of Phthalic anhydride PU coatings formed with TDI

Dynamic mechanical analysis

DMA is a useful method for analysis of elastic and loss modulus of polymers as a function of temperature, frequency or time or both. The DMA was characterized by storage modulus (E`), loss modulus (E``) and loss factor (tan δ), which can be elaborated by the ratio of loss modulus. All these parameters are function of temperature and frequencies. Normally magnitude of tan δ can be used to predict the damping behaviour of polymeric material. This property is essential for the material selection. Generally materials which are having a high and wide loss factor peak can be used as good damping materials.

Comparing samples where ratio of DEG is different but amount of phenolic resin is same exhibit more right tan δ as compare to the sample having different ratio of phenolic resin taken. Hence coatings modified from DEG blended with phenolic resin show better performance than coatings only modified from phenolic resin due to better crosslinking [21].
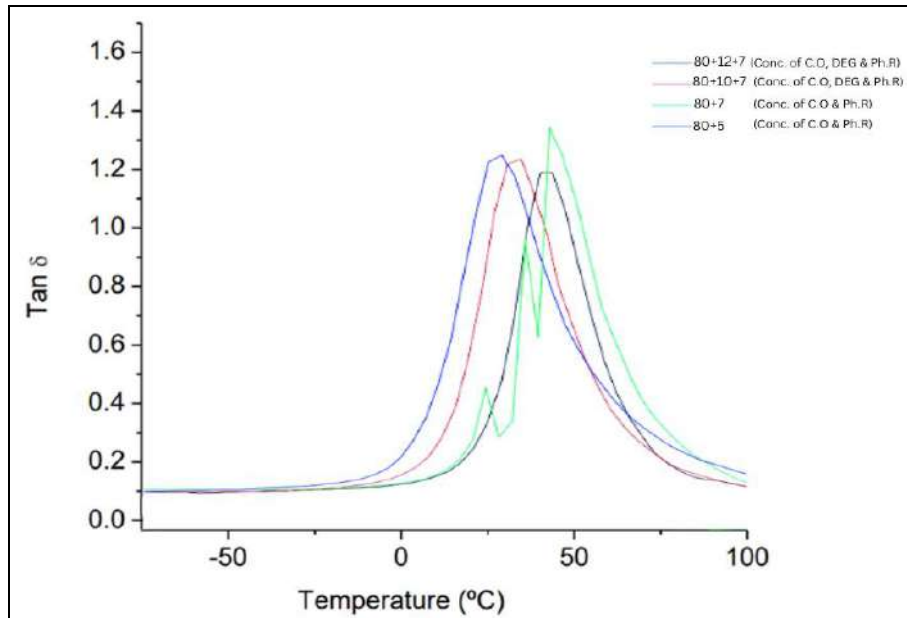
Fig 7: DMA Spectra of PU Coatings

3.2 Performance Properties

According to Indian Standard procedures, the performance characteristics of each created polyurethane coating were assessed, and their performances were compared. The gel times, hard dry times, mixing times, surface dry times, tack free periods, and chemical and solvent resistance of the produced coated panels were evaluated.

Physico-Chemical Properties

For verification of the successful completion of the reaction, two different types of polyols modified with phenolic resin and phenolic resin combined with phthalic anhydride in varying concentrations as shown in Tables 5.11 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 formulation for coatings, polyol, a UV-resistant compound, and diisocyanate were used to make the polyurethane coatings. It was discovered that the polyurethane coatings created with phthalic anhydride + phenolic resin modified polyols had a little shorter drying time and gel time than those prepared with phenolic resin modified polyols. Also, it was noted that the drying durations for the coatings with various phenolic resin concentrations did not significantly differ from one another. In case of phthalic anhydride modified polyols, polyurethane coatings made with maximum amount i.e., B_3 of took slightly lesser time to dry in comparison to B_1 and then B_2 set of panels.

Chemical and Solvent Resistance

The different polyurethane coatings' acid, water, and toluene resistance was examined using the immersion technique for a predetermined amount of time. All of the coating sets responded well when tested with toulene and water. The coatings' gloss remained constant throughout the investigation. Table 5.12 displays the results for chemical and solvent resistance.

Table 1: Physico-chemical characteristics of two-component PU coatings produced with TDI and P. An modified polyol

Coating system	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1. C.O+Ph.resin					
A1	10 sec	3 hr 40 min.	3 hr 35 min.	21 hr 25 min.	25 hr 15 min.
A2	10 sec	4 hr 25 min.	15 hr 35 min.	21 hr 15 min.	25 hr 55 min.
A3	10 sec	3 hr 45 min	16 hr 15 min.	21 hr 25 min.	24 hr 15 min.
2. C.O+Ph.resin+P.An					
B_1	10 sec	3 hr 30 min.	3 hr 25 min.	21 hr 15 min.	24 hr 55 min.
B2	10 sec	4 hr 15 min.	15 hr 15 min.	21 hr 05 min.	25 hr 25 min.
B3	10 sec	3 hr 25 min.	16 hr 25 min.	21 hr 15 min.	23 hr 55 min.

Table 2: Chemical resistance of the two-component aliphatic polyurethane coatings created by P.A.N. modified polyols with TDI

Coating system	2% Acetic Acid	2% Sulphuric Acid	Toluene	Water
1. C.O+Ph.resin				
A_1	a	a	a	a
A2	b	a	b	a
A3	a	a	a	a
2. C.O+Ph.resin+P.An				
B_1	a	b	a	a
B2	a	c	a	a
B3	a	a	b	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 along with phthalic anhydride. The FTIR spectra provide useful information to establish the existence of certain functional groups needed for interacting with diisocyanates. The UV-VIS absorption spectra show that the polyurethane coating formed from TDI has a conjugated structure due to the presence of aromatic rings. where a 395 nm absorption peak is seen on the TDI-PU spectrum is due to the conjugative effect between carbamate and benzene ring, which can lower the energy level of π * excited state. XRD studies tell about the structural characteristics of material. One broad peak is observed from the data. This broad curve tells about the amorphous nature of materials. DMA study explains that on comparing samples where ratio of DEG is different but amount of phenolic resin is same exhibit more right tan δ as compare to the sample having different ratio of phenolic resin taken, hence coatings modified from DEG blended resin show better performance than coatings only modified from phenolic resin due to better crosslinking.

Physico-chemical properties observed for PU coatings prepared with phenolic modified polyols and Phthalic anhydride modified polyols similar curing times of coatings with varying amount of modifiers. Chemical resistance was also checked for all the prepared PU coatings that are in good concurrence without harming the coatings.

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