



Synthesis of two component polyurethane coatings blended with Phenolic resin

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Abstract: In this work, modified UV curable polyurethane was developed from isophorone diisocyanate (IPDI) and 4, 4-methylene diisocyanate (MDI). The rigid moiety was incorporated into the polyurethane's main chain to enhance its heat resistance. The structure of the copolymer was verified by Fourier transform infrared spectroscopy (FT-IR). The prepared coating is utilized to examine features like gel time, surface dry, tack-free, and hard surface drying times. The physicochemical characteristics of castor oil-based modified polyols produced using phenolic resin and diethyleneglycol were discovered to have undergone considerable alterations. Variation in the physico-chemical parameters of synthesised polyol gives information for achieving appropriate polyurethane curing.

Keywords: phenolic resin, diethyleneglycol, castor oil, isophorone diisocyanate and 4, -methylene diisocyanate.

1. Introduction:

Because of a variety of environmental and global issues in the 21st century, polymer investigations are putting a significant amount of awareness and increased focus on research that is based on materials derived from renewable resources and discovering implementations for those components along with their performance. Polyurethane production now requires approximately 90 percent of the polyol derived from petroleum. This polyol is based on polyether [1]. The class of renewable substances known as vegetable oils is often regarded as the most significant globally. Castor, palm, linseed, soy bean, coconut, sunflower, and canola oils are examples of the types of oils that may be extracted from different oilseeds and processed into vegetable oils [2-5]. Vegetable oils are one of the most plentiful, cheapest, and most readily renewable natural resources [6]. Polyurethane is a substance that has been discovered to have a wide range of uses, including coating, paint, foam, thermosetting, thermoplastic elastomers and fibres. It almost appears like this material has some kind of magical properties. In reality, the term "polyurethane" refers to the end product of the reaction that takes place when a polyol and either a diisocyanate or a polyisocyanate are joined [7]. A polyurethane film includes groups such as ester, ether, amide, and urea. As a result of the structural likeability of polyurethane coatings, the industry that makes coatings has given them an

ever-increasing amount of significance [8]. Excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance, and a broad range of mechanical strength are just some of the reasons polyurethane (PU) have gained significant uses in the coating industries [9-11]. These qualities have led to PU coatings emergence as the coatings of preference for a wide variety of uses, including chemical or UV resistance, vehicle finishing and commercial maintenance [12]. Coatings applied to surfaces have two purposes: decoration and protection. In order for coatings to continue performing their tasks for as long as feasible, it is important to find strategies to reduce the damaging effects such as cracking and fading that they endure. Moreover, UV resistant coatings give excellent scratch and chemical resistance, and implementation of these coatings is becoming common in technologies where exterior applicability is necessary [13].

The main objective of this study is to synthesize two component polyurethanes coatings using castor oil and isophorone diisocyanate (IPDI) and 4, 4-methylene diisocyanate (MDI).

2. Experiment

2.1. Raw Materials

Castor oil (Shivathene Linopack Ltd. Parwanoo, Himachal Pradesh), Phenolic resin (Haryana scientific private Ltd., Haryana), Diethyleneglycol (Krishna chemicals private Ltd., Delhi), Isophorone diisocyanate (IPDI) and 4, 4-methylene diisocyanate (Garg chemicals, private Ltd., Delhi), Acetone (Sisco Research Laboratory, AR grade), Hydrochloric acid (Krishna chemicals private Ltd, Delhi), Sulphuric acid (Ashoka scientific Ltd. Haryana), Nitric acid (Himedia Laboratories Pvt. Ltd., Mumbai), Acetic acid (Garg chemicals private Ltd., Delhi).

2.2 Preparation of two component polyurethane coating

The following two procedures were used to synthesise modified polyols and isocyanates, which make up two component polyurethane coatings.

Step 1: Synthesis of modified polyols:

In order to provide modified polyols, a chemical reaction was carried out in a flask with three necks, one of which had a thermometer, one of which had a nitrogen intake, and one of which had a reflux condenser.

There were three separate sets of polyols produced, each with a distinct blending of polyols. In the first series of polyol castor oil is heated at a certain temperature in three round bottom flasks before phenolic resin and various concentrations of diethylene glycol are gently added. The concentration of diethanolamine is altered with each set in the second series of polyol castor oil and phenolic resin.

The reactions took place at a temperature of 120–160 °C for about 6-7 hours after which the sample was dried and put into an airtight glass jar for analysis of various physical and chemical properties .

Step 2: Preparation of polyurethane coatings:

After that, each of the chemically modified polyols that had been created underwent a reaction with isophorone diisocyanate (IPDI) and 4, 4-methylene diisocyanate at room temperature 25 °C and 70% relative humidity. The reaction mixture of polyol and isocyanate was then fully mixed and coated on the glass panels for the observations of their curing periods such as mixing time, gel time, tack free time, surface dry time and hard dry time. After that, these coated panels were placed in an oven preheated to 60 °C for around 5-6 hours to complete the post-curing process. After that, the chemical and water resistance of these covering panels was investigated at this time. For these studies, 5% solutions of ethanol, acetic acid, nitric acid and hydrochloric acid were made. Then after, the coated panels were immersed into solutions of acids, ethanol, and water at 72 hours for the purpose of studying the impacts of these solutions, including their consequences on the panels' physical appearance, gloss and peel off.

3. Results and Discussion

Curing properties such as mixing time, surface dry time, gel time, tack free time and hard dry time of two component polyurethane coating have been studied(Table 2). Chemical resistance of the glass coated panels was also checked. Spectroscopic characterizations like FTIR and UV-VIS spectroscopy have been also performed for the prepared modified polyols.

3.1. Spectroscopic characterization

FTIR STUDY

FTIR spectra of the synthesized castor oil based modified polyols were achieved through Perkin Elmer Spectrophotometer. The spectra show informative results in order to confirm the presence of certain functional groups required for the reacting with diisocyanates. A broad peak at 3387 and 3458 Cm^{-1} confirms the formation of polyol in all the IR spectra as this is the key band of free hydroxyl group. The peaks at 2933, 2925 and 2862 Cm^{-1} shows the presence of C-H stretching of CH_2 group present in the compound [14]. Peak at 1739 Cm^{-1} confirms the presence of ester formation. A peak of aromatic ring has been obtained at 726 Cm^{-1} . The FTIR spectra obtained for phenolic resin modified polyol (I₁-I₁) and DEG modified polyol (M₁-M₁) are shown in figure 1.1 and 1.2 . The remaining polyol with varying concentrations of phenolic resin i.e., I₂-I₂, I₃-I₃, I₄- I₄ and modified polyol of DEG with varying concentration i.e., M₂-M₂, M₃-M₃, M₄-M₄ show peaks position almost at same stretching of M₂- M₂ in the figures.

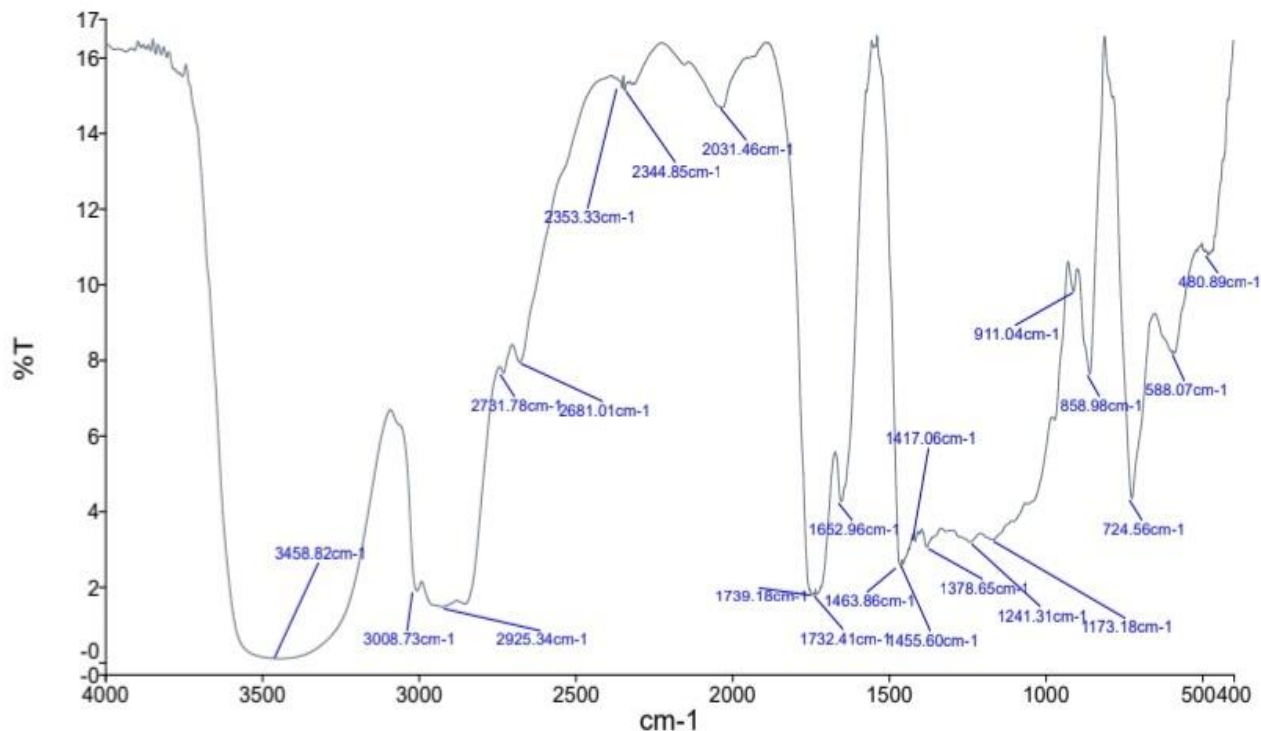


Figure1: FTIR spectra of polyol I₂-I₂

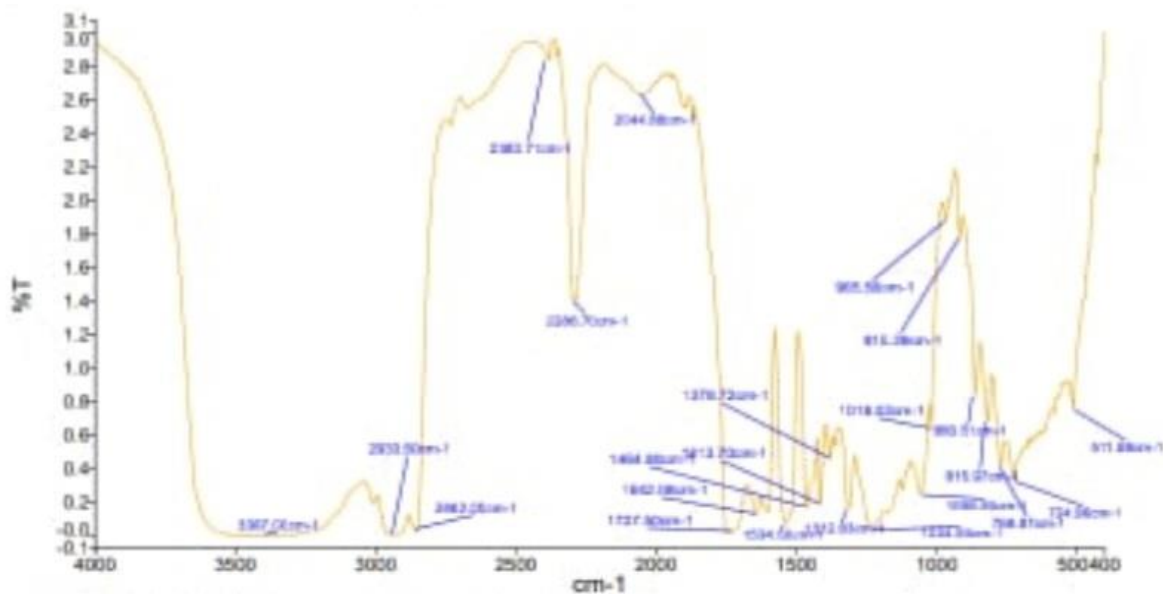


Figure 2: FTIR spectra of polyol M₂-M₂

NMR spectra:

¹H-NMR spectroscopic investigation of the prepared chemically modified polyols has been done using Bruker Spectrospin DPX-300. Peak obtained at 3.6 ppm is for CH₂OH. Peak obtained at 5.2 ppm indicates presence of C=CH group [15]. Peak obtained at 4.2 ppm indicate presence of acetate protons. It has been observed that as the amount of

phenolic resin increases peak of aromatic protons also increases, which shows that maximum amount of phenolic resin and diethylene glycol reacted with castor oil that favours modified polyol formation.

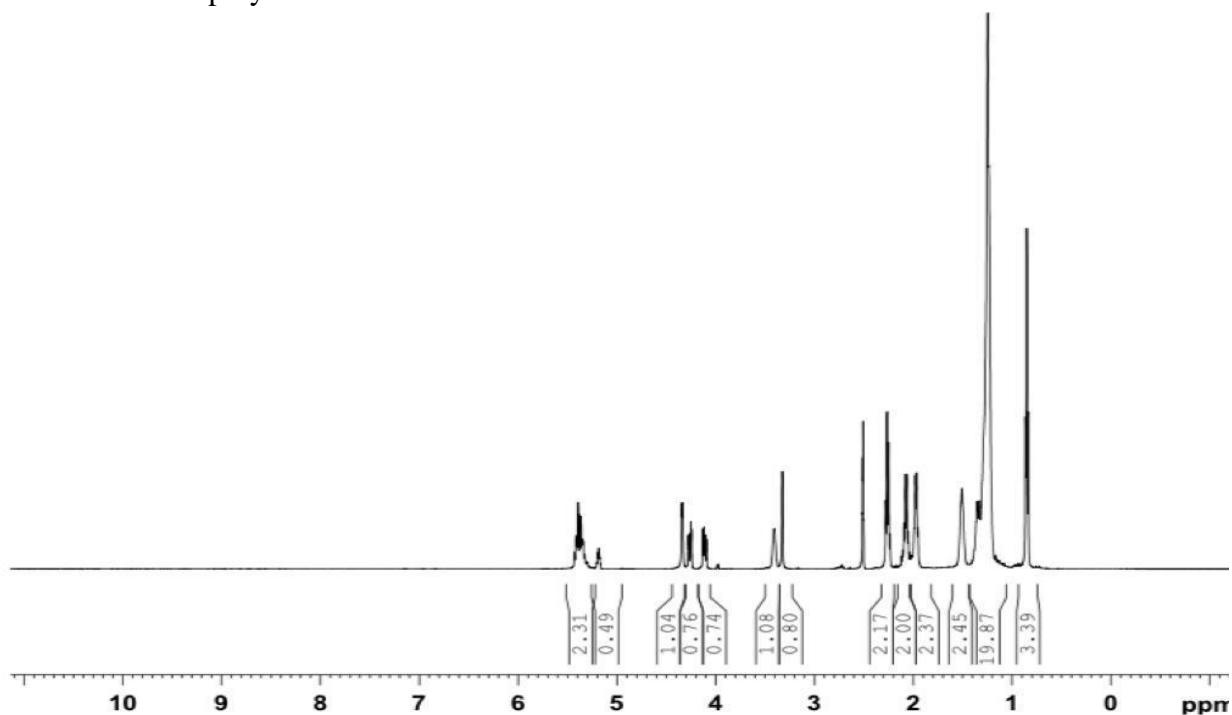


Figure 3: NMR spectra of polyol I₂-I₂

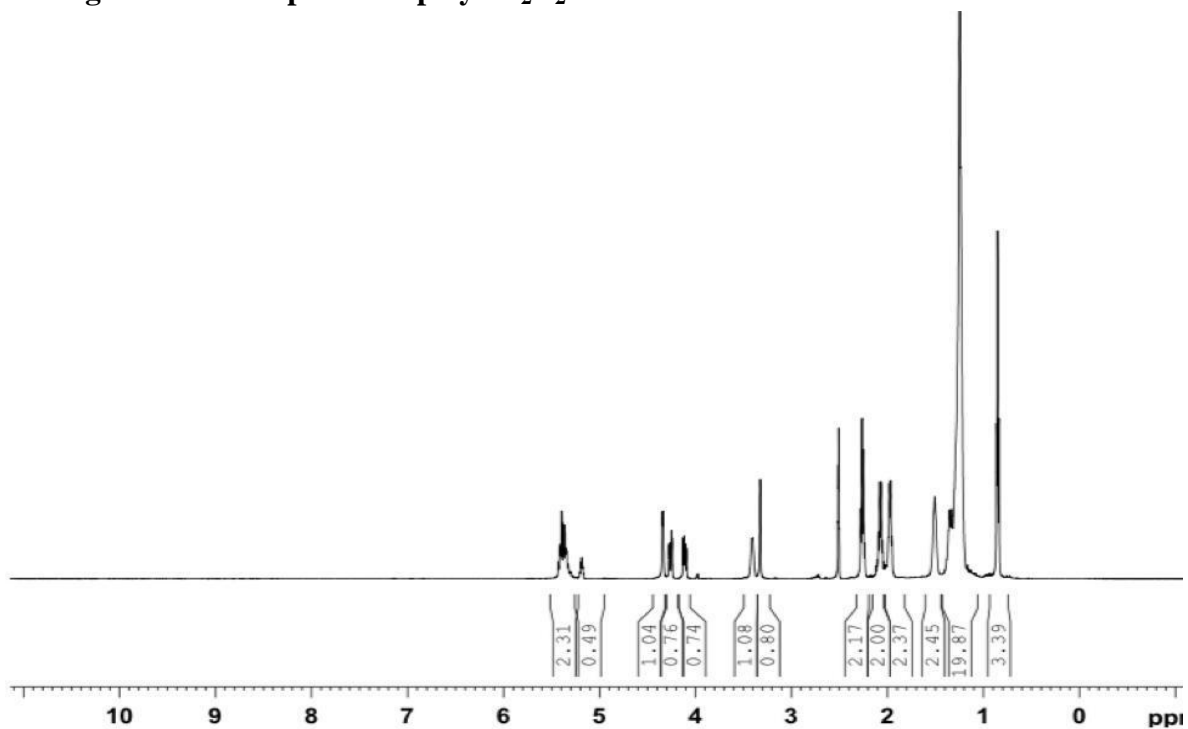


Figure 4: NMR spectra of polyol M₂-M₂

UV-VIS Spectra:

Aliphatic polyurethane coatings were evaluated for their UV resistance exposure to ultraviolet (UV) radiations for a specific length of time using UV-VIS spectroscopy. Optical absorption spectra for all the coatings at room temperature in the wavelength range of 200- 1100 nm with Shimadzu Double Beam UV-VIS Spectrophotometer. It was observed that there was almost a negligible shift in the absorption maximum i.e., λ_{max} for coatings prepared with BHT. Before the exposure of UV rays the coatings were colourless but after exposure these were converted into slightly yellowish. So we can say that an optimum amount of UV resistant compound favours the resistancy in particular coating panel above which it reduces the resistance against UV radiations of coatings. Hence, we conclude that coatings made with phenolic resins along with DEG better performed in comparison to coatings made only with phenolic resin modified polyols because of better cross linking among the polymer.

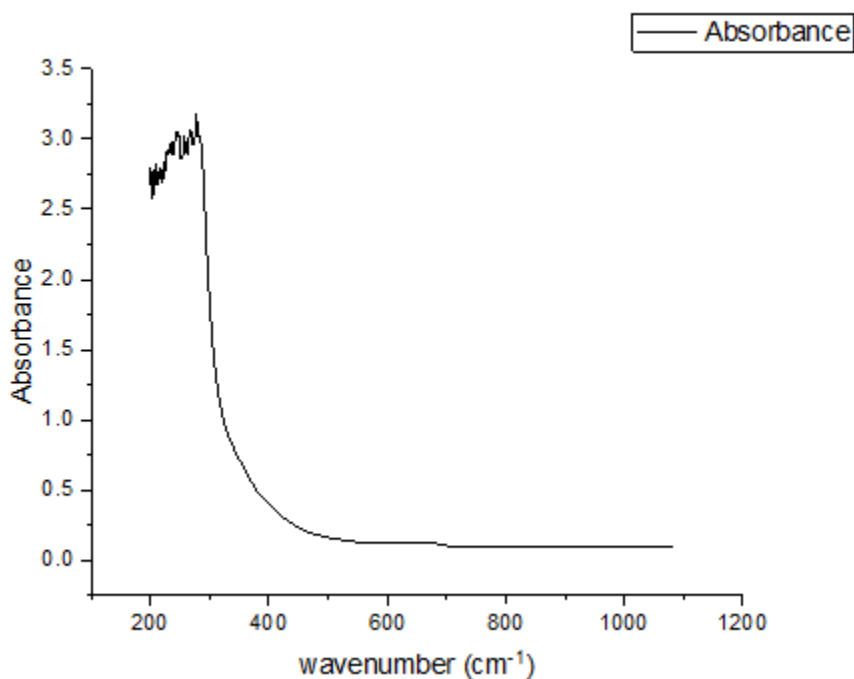


Figure 5: UV-VIS spectra of polyol I₂-I₂

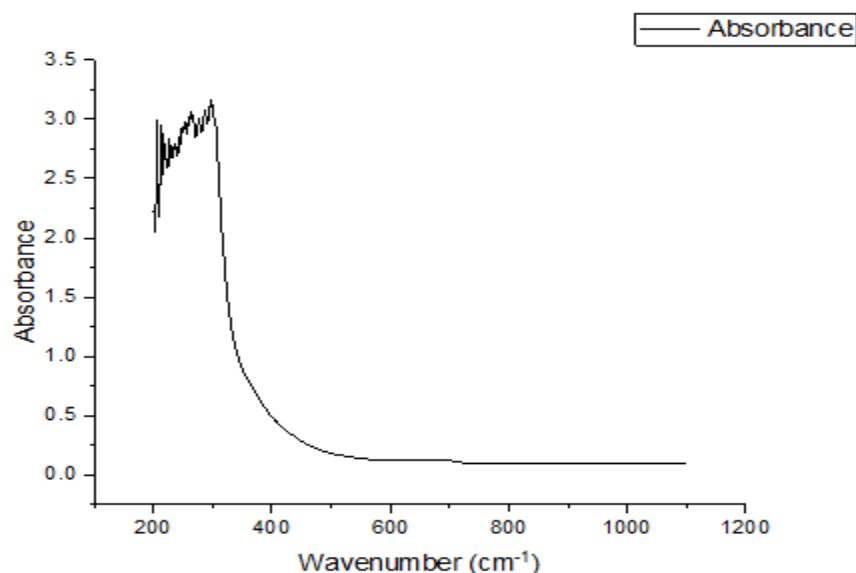


Figure 6: UV-VIS spectra of polyol M₂-M₂

3.2 Physical Characterization of coating panels

3.2.1 Physico- chemical properties

Two different types of modified polyols with various ratios of the modifiers were reacted with TDI and IPDI to create two component polyurethanes that were coated on glass panels. It was discovered that one set of polyol with different concentrations had a very little variation in the curing timeframes. If coating samples were generated either with MDI and IPDI, similar types of differences in curing periods have been seen within the second group of polyols. Additionally, phenolic modified polyols have showed some modest variance when compared to DEG modified polyols.

The physico- chemical properties for MDI and IPDI based coating sample in table 1 and table 2.

Table 1: Physico-chemical properties of two component PU coatings with 4, 4-methylene diisocyanate(MDI)

Polyols	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1. C.O+Ph.resin					
A ₁	10 sec.	4 hr 40 min.	17 hr 10 min.	21 hr 30 min.	23 hr 45 min.
A ₂	10 sec.	3 hr 55 min.	15 hr 55 min.	20 hr 35 min.	23hr 57 min.
A ₃	10 sec.	4 hr 05 min.	16 hr 50 min.	22 hr 10 min.	25 hr 55 min.
2. C.O+Ph.resin+DEG					
B ₁	10 sec	3 hr 45 min.	17 hr 30 min.	19 hr 45 min.	24 hr.
B ₂	10 sec	3 hr 25 min.	16 hr 40 min.	21 hr 45 min.	25 hr 55 min.
B ₃	10 sec	3 hr 40 min.	16 hr 55 min.	20 hr 20 min.	24 hr 35 min.

Table 2: Physico-chemical properties of two component PU coatings with Isophorone diisocyanate (IPDI)

Polyols	Mixing time	Gel time	Surface dry time	Tack free time	Hard dry time
1. C.O+Ph.resin					
A ₁	10 sec.	3 hr 50 min	16 hr 13 min.	20 hr 50 min.	22 hr 30 min.
A ₂	20 sec.	3 hr 55 min.	15 hr 17 min.	21 hr 55 min.	23 hr 25 min.
A ₃	10 sec.	3 hr 50 min.	16 hr 15 min.	20 hr 55 min.	22 hr 35 min.
2. C.O+Ph.resin+DEG					
B ₁	10 sec	4 hr 45 min.	17 hr 15 min.	22 hr.	23 hr 35 min.
B ₂	10 sec	3 hr 35 min.	16 hr 10 min.	21 hr 50 min.	22 hr 30 min.
B ₃	10 sec	3 hr 45 min.	16 hr 10 min.	21 hr 55 min.	24 hr 37 min.

3.2.2 Chemical and Solvent Resistance

Chemical agents such as sulphuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), and acetic acid were used to alter the physical features of the manufactured coated panels, such as colour change, gloss, and peeling (CH₃COOH). After 72 hours, the coated panels that had been immersed in the solutions were examined. Following 72 hours of observation, every coating sample demonstrated excellent chemical resistance. No coating panel sample showed any colour fading. Additionally, despite the lengthy presence of chemicals, the coating's shine was still visible on the panels. Thus, it was noted that all of the coated panels shown high resistance to chemicals, water, and solvents.

4. Conclusion

In the current investigation, phenolic resin and DEG were used to modify castor oil-based polyol to create two-component polyurethane coatings. FTIR analysis of the modified polyol reveals the presence of all the appropriate functional groups needed for the reaction with isocyanate to create polyurethane. According to an NMR research, the synthesis of modified polyols is favoured as the quantity of modifier increases. Due to better crosslinking, a UV-VIS investigation demonstrates that DEG modified PU coatings function better than simply phenolic resin modified polyols. Physical and chemical characteristics such as gloss time, hard time, and gel time exhibit a similar pattern with different concentrations. All the coated panels' chemical resistance has also been examined and each panel exhibits excellent chemical resistance.

5. Referances

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