

Study of polyurethane surface coatings based on (rosinified phenolic resin-castor oil) blends with diisocyanates

Bhaumik M. Patel and Hasmukh S. Patel*

Department of Chemistry, Vallabh Vidhayanagar, Sardar Patel University, Vallabh Vidhayanagar, Gujarat, India

ABSTRACT

Surface coating formulations were prepared by blending of rosinified phenolic resin with castor oil of different % weight ratio was carried out. Such obtained polyols were treated stoichiometrically hexamethylene diisocyanate (HMDI) and diphenylmethane diisocyanate (MDI) to afford polyurethane syrups. FT-IR analyses were monitoring for these polyurethane. These produce polyurethane syrups (i.e. resins) resins were casted into film. The result of polyurethane film were characterized for surface drying time, tack-free time, mechanical properties like scratch, impact, pencil hardness, adhesion and flexibility. The chemical properties like acid, alkalies and solvent resistance of these coats have also been checked.

Keywords: Castor oil, Rosinified phenolic resin, Polyurethane, Polyol, Hexamethylene Diisocyanate (HMDI), Diphenylmethane diisocyanate (MDI), Coating, Blend

INTRODUCTION

As the first commercial synthetic resin, phenolic resin have been widely used as adhesives composites, moldings, coatings, industrial laminates, abrasive materials, foundry resin, friction materials and matrix materials due to their excellent flame resistance, dimensional stability and chemical resistance. [1] Phenolics are continue to have an important role in the coating industry because of their versatility, coatings properties, and reasonable price. However, Phenolic resin is brittle and not very tough, like many other thermosetting resins. Thus, modification of phenolic is an important subject for its further application more pertinent to paints. Some research publications show that phenolic resins have been used to in order to get the modified polyol for polyurethane formation [2-5]. However, the reports indicate that phenolics based polyurethane used as a composite, adhesive, foam, etc. [6-21]

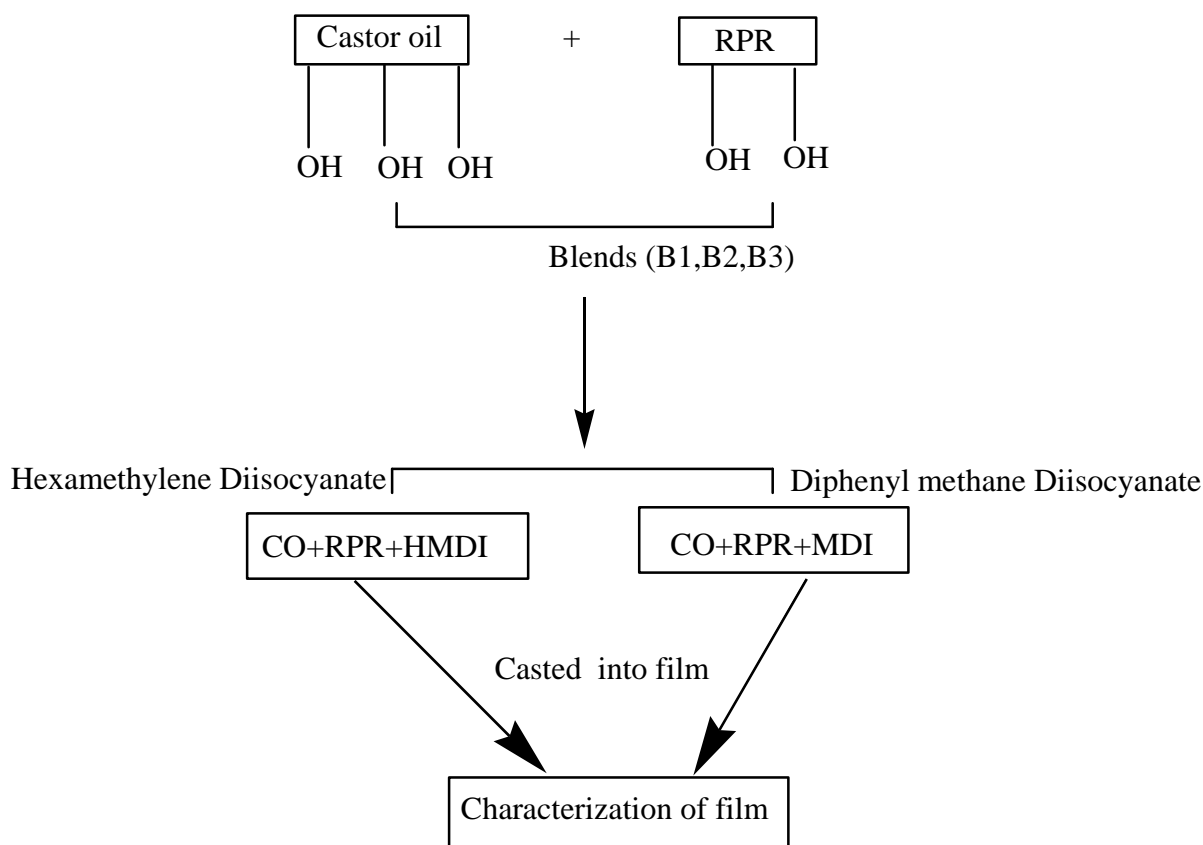
One of the most natural rosinified phenolic resins are used in printing inks, in oil lacquers and as additives to alkyd paints because good compatibility with natural oils in which they improve the drying and shine. It can be polymerized by cooking with vegetable oils to make Phenolic paints with fast drying, good hardness and high gloss. [22]

Castor oil (CO) sometimes described as a triglycerides of ricinoleic acid, is one of the naturally occurring glyceride that approaches being a pure compound. Castor oil (CO) serves as raw material for the manufacturing of number industrial utility products [23-25]. Castor oil known preliminary for its medicinal use as a cathartics, is now also used primarily as an industrial raw material for the manufacturing of industrial products used in coatings, urethane derivatives, surfactants, dispersant, cosmetics, textile and lubricants. [26, 27]

Term polyurethane (PU) originally referred to coating system that utilized high reactivity of isocyanates for chemical hardening. Polyurethane (PU) chemistry is based on reaction of a diisocyanate with compounds containing

an active hydrogen atom to produce urethane linkages. There are many compounds that contain active hydrogen like water, alcohol, amines, hydroxyl group, acids etc. Such kind of reaction occurs at room temperature or at slightly elevated temperature. Due to such high reactivity of isocyanates with variety of compounds, it is possible to formulate urethane coating systems with different compositions and methods of applications. Polyurethanes are most widely used in coating industry as they exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance properties [28] and wide range of mechanical strength.

Looking to the survey of above three components i.e. RMP, CO & PU the present aspect comprises the surface coating formulation based on blending of RMP, CO and Diisocyanates. Thus the work is scanned in following scheme.



Scheme: 1 Formation of Polyurethane Surface Coatings

MATERIALS AND METHODS

Materials

Castor oil was purchased from local market. Rosinified Phenolic Resin (RPR) was purchased from local market. Dibutyltin dilaurate (DBTDL) used as a catalyst which was purchased from himedia. Hexamethylene diisocyanate (HMDI), and Diphenylmethane diisocyanate (MDI) were purchased from the bayer, (Dubai). Xylene used as a solvent was purchased from the S.d.fine chemical limited, (Mumbai). All other chemicals used were of pure grade.

Blending of Rosinified phenolic (RPR) resin and Castor oil (CO)

To prepare castor oil and rosinified phenolic resin blends, involving a physical mixing of both as described below: Three necked flask equipped with a mechanical stirrer, castor oil was charged and under continuous stirring desired amount of specific rosinified phenolic resin (as shown in Table 1) were added gradually over the period of half an hour. Upon the completion of addition the reaction mixture was stirred for an hour after which it was kept aside in a cylindrical glass container for overnight to check any tendency of separation of the two layers. In neither case separation of the two layers was observed. The physical properties of resultant above different percentage composition blends (RPR-CO) are given in Table -1.

TABLE:-1 Composition of (RPR: CO) and Physical Properties

Sr. No.	Composition RPR+CO	OH Value in mg of KOH/gm	Acid value	Colour	-OH Equivalent Weight	Moisture content, %
B1	40:60	115.82	8.40	Pale yellow	484.84	0.055
B2	50:50	103.18	10.65	Pale yellow	543.47	0.065
B3	60:40	90.36	12.30	Pale yellow	613.76	0.065

Synthesis of polyurethane:-

Blends of RPR-CO were taken in three necked flask which was equipped with mechanical stirrer, reflux condenser and thermometer. The stoichiometric amount of Hexamethylene diisocyanate (HMDI) were also using diphenyl methane diisocyanate (MDI) was added gradually in presence of dibutyltin dilaurate (DBTDL) catalyst. The reaction was performed at 50-65 °C with continuous stirring for 3-4 hrs. The prepolymer was isolated as a viscous liquid. As the reaction mix. becomes pourable viscous liquid. It was poured in to the glass cavity. It was kept at room temperature for 24 hrs curing. These films were used for further study and characterization.

TABLE:-2 PU Compositions Based on (RPR-CO) Blends for MDI and HMDI (Weight of Diisocyanates/10gm of polyol)

Sr. No.	Composition RMP+CO	HMDI		MDI	
		H1	H2	M1	M2
1.	40:60	5.222	6.270	2.732	3.278
2.	50:50	4.600	5.520	2.409	2.890
3.	60:40	3.983	4.779	2.090	2.508

Panel Preparation

The mild steel panels were first degreased in alkali solution and subsequently swabbed with xylene to remove any type of oily material or contaminant from the surface. After xylene has been evaporated the panels were coated by the above prepared coating composition.

FILM CHARACTERIZATION

The coated panels were examined for drying time, adhesion test, flexibility test, scratch hardness, pencil hardness, impact resistance and chemical resistance properties by standard methods. The results are given in tables and respectively.

Drying Time

The mild steel panels were used to determine the air drying time of films of various blends. The panels were prepared in a similar manner written above and coating compositions were applied. The films were checked for 'surface dry' and 'tack-free dry' stages at regular interval of time. The results of drying time determination are given in Table-3.

Adhesion Test (ASTM D 3359)

Adhesion of films were determined by employing cross-hatch adhesion test and panels for the test were prepared exactly in a similar manner to that of drying time determination test. Cross-hatch adhesion test was carried out after 168 hour of coating application. Adhesion test was carried out using reported method [29]. The results are given in Table-3.

Flexibility (ASTM D 622)

For the determination of flexibility, mild steel panels were used. The coating compositions were applied and cured in the same manner as mentioned above. Flexibility test were carried out using mandrels having specific rod diameter. Generally 1/8 inch rod diameter mandrel was used and if film passed through 1/8 inch mandrel then it was said to be passed for the flexibility test. The results are given in Table-3.

Scratch Hardness

In this method, a hand operated instrument was used in which test panel was kept on a sliding base with coated side upward and scratched under specific load with a needle which was in contact with film on test panel. The load was kept increasing till the film was scratched which was indicated by a light bulb that glows when film was scratched. The results are given in Table-4.

Pencil Hardness

In this method the use of pencil having different hardness are used. Sharp tipped pencils having hardness 4B (soft) and 6H (hard) were used to scratch the film. The pencil was held approximately at an angle of 45° to the film and with uniform pressure pulled down over the length of the film. The test was repeated till a pencil with specific

hardness was able to scratch the film and hardness off that pencil was reported as the pencil hardness test. The results are given in Table-4.

Impact Resistance (ASTM D 2794)

The coated test panels for impact resistance test were prepared in the same manner as described above. The test was carried out after 168 hour of coating application. The coated panel was kept on a platform (coated side upward). The panel was then indented with an object of specific weight from the varying heights. The test was repeated by increasing the height from which the object falls till the film was cracked or detached. The results are given in Table-4.

TABLE:-3 Properties of Films Prepared from PU Compositions Based on (RRP-CO) Blends with MDI and HMDI

Polyurethane code	Drying time in minutes		Adhesion	Flexibility
	Surface dry	Tack-free dry		
B1PUH1	150	240	F	p
B2PUH1	145	235	P	p
B3PUH1	140	230	P	p
B1PUH2	135	232	P	P
B2PUH2	130	227	P	P
B3PUH2	125	222	P	p
B1PUM1	60	120	P	P
B2PUM1	55	115	P	P
B3PUM1	50	110	P	F
B1PUM2	55	80	P	P
B2PUM2	50	75	P	P
B3PUM2	45	70	P	F

P=Pass, F=Fail

Table: 4 Mechanical Properties of PU cured coating from (RPR-CO) blends with MDI and HMDI

Polyurethane code	Scratch hardness in gms.	Pencil hardness	Impact resistance in-lb
B1PUH1	1200	1H	125
B2PUH1	1200	1H	130
B3PUH1	1450	2H	135
B1PUH2	1600	3H	130
B2PUH2	1800	4H	145
B3PUH2	2000	4H	150
B1PUM1	2200	2H	170
B2PUM1	2350	3H	175
B3PUM1	2500	4H	180
B1PUM2	2800	5H	200
B2PUM2	3000	5H	210
B3PUM2	3250	5H	225

Table: 5 - Chemical Properties of PU curd coating from (RPR-CO) blends with MDI and HMDI

Polyurethane code	Acid resistance 5% HCl 24 hrs.	Alkali resistance 3% NaOH 2 hrs.	Water resistance (Dist. Water) 168 hrs.
B1PUH1	2	3	3
B2PUH1	3	4	3
B3PUH1	4	4	3
B1PUH2	4	4	4
B2PUH2	5	5	5
B3PUH2	5	5	5
B1PUM1	4	5	5
B2PUM1	5	5	5
B3PUM1	5	4	5
B1PUM2	5	5	5
B2PUM2	5	5	5
B3PUM2	5	5	4

0 = film completely removed

1 = film removed and particularly cracked

2 = film partially cracked

3 = loss in gloss

4 = slight loss in gloss

5 = film largely unaffected

Determination of Chemical resistance properties (ASTMD 1308)

The assessment of chemical resistance of the films to various chemicals, mild steel panels were used which were prepared, coated and cured as mentioned above. The immersion method was utilized to assess the chemical resistance of films in which the panels were immersed vertically in the baths containing solutions of different chemicals with specific concentration at room temperature for the specific time period. Upon completion of the

specified time period the panels were removed from the baths and allowed to dry before visual examination. The results of resistance against chemicals are given in Table-5.

The drying time of films based on PU compositions is much lower than that of RPR-CO blends. This can be attributed to presence of urethane linkages which is known for the fast drying characteristic.[21] Comparison of drying time of PU films based on MDI and HMDI shows that the PU films based on MDI have higher drying time than PU films based on HMDI. This can be due to structural difference in both isocyanates; MDI is aromatic while HMDI is aliphatic. Also, results of adhesion test and flexibility suggest that, these films give good adhesion and flexibility. Flexibility of all the films was measured by using 1/8" mandrel as per ASTM D 622. Excellent scratch hardness was obtained from the films, prepared from these blends. The pencil hardness and impact resistance are also good for such kind of films. Chemical resistance properties of all the films give satisfactory results.

CONCLUSION

Room temperature curing composition can be prepared easily and give satisfactory results. Drying time of films based on MDI shows faster drying than compared to PU films based on HMDI. PU films based on MDI shows improved scratch hardness than PU films based on HMDI. Also results of scratch hardness, pencil hardness and resistance against chemicals are higher in case of PU films prepared from MDI as compared with PU films prepared from HMDI.

Acknowledgement

The authors thankful to Head of the Department, for providing research facilities.

REFERENCES

- [1] Wang FY, Chen CM, Wu WJ, *Journal of applied polymer science*, **2001**, 80,188-196.
- [2] Chen CM, Seng HT, Wu HD, *Journal of Applied Polymer Science*, **1998**, 69, 1119-1127.
- [3] Vashish U, Rani G, Ali V, Kaushal J. Alam T, Alhadi SA, Mohd I, *J.Chem.Chem.Eng*, **2011**, 738-746.
- [4] Mohapatra DK, Nayak PL, Lenka S, *Journal of Polymer Science: Part A: Polymer Chemistry*, **1997**, 35, 3117-3124.
- [5] Milanese AC, Odila HM, Jacobus CH, **2012**, 15 (2): 191-197.
- [6] Shakeb AMF, *Surface Coatings international Part B: Coating Transactions*. **2005**, 88, 83-156.
- [7] Yokoyama N, *Journal of Applied Polymer Science*, **2006**,102, 2099-2106.
- [8] Gotfryd AZ, *Progress in organic coating*, **2004**, 49,109-114.
- [9] Mishra DK, Mishra BK, Lenka S, Nayak PL, *Polymer Engineering and science* **1996**, 36(8), 1047-1051.
- [10] S. Jang, US 3,776,869, (**1973**).
- [11] Jiang H, Zhang L, Tong L, Chen J, Xinfu L, **2010**, 137-141.
- [12] Ullmann's encyclopedia of industrial chemistry, (**2003**), 31,345-352.
- [13] Lin J, Wang W, Wen X, Qucaipihui Z, Zheng D, Cheng J, Yang Z, *Pigment and Resin Technology*, **2012**, 41, (6), 351-358.
- [14] Kattimuttathu SI, Vadi KS, *Ind. Eng. Chem. Res.*, **2005**, 44, 4504-4512.
- [15] Kothandaraman H, Sultan NA, **2006**, 1017-1024.
- [16] Gopalakrishnan S, Linda FT, *J. Chem. Pharm. Res.*, **2011**, 3(2):848-862.
- [17] Zheng J, **2000**.
- [18] Subrayan P, Zhang S, Jones FN, Swarup V, Yezrielev AI, *Journal of applied Polymer science*, **2000**, **77**, 2212-2228.
- [19] Gopalakrishnan S, Linda FT, *J. Chem. Pharm. Res*, **2010**, 1(4), 252- 261.
- [20] Patel BK, Patel HS, Desai SN, *Pelagia Research Library*, **2012**, 3(5):1052-1057.
- [21] Yuan H, Xing W, Yang H, Song L, Hu Y, Yeoh HG, *Polymer International*, **2012**.
- [22] Knop A, Scheib W, Springer- Verlag Berlin Heidelberg New York **1979**.
- [23] Naughton FC, *J. Oil & Color Chemists Assoc.*, **1974**, 51, 65.
- [24] Achaya KT, *J. Oil & Color Chemists Assoc.*, **1971**, 48, 759.
- [25] Lakshminarayana G, *J. Oil Technol. Assoc. India*, **1981**, 13, 75.
- [26] Lakshminarayana G, Paulose MM, Vishwanadham B, Laxminarayana J, Ramalingaswamy PA, *J. Am. Oil Chem. Soc.*, **1991**, 68, 179.
- [27] Chandra S, Gupta RK, *Pigment & Resin Techn.*, **1994**, 23, 7.
- [28] Potter TA, Schmelzer HG, Baker RD, *Prog. in Org. Coatings*, **1984**, 12, 32.
- [29] Patel HS, Patel BK, Patel KB, Desai SN, *Int. J. Poly. Mater.*, **2009**, 59, 25.