List of Publications

1. The Effect of Chain length of Polyethylene glycol on properties of Castor oil based Polyurethane Elastomers.
   V. Bhardwaj, **K. Somani,** S. Kansara
   Journal of Macromolecular Science, Pure and Applied Chemistry,
   39 (1&2), 2002, 115.

2. Study of Thermal properties and crystallinity of polymeric materials,
   Proceedings of National Workshop on "Engineering Materials " ERDA, Baroda, 11-12th March, 2003.
   Utkarsh Shukla, **Keyur Somani**, Animesh kumar Rakshit

3. Castor oil based Polyurethane Adhesives for wood to wood bonding.
   Keyur Somani, Natvar Patel, Sujata Kansara,
   Animesh Kumar Rakshit
   International Journal of Adhesion and Adhesives, **23** (4) 2003, 269.

4. Polyol from Castor oil and Epoxy resin for Polyurethane coatings.
   Keyur Somani, Natvar Patel, Sujata Kansara,
   Animesh Kumar Rakshit
   European Coating Journal ,**11**, 2003, 35.

5. High Solids Polyurethane coatings from Castor oil based polyester-polyols.
   K. Somani, R. Parmar, N. Patel, S. Kansara
   International Journal of Polymeric Materials. **53** (3) 2004, 283.

6. Effect of chain length of Polyethylene glycol and crosslink density on Sorption and Diffusion of organic solvents through castor oil based Polyurethanes.
   Keyur Somani, Natvar Patel, Sujata Kansara,
   Animesh Kumar Rakshit
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THE EFFECT OF CHAIN LENGTH OF POLYETHYLENE GLYCOL ON PROPERTIES OF CASTOR OIL BASED POLYURETHANE ELASTOMERS

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ABSTRACT

Polyurethane (PU) elastomers from castor oil based polyol, polyethylene glycol (PEG) of various molecular weight (200, 400, and 600) and toluene diisocyanate were prepared in the form of transparent sheets. The sorption, mechanical and thermal properties have been studied. The solubility parameter, molecular weight between two crosslinks and degree of crosslinking of PU samples were calculated from equilibrium swelling experiments. The kinetic study of swelling revealed that sorption is anomalous in nature in all the samples. Diffusion coefficient (D) and sorption coefficient (S) were found to decrease with an increase in chain length of PEG. The stress-strain data showed that the elastomers obtained using PEG-200 gave the best mechanical properties. The thermal degradation of all elastomers starts at ~250°C, regardless of the PEG chain length. The values of activation energy of degradation were in the range of 60–72 kJ/mole.

Key Words: Polyethylene glycol; Castor oil; Polyurethane elastomers; Solubility parameter

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INTRODUCTION

Polyurethanes are known for their industrial applications due to high strength, resiliency, and good resistance to abrasion. A great number of factors such as extent of crosslinking, nature of polyol and diisocyanate and curing conditions are known to affect the properties of polyurethanes [1–5].

Efforts have been made during the past few decades to replace these expensive polyols with low cost natural vegetable oils or their derivatives in the production of PU products [6–8]. Among the vegetable oils, castor oil stands out for the synthesis of polyurethane elastomers as it possesses double bonds, as well as three hydroxyl groups. Moreover, castor oil possesses good compatibility with polyethylene glycol (PEG) in all proportions so that PEG can be effectively blended with castor oil or its derivatives to obtain castable polyurethane elastomers with improved application properties.

In the present study, we report the synthesis of PU by blending castor oil based polyols and PEG of various molecular weights for producing PU. The effect of molecular weight of polyols on physical, transport, mechanical and thermal properties have been studied.

EXPERIMENTAL

Materials

The castor oil based polyol designated R-60 in the study having hydroxyl equivalent weight 220 and having five hydroxyl groups per mole were supplied by H.K. Agencies, Ahmedabad. Polyethylene glycols (PEG) of molecular weight 200, 400, and 600 used in the study were purchased from Sisco Chem. Industries, India and were dried over anhydrous Na_2SO_4 to remove traces of water. All the solvents used were of analytical grade and were further purified by distillation. Toluene diisocyanate (TDI) and dibutyl tin dilaurate (DBTDL) were purchased from Fluka, Switzerland, and used as received.

Preparation of Prepolymer (PUR-60)

In a four-neck flask, equipped with a mechanical stirrer, thermometer, nitrogen gas inlet and outlet, calculated quantity of R-60 was placed in the flask. The required quantity of TDI was added gradually to R-60, maintaining a temperature of reactants of about 25°C until the addition of TDI was completed. The reactants were stirred for one hour to complete the reaction. The ratio of NCO/OH was maintained at 2.

Preparations of Elastomers (PUP)

Castable polyurethane elastomer was prepared by allowing the reaction of prepolymer PUR-60 with required quantities of PEG-200, PEG-400, and PEG-600, respectively along with the catalyst DBTDL (0.01 wt% total charge) by maintaining the final ratio NCO/OH 1.5. The reactants were weighed in a beaker, stirred well, and degassed under reduced pressure (2–5 mm of Hg.). The resin was then transferred to a previously leveled glass mold kept at 60°C and left overnight for curing. The samples in the form of sheets of about 1 mm. thickness were removed from the mold and finally cured at 80°C for 15 hours.

Swelling Experiments

Equilibrium swelling experiments were performed at $30 \pm 0.5°C$ to determine solubility parameter of polyurethane samples. The swelling was carried out in various solvents ranging their solubility parameter value (δ) from 7.4 to 14.5 $(\mathrm{cal/cm^3})^{1/2}$. From the plots of equilibrium swelling volume Q vs. δ (Fig. 1) acetone gave a maximum value of Q in all three samples and hence, was used for further sorption kinetics studies.

In the kinetic experiments, a so-called pat and weight technique was used for liquid sorption [9]. Samples, after taking the dry weight, were placed in acetone in a standard joint test tube, which was maintained at a temperature of $30 \pm 0.5°C$. The specimens were taken out at regular intervals, and solvents adhering to the surface was rubbed off, weighed immediately, and replaced in solvent. This procedure was continued till equilibrium swelling was achieved. This was repeated for three specimens from each network in order to ensure the reproducibility of the values. The time taken for wiping out the solvent from the sample surface was kept to a minimum in order to minimize error due to solvent evaporation.

Mechanical Testing

The tensile strength, percentage elongation, and modulus were determined according to ASTM-D 412. Shore A hardness of all the samples were measured by means of a type A Shore Durometer at room temperature as per ASTM- A 2240.

Thermogravimetry

The thermogravimetric analysis of PUP samples were carried out using Shimadzu TG -30 thermal analyzer at a heating rate of 100°C/min in air.

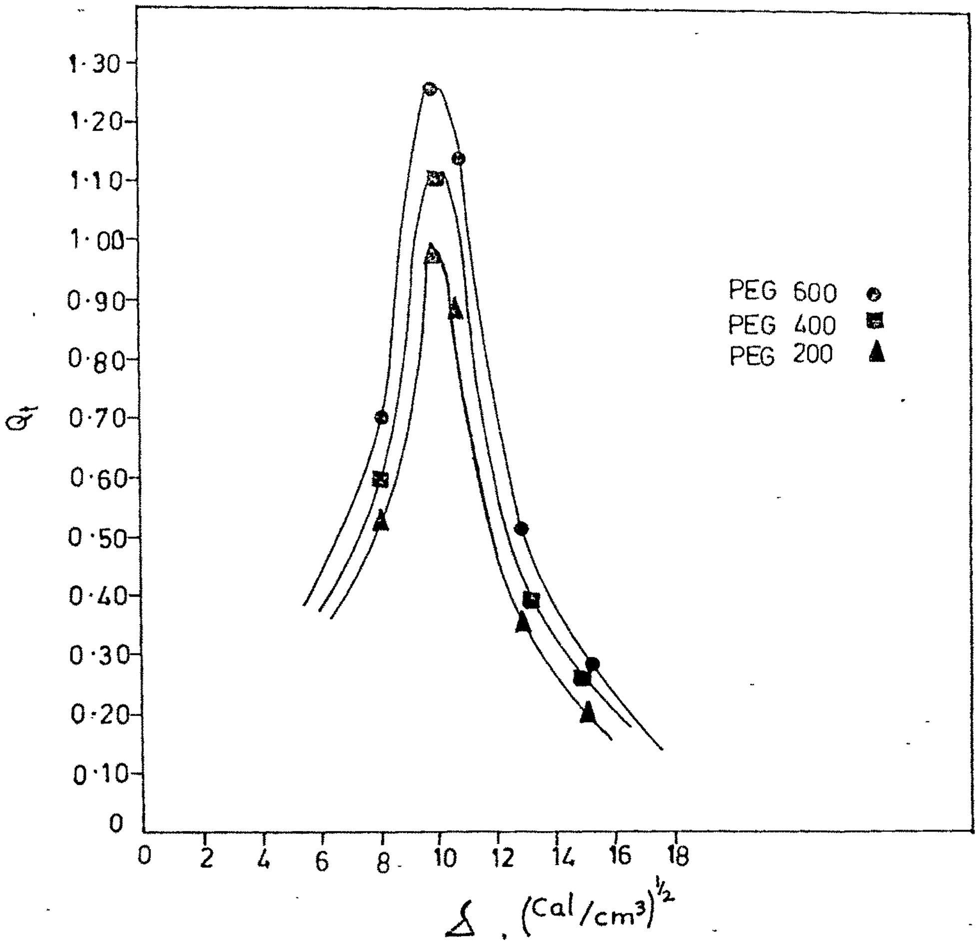

Figure 1. Plot of volume equilibrium of solvents (Q_t) vs. solubility parameter of solvent (δ).

RESULTS AND DISUSSION

Polyurethanes prepared by a transfer molding technique were in the form of yellow transparent films. The densities of polymer films were determined by a floatation method. Results are summarized in Table 1.

Table 1. Physical Parameters of Polyutrethanes

PU	Density g/cm^3	V_p	M_c gm./mole	N × 10^3 mole/cc	v × 10^3 mole/gm.
PUP-200	1.125	0.475	690	1.63	0.73
PUP-400	1.113	0.447	820	1.36	0.61
PUP-400	1.107	0.363	1360	0.81	0 37

The equilibrium degree of swelling (Q), which is the reciprocal of volume fraction of polymer in the swollen state (V_p), was calculated from the swelling data of PUP samples in various solvents using the following relations:

$$Q = 1/V_p$$

$$V_p = \frac{w_p/d_p}{w_p/d_p + w_s/d_s}$$

where,

w_p = dry wt. of polymer
w_s = wt. of solvent taken up at equilibrium
d_p = density of polymer
d_s = density of solvent

In order to determine the solubility parameter of PUP samples, Q was plotted against δ of solvents studied. From the plot (Fig. 1) it was found that acetone $= (9.9\ \mathrm{cal/cm^3})^{1/2}$ gave a maximum value of Q for all samples studied and hence, was used for further sorption studies. The average molecular weight between two crosslinks (M_c), which is a direct measure of crosslink density, was measured from the well-known Flory-Rehner equation shown below:

$$M_c = \frac{-d V_1 (V_p)^{1/3}}{\ln(1 - V_p) + V_p + \chi_{12} V_p^2}$$

where,

V_1 = molar vol. of solvent
d = density of network
χ_{12} = polymer-solvent interaction parameter which was calculated using the Equation [11]:

$$\chi_{12} = B + \frac{V_1 (\delta_p - \delta_s)^2}{RT}$$

where,

δ_p = solubility parameter of polymer
δ_s = solubility parameter of solvent
R = gas constant
T = absolute temperature
B = Lattice constant which is generally taken as 0.34 for good solvent.

The degree of crosslinking (ν) and number of chains per unit volume (N) were also calculated using the following relations [12, 13]:

$$\nu = \frac{1}{2M_c} \quad N = \frac{d}{M_c}$$

The values of V_p, M_c and for all samples studied in acetone are summarized in Table 1. It can be seen from the Table that V_p decreases with an increase in chain length of PEG. As the distance between two crosslink points increases with an increase in chain length (for a given NCO/OH ratio) of highly flexible PEG the free volume available also increases and hence, V_p decreases. The increase in chain length increases the distance between two crosslink points resulting in a less dense crosslinked structure and therefore, M_c increases with the increase in molecular weight of PEG incorporated into the network (Table 1).

Kinetics of Swelling

The sorption of penetrating species into polymer matrix is quantified in terms of mole percent uptake. The mole percent uptake (Q_t) at each time interval, from the results of swelling experiments was calculated using the following relation [12]:

$$Q_t = \frac{m_e/m_r}{m_i} \times 100$$

where,

m_e = mass of solvent taken up at equilibrium
m_r = relative molar mass of solvent
m_i = dry mass of sample.

At equilibrium swelling, Q_t was considered to be Q_∞, mole percent uptake at infinite time, the values of which are tabulated in Table 2. The sorption curves of PUP networks which are shown in Fig. 2 were obtained by plotting Q_t vs. $t^{1/2}$. From the curves it is clear that uptake capacity increases

Table 2. Values of Q_∞ and n for PUP

PU	Q^∞	k	n
PUP-200	1.323	0.016	0.58
PUP-400	1.489	0.063	0.54
PUP-600	2.134	0 076	0.45

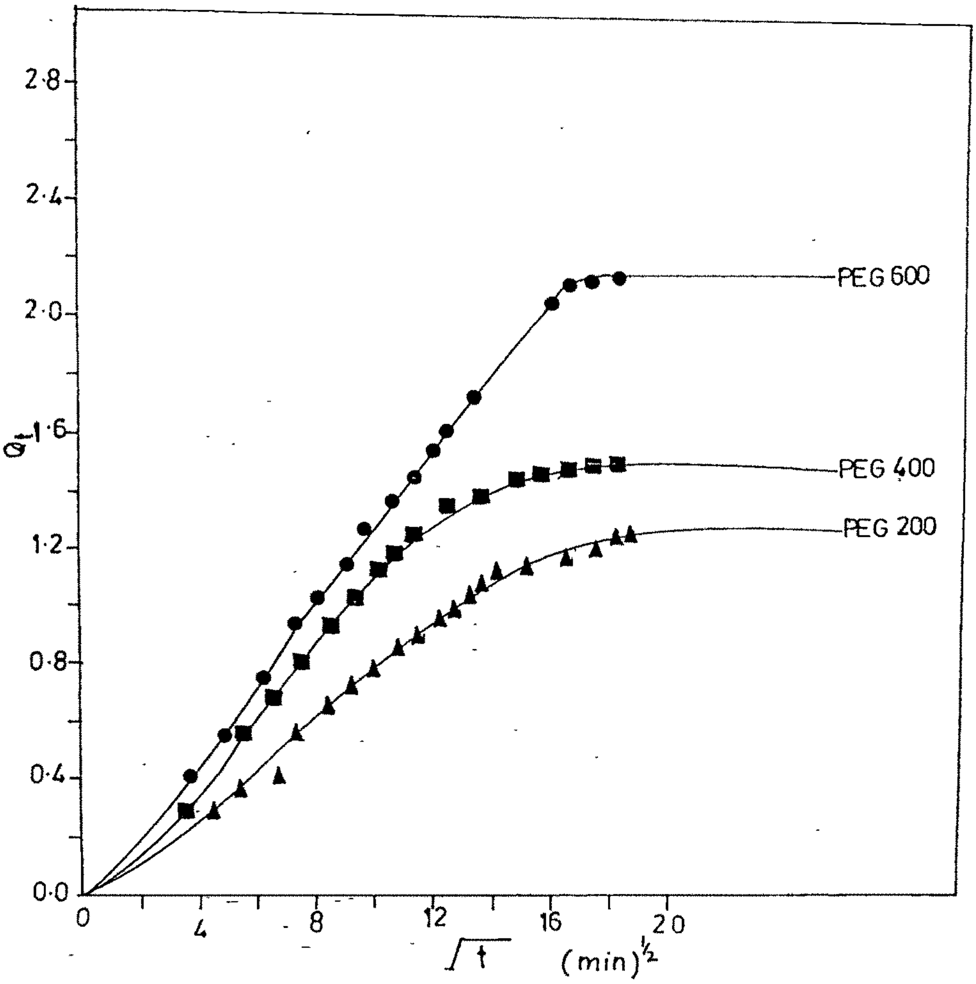

Figure 2. Sorption curves of PUP samples, (Q_t) vs. $(t)^{1/2}$.

in the order PUP 200 < PUP 400 < PUP 600 at a given time. This shows that the solvent uptake capacity is affected by ethylene oxide chain length. The equilibrium swelling Q_∞ also follows the same trend (Table 2). Incorporation of PEG-600 into R-60 polyol resulted into a PU network of maximum flexibility and thus sorption capacity would be maximum. Decreasing the chain length by introducing PEG-400 and PEG-200, respectively in place of 600, the network structure becomes progressively more rigid and then is less able to accommodate the solvent molecules.

To understand the mechanism of sorption the values of Q_t and $Q\infty$ were substituted into the general expression [14], which describes the transport kinetics.

$$Q_t/Q = kt^n$$

where k is a constant which depends on the structural characteristics of the polymer and its interactions with solvent. The value of n determines the mode of transport. When $n = 1/2$, diffusion obeys Fick's law. Fickian diffusion occurs when segmental mobility of the polymer chain is faster than the rate of diffusion of penetrant molecules. When $n = 1$, the diffusion is said to be non-Fickian, which occurs when diffusion is much faster than polymer chain relaxation processes. In the present system, the values of k and n were obtained from the linear plot of log $(Q_t/Q\ )$ vs. log t (Correlation coefficient > 0.9) and are presented in Table 2. In all cases, the magnitude of n is nearly 0.5. This suggests that the diffusion process is Fickian in nature.

The transport of penetrant molecules through polymers is also quantified by another term, permeability, P. The permeability of small molecules in polymers usually occurs through the following steps:

(1) sorption of penetrating species into polymer matrix.
(2) diffusion of penetrating species through polymer matrix.
(3) desorption of penetrating species through polymer wall.

The sorption coefficient S which gives an idea about the equilibrium sorption of solvent, was calculated using the Equation [15]:

$$S = \frac{m_\infty}{m_p}$$

where,

m_∞ = mass of solvent taken up at equilibrium.
m_p = initial mass of polymer.

The diffusion coefficient D which is a measure of the penetrant molecules to move among the polymer segment was calculated from the following relation [16]:

$$D = \pi(h\theta/4Q_\infty)^2$$

Table 3. Values of Diffusion Coefficient, Sorption, and Permeability of PUP System

PU	$D \times 10^9$ m^2/sec	S	$P \times 10^9$ m^2/sec
PUP-200	7.4	0.77	5.7
PUP-400	5.2	0.46	2.4
PUP-600	2.4	0.24	0.6

where,

θ = slope of the linear portion curve (Fig. 2)
h = thickness of sample.

The values of S and D are summarized in Table 3. It can be seen from the results that for the same ratio of NCO/OH, diffusion coefficient, as well as sorption coefficient, increases with an increase in crosslink density and decreases in number of -CH_2O- repeat units. The maximum values of D and S of PUP network having the least number of ethylene oxide units indicate that acetone molecules are absorbed and accommodated mainly by castor oil and isocyanate counterparts, rather than the linear chain molecules of PEG in the network. The permeability coefficient, P which gives the combined effect of both D and S was calculated using the equation:

$$P = D \times S$$

The values of P also follow the similar trend. The values of D, M_c and V_p were used to establish the following relationship proposed for swollen polymer networks [17]:

$$D \sim V_p\beta$$

$$D \sim M_c\gamma$$

where β and γ are empirical constants. Straight lines shown in Fig. 3 represent these power laws.

Mechanical Properties

The tensile properties in terms of tensile strength, modulus and % elongation evaluated from stress-strain curves are tabulated in Table 4. The data show a gradual increase in all mechanical properties studied with a decrease in molecular weight of polyol incorporated with the R-60 polyol. The ratio of NCO/OH, when maintained the same in all PUP samples, the higher molecular weight polyol (PEG 600) which is linear in nature causes formation of a weak polymer network as a result of (1) directly decreases in crosslink density and; (2) indirectly not allowing uniform distribution of load throughout the network due to of its longer chain length. In otherwords, when the load is applied to the network, polyol PEG-600 because of its high flexibility throw away, the load to the rigid part (castor oil and TDI) of the network and creates stress con-

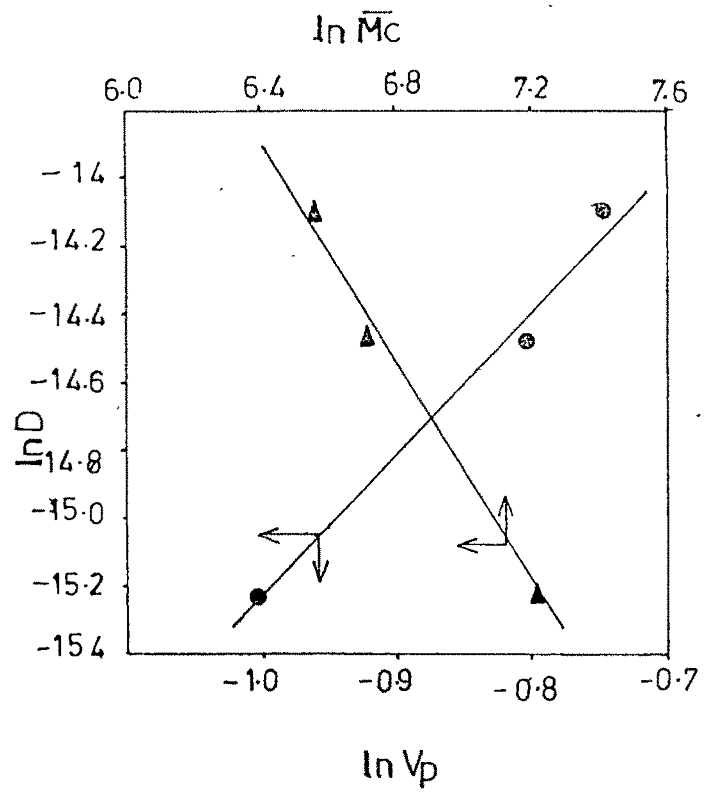

Figure 3. Log-log plot of diffusion coefficient (D) vs. M_c and V_p.

centration at that region. Ultimately, the rupture takes place at low load and elongation values of. Thus, the lack of mutual co-ordination to share the load applied, results in a decrease in tensile strength, elongation, and modulus.

When polyol PEG-200 is used, the shorter length of flexible chain contributes to bare load along with R-60 part coordinately which leads to an increase in tensile properties of the PUP-200 system. Hardness of PUP samples are also shown in Table 4. As can be seen from the Table, hardness

Table 4. Mechanical Properties of PUP System

	PUP-200	PUP-400	PUP-600
Tensile strength × 10^{-5}(N/m^2)	133	35	10
% elongation	248	127	48
Modulus × 10^{-5} (N/m^2)	29.4	24	22
Hardness × 10^{-5} (N/m^2)	86	64	50

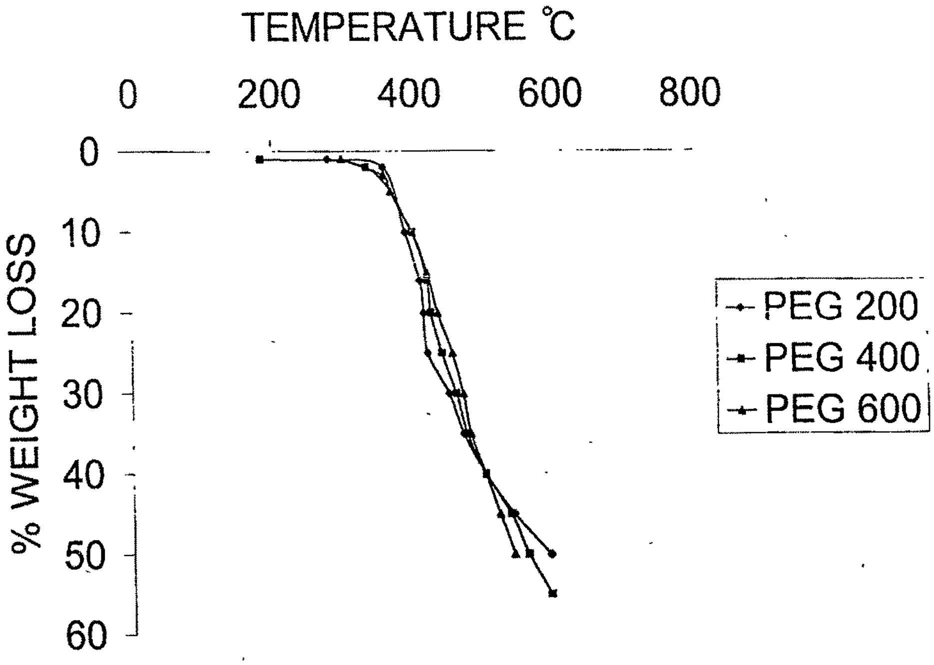

Figure 4. Thermograms of PUP samples.

of PUP increases with a decrease in the chain length of PEG. This is according to expectation. As chain length is decreased, crosslink density increases, which results into more rigid network.

Thermal Analysis

Thermograms of PUP samples are shown in Fig. 4. As can be seen from the thermogram, all the PUP samples, regardless of the chain length of polyol used, undergo spontaneous decomposition at ~ 270°C. Once the degradation has started, weight loss is rapid. The initial decomposition may correspond to urethane bond break which starts at ~ 270°C leading to the formation of carbon dioxide, alcohols, amines, carbon monoxide, etc. [18–19]. The decomposition beyond ~ 350°C may be due to polyol. Since one of the polyols used in this study is based on castor-oil, the main chain scission may occur with formation of 10-undecanoic acid and heptanal as evidenced by thermal degradation of ricinoleic acid [20]. Activation energy, which is a quantitative measure of thermal stability, was determined by Broido's method. The values of activation energy lie between 60–72 kJ/mole, indicating reasonably good thermal stability of the polyurethane elastomers.

CONCLUSION

Polyurethane (PU) elastomers synthesized from castor oil based polyol and linear polyethylene glycols(PEGs) were transparent films showing rubbery to tough characteristic behavior depending on the molecular weight of PEG. Diffusion coefficient and sorption coefficient were found to be dependent on the crosslink density and structure of the network. Polyurethane elastomers containing PEG-200 showed the best mechanical properties.

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REFERENCES

1. Buist, J.M. Development in Polyurethane-1. Applied Science Publishers Ltd.. London, 1978.
2. Bastids, S. J. Apply. Polym. Sci. **1995,** *56*, 1487.
3. Lin, I.S.; Biranowski, J.; Lorenz, D.H. Urethane Chemistry and Applications; Edwards, K.N., Ed.; ACS Symposium Series, 172, Chapt. 34, 1981; p. 523.
4. Rajalingan, S.; Radhakrishnan, G. Polym. Inter. **1995,** *25*, 87.
5. Desai; S.; Thakore, I.M.; Devi, S. Polym. Inter. **1998,** *47*, 172.
6. Qipeng, G.; Shixia, F.; Qingyu. Z. Eur. Polym. J. **1990,** *26*, 1177.
7. Patel, P.; Suthar, B.P. Polymer **1990,** *31* (2), 339.
8. Ding, H.; Zhang, L.; Zhang, N. Hebi Gongye-Xaxe Xuebao **1996,** *25* (2), 37.
9. Fieldson, G.T.; Barbari, T.A. Polymer **1993,** *34*, 1146.
10. Flory, P.; Rehner, J. J. Chem. Phys., **1943,** *11*, 521.
11. Hiaw, H.; Ping, Z.H.; Xie, J.W.; Yu, T.Y. J. Polym. Sci., Part A, Polym. Chem. **1990,** *28*, 585.
12. Mathew, A.P.; Packirisanry, S.; Thomas, S. Polymer **1995,** *36*, 4935.
13. Saikumar, C.; Rajadurai, S.; Thyagarajan, G. J. Polym. Mater. **1987,** *4*, 139.
14. Tetsuya, T.; Keito, Y.; Kazuo, Y.; Shuji, M. Polymer **1950,** *36*, 2941.
15. Martin, G.C.; Enssani, E.; Shen, M.J. Appl. Polym. Sci. **1981,** *26*, 1465.
16. Berens, A.R.; Hopfenberg, H.B. Polymer **1978,** *19*, 489.
17. Chee, K.K. Polymer Gels and Networks **1995,** *5*, 95.
18. Jellinek, H.H.G.; Dankle, S.R. Degradation and Stability of Polymers, Vol. 1, Chapt. 2; Jellinek, H.H.G., Ed.; Elsevier, 1983; p. 91.
19. David, D.J.; Staley, H.B. Analytical Chemistry of Polyurethanes, Vol. XVI, Part III, High Polymers, p. 365, 1974.

20. Saunders, J.H.; Frisch, K.C. Polyurethane Chemistry and Technology, Part I, Chemistry of High Polymers, Vol. XVI, Interscience Publisher, Chapt. 2, p. 51, 1963.
21. Broido, A. J. Polym. Sci. **1969**, *A2* (7), 1761.

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Castor oil based polyurethane adhesives for wood-to-wood bonding

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Abstract

Most adhesives are polymeric adhesives and if made from renewable sources they will have low cost and biodegradability which are of importance. In view of these properties we synthesized polyurethane (PU) adhesives from three different polyester polyols, obtained by reacting a castor oil derivative and diols (glycols) with diisocyanate adducts, where different NCO/OH ratios were used to give various compositions. The polyols and PUs were characterized by FTIR spectroscopy. The effect of NCO/OH ratios, types of isocyanate adducts and chain length of glycols were studied, by determining wood-to-wood adhesion strength, i.e. by lap shear strength measurement. The change in lap shear strength after being placed in cold water, hot water, acid or alkali solutions was tested. Thermal stability of these PU adhesives was determined by thermogravimetric analysis.

Keywords: A. Adhesives for wood; A. Polyurethane; C. Lap shear; Castor oil

1. Introduction

Generally, several kinds of commercial polyurethanes (PUs) are used to prepare solvent-based adhesives but due to their unknown formulations, their performance cannot be predicted and variation from batch to batch may produce significant differences in properties. A few studies dealing with the preparation of PUs from raw materials and their application as adhesives have been carried out [1–5]. PU adhesives are widely used in different industries. Due to the versatility of PU chemistry, there are many different types of PU adhesives [6]. These normally consist of polyol (polyester or polyether type), isocyanate and other additives. Since the performance of an adhesive is related to its viscoelastic properties, in addition to its surface free energy and that of the adherend [7], the relationship between composition and properties are of great importance. The performance or behavior of a wood adhesive system is dependent on a wide range of variables, such as surface smoothness of wood substrate, presence of wood extractives, pH and amount of debris present, which are related to the environment, such as the level and rate of a change in both temperature and relative humidity [8]. The bonding mechanism of adhesives is due to complex chemistry of the cellulosic substrate, i.e. hydrogen bonding with some adhesive and attractive weak Vander Walls forces with others [9]. Adhesives based on urea formaldehyde and phenol formaldehyde, are the major adhesives used for bonding wood [10–12], but some of these adhesives are very sensitive to hydrolysis [13,14] and stress scission [15]. Polyacrylate-type adhesives are also used as wood adhesives but it has some disadvantages such as shorter pot life, higher cost and limited durability. Literature studies reveal synthesis of different types of PU adhesives [16,17] made from synthetic chemicals. Extensive research work on synthesis of castor oil based PU is reported in literature [18–20], but there are very few studies dealing with the use of castor oil based PU as adhesives. Hence this effort to synthesize castor oil based polyol is utilized in the PU adhesives. Castor oil has two reactive sites, the double bond of the unsaturated fatty acid and the carboxyl group, linking the acid to the glycerol. Castor oil is used in the synthesis of IPNs of PU. It is a highly crosslinked polymeric structure and it acts as a very good adhesive for metal to metal bonding, Zhang et al. [21] and

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Hang-Quan et al. [22] synthesized IPNs from castor oil based PUs. Rajaswamy et al. [23] synthesized semi-IPNs from polychloroprene and castor oil based PUs which are good adhesives for rubber to rubber bonding. The present work describes the development of PU adhesives by reacting three different castor oil based polyester polyols of different chain lengths, with aromatic isocyanate as well as aliphatic isocyanate adducts, with different NCO/OH ratios. The polyester polyol and PU adhesives were characterized by FTIR spectroscopy. These PU adhesives were applied on to wood substrates. Lap shear strength was measured using standard methods and the extent of crosslinking in adhesives was monitored by measuring the adhesive strength (green strength) as a function of time. Thermal stability of the PU adhesives was also checked.

2. Experimental

2.1. Materials

Castor oil (Jayant Oil Mills, Vadodara, India) was used after vacuum drying in oven for 24 h at 100°C. Ethylene glycol, diethylene glycol and triethylene glycol (Merck, USA) were used as received. The catalyst dibutyltindilaurate (DBTDL) (Merck, USA) was used without any further purification. Aromatic isocyanate and aliphatic isocyanate (Grand Polycoats, Padra, India) were characterized for their physical properties, as shown in Table 1. Methyl ethyl ketone (MEK) (Suvidhinath Laboratory, Vadodara, India) was used after distillation and drying with molecular sieves (4 Å).

2.2. Preparation of polyester polyols

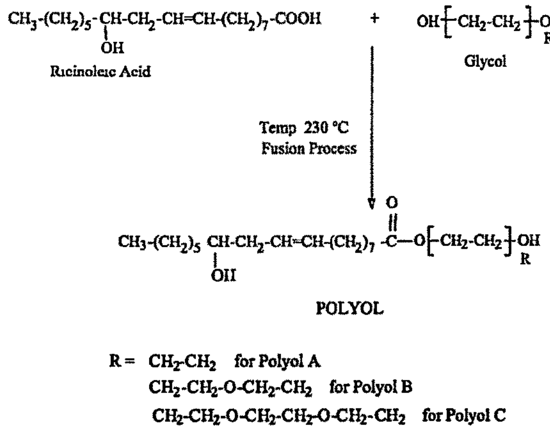
A dry process (fusion process) was employed for the synthesis of polyols, in which a reaction kettle equipped with a mechanical stirrer and provision for nitrogen flushing was charged with dry ricinoleic acid (0.5 mol) and 0.5 mol of respective glycols. (For synthesis of polyol A, B and C ethylene glycol, diethylene glycol and triethylene glycol were charged, respectively, 1:1 molar ratio). The temperature was raised slowly with continued stirring and was maintained at 230°C for 3 h. The water formed during the reaction was removed from the top of condenser by vacuum evaporation. The acid value of the contents were measured periodically. A gradual decrease in acid value showed the progress of reaction. The reaction was finally stopped at an acid value near to zero. The final traces of water were removed from the resin by continuously applying vacuum along with bubbling of nitrogen gas. Finally, polyol was cooled to 40°C and the acid value was determined. The reaction sequence is shown in Scheme 1. Hydroxyl value of these three different polyester polyols was determined by the acetic anhydride-pyridine method [24]. The properties of the polyols such as hydroxyl value, non-volatile matter and viscosity, are presented in Table 2.

2.3. Adhesive preparation

Preparations of adhesives were carried out by reacting polyester polyol with either the aromatic isocyanate adduct or aliphatic isocyanate adduct, along with the DBTDL, (0.05% w/w of total composition). The compositions were of various NCO/OH ratios. The composition and designation codes of the adhesive systems are shown in Table 3. The adhesives were diluted by MEK, to give an appropriate viscosity for effective application on to the wood strips.

2.4. Wood specimen preparations

As per test sample requirements, teak wood pieces (longitudinal) were cut into 300 x 25 x 3 mm^3 strips and polished using sandpaper grit no. 60 (250 μm).



Scheme 1. Synthetic scheme of polyols.

Table 1
Physical properties of isocyanate adducts

Type of isocyanate adduct	Free isocyanate content (%wt)	NCO equivalent weight	Non-volatile matter (%wt)	Specific gravity at 30°C	Viscosity at 30°C by FC-B IV (s)
Aromatic	12.5	336	75	1.02	210
Aliphatic	16.5	255	75	1.05	175

Table 2
Composition code and physical properties of castor oil based polyesters polyols

Designations of polyols	Hydroxyl value (mg KOH/g)	Hydroxyl equivalent weight (g)	Viscosity at 30°C FC B-IV (s)	Non-volatile matter (%)
Polyol A	306	183	124	99.1
Polyol B	265	210	137	99.5
Polyol C	249	225	168	99.3

Table 3
Designation code and composition of adhesives and gel time of adhesives

Type of polyol	Designation of adhesive composition code	Type of isocyanate adduct	NCO/OH ratio	Amount of polyol (g)[a]	Amount of isocyanate adduct (g)[a]	Gel time at 30°C (min)
Polyol A	A-Aro 1	Aromatic	1.0	3.52	6.48	115
	A-Aro 2	Aromatic	1.3	2.95	7.05	110
	A-Aro 3	Aromatic	1.7	2.43	7.57	100
	A-Ali 1	Aliphatic	1.0	4.18	5.82	235
	A-Ali 2	Aliphatic	1.3	3.56	6.44	210
	A-Ali 3	Aliphatic	1.7	2.97	7.03	203
Polyol B	B-Aro 1	Aromatic	1.0	3.86	6.14	130
	B-Aro 2	Aromatic	1.3	3.26	6.74	120
	B-Aro 3	Aromatic	1.7	2.70	7.30	110
	B-Ali 1	Aliphatic	1.0	4.53	5.47	235
	B-Ali 2	Aliphatic	1.3	3.89	6.11	230
	B-Ali 3	Aliphatic	1.7	3.28	6.72	195
Polyol C	C-Aro 1	Aromatic	1.0	4.69	7.00	135
	C-Aro 2	Aromatic	1.3	4.05	7.84	120
	C-Aro 3	Aromatic	1.7	3.42	8.67	115
	C-Ali 1	Aliphatic	1.0	4.22	4.78	240
	C-Ali 2	Aliphatic	1.3	4.01	5.89	200
	C-Ali 3	Aliphatic	1.7	3.89	7.48	180

[a] In all systems, the composition with 0.05% dibutyltindilautrate was added as a catalyst.

2.5. Wood bonding and testing

Using a brush, the adhesive solution was applied on both pieces of the wood strips for a thickness of 0.1 mm and a lap joined giving $25 \times 30\,\mathrm{mm}^2$ area of overlap. A load (2.5 kg) was placed over the contact points of wood pieces and left overnight. After that, the wood joints were kept at room temperature (30°C) and at a relative humidity of $50 \pm 5\%$ for 7 days. Each wood joint specimen was tested for lap shear strength using a Zwick UTM model 1445 according to ASTM D 906-82 (1987).

2.6. Spectroscopic analysis

FTIR spectra of polyol and PU samples (film) were recorded on a Nicolet Impact 400 spectrophotometer. PU films (around 100 µm) were prepared by spontaneous evaporations at room temperature of adhesive solution placed on mercury. The number of scans per sample was five. Polyols were taken as neat and number of scans per sample were two.

2.7. Thermogravimetry

Thermogravimetric analysis (TGA) was performed under air from 30°C to 500°C, at a heating rate of 10°C/min. on Shimadzu Thermal (DT-30B) Analyzer.

3. Results and discussion

3.1. Infrared spectroscopy

In the spectra of polymeric films of the adhesives, the characteristic carbonyl stretching was observed at $1735\,\mathrm{cm}^{-1}$, indicating the presence of a urethane linkage. The absorption peaks resulting from –NH stretching and bending vibrations were observed at 3330 and $1560\,\mathrm{cm}^{-1}$, respectively. The band observed at $2273\,\mathrm{cm}^{-1}$ indicated the presence of unreacted NCO in the higher NCO/OH ratio samples (i.e. 1.3 and 1.7). The double bond in the polyol moieties was observed as a medium intensity peak at 1635 cm^{-1}. The OH stretching band at 3400 cm^{-1} indicated the presence of free hydroxyl groups. In the cases of diethylene glycol and triethylene glycol, the presence of C–O–C ether linkage is indicated with a band observed at 1904 cm^{-1}. The band observed at 2949 cm^{-1} of is due to the –CH stretching. The presence of free functional hydroxyl groups in polyols (A, B, C) and the expected structure of the PU adhesive were confirmed by FTIR spectroscopy (Figs. 1a–c and Figs. 2a–c, respectively).The formation of PU is clearly indicated, due to the absence of a –OH absorbance band associated with the polyol and the presence of a –NH band of PU.

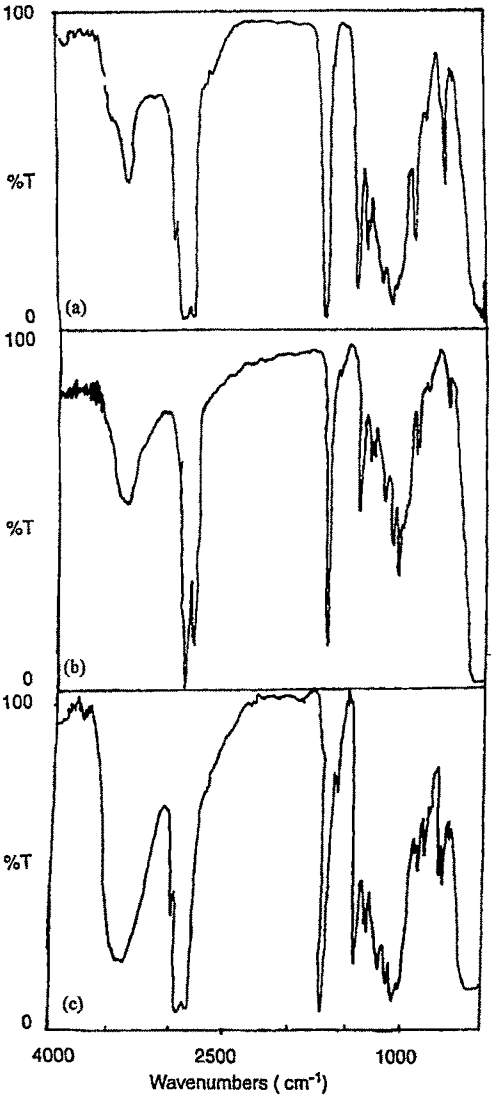


Fig. 1. FTIR spectrum of polyester polyols A, B and C.

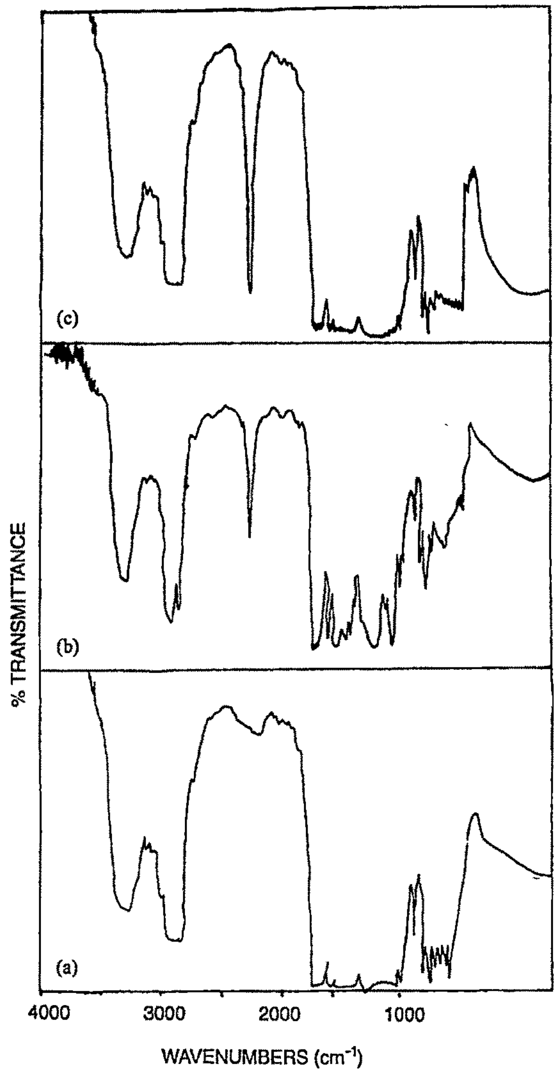


Fig. 2. FTIR spectrum of PU a (B Aro 1), b (B Aro 2) and c (B Aro 3).

3.2. Gel time

The gel time or pot life is an important property of adhesive systems, with respect to their application, as this indicates the maximum time during which the system remains in a fluid state for use. The results, shown in Table 3, indicate that the adhesive containing an aromatic isocyanate adduct gelled (cured) faster than the aliphatic isocyanate adduct. Also, as the NCO/OH ratio in each formulation increased, curing time decreased. The adhesive composition A-Aro 3 cured faster compared to all other compositions synthesized in this study. This was because of the presence of higher NCO/OH ratio (1.7), as well as the higher hydroxyl value of polyol A in A-Aro 3.

Table 4
Lap shear strength of adhesives

Systems	Polyol with aromatic isocyanate adduct having NCO/OH ratio	Lap shear strength ($N/m^2 \times 10^5$)	Lap shear strength ($N/m^2 \times 10^5$)	Polyol with aliphatic isocyanate adduct having NCO/OH ratio	Systems
A-Aro 1	1.0	93.0	13.1	1.0	A-Ali 1
A-Aro 2	1.3	96.7	12.3	1.3	A-Ali 2
A-Aro 3	1.7	94.3	13.8	1.7	A-Ali 3
B-Aro 1	1.0	70.7	6.5	1.0	B-Ali 1
B-Aro 2	1.3	90.4	7.5	1.3	B-Ali 2
B-Aro 3	1.7	77.3	8.6	1.7	B-Ali 3
C-Aro 1	1.0	56.3	<5.2	1.0	C-Ali 1
C-Aro 2	1.3	82.5	6.3	1.3	C-Ali 2
C-Aro 3	1.7	73.3	7.2	1.7	C-Ali 3

3.3. Effect of presence of different polyols in polyurethane adhesives and NCO/OH ratio on adhesion

The lap shear strengths of all the systems were determined and the results are shown in Table 4. It is seen that the lap shear strengths of the systems initially increase with increase in NCO/OH ratio, but then decrease at much higher NCO/OH ratios. As the NCO/OH ratio increases (i.e. greater crosslink density), the rigidity and strength of the adhesive bond increases. However, beyond a critical value, increase in NCO/OH ratio increases the stiffness, which is responsible for decrease in adhesion strength. Among all the systems for a particular NCO/OH ratio in PU adhesive, the chain length of the polyol increases from polyol A to polyol C. Polyols A, B, C were synthesized from ethylene glycol, diethylene glycol and triethylene glycol, respectively. The presence of the shorter chain length in polyol A resulted in a decrease in molecular weight between two crosslink points and increase in crosslink density, whereas the presence of ethylene oxide linkages in polyol B and C increases the flexibility and distance between two crosslink points. Both these factors are responsible for a higher lap shear strength of polyol A, compared to polyols B and C. The system A-Aro2 having a NCO/OH ratio of 1.3 exhibits the best adhesive performance.

However, in the PU adhesive systems containing the aliphatic isocyanate adducts, as the NCO/OH ratio increased, the lap shear strength shows a little decrease. Comparative studies of PU adhesives containing aliphatic isocyanate adducts and different polyols indicate that the PU system containing A Ali 1 showed a better lap shear strength compared to all other systems under investigation. Lap shear strength of these castor oil based adhesives is 10 times greater than that found for the commercially available wood adhesives [25].

3.4. Effect on chemical resistance

Wood pieces bonded with the adhesives, prepared from different polyols with aromatic isocyanate adducts, were kept in cold water (30°C) for 24 h and then dried at room temperature for 24 h. Lap shear strength was determined as mentioned earlier. Similarly, bonded pieces were immersed in hot water (100°C) and in acid (pH 2) and alkali solutions (pH 10) both at 80°C for 1 h and then dried at room temperature for 24 h. After immersion, lap shear strength was determined. The results are shown in Table 5. The results indicate good resistance to both cold and hot water. The acid solution (pH 2) had a negative effect on adhesion, because polyester is easily hydrolyzed in the presence of acid, resulting in deterioration in adhesive strength. In the alkali solution (pH 10), the adhesion decreased to some extent in terms of lap shear strength, probably because of alkaline hydrolysis.

3.5. Study of green strength and curing time

Green strength is one of the important properties of the adhesives. It shows the ability of an adhesive to hold the substrates together when brought into contact and before the adhesive develops ultimate stronger properties with full cure. It is the strength measured before complete curing of adhesive, i.e. before achievement of ultimate strength. For these purposes, different polyols with aromatic isocyanate adduct having a NCO/OH ratio of 1.3 was selected. The curing properties of these PU adhesives were monitored using lap shear strength tests for a number of days. The results (shown in Table 6), indicate that over a period of time, the lap shear strength increased up to 7 days and beyond which, it leveled off. This may be due to the ongoing crosslinking process during storage as the MEK gets eliminated from the system quite easily (b.p. 79°C).

3.6. Thermal analysis

From TGA, it was concluded that two stages of degradation occurred during heating. The first stage is due to the breaking of urethane links, which starts at ~260°C leading to the formation of CO_2, alcohols,

Table 5
Lap shear strength of different adhesives after soaking in chemicals

System	NCO/OH	Lap shear strength ($N/m^2 \times 10^5$) (before)	After treatment lap shear strength ($N/m^2 \times 10^5$)			
			Cold water	Hot water	Acid solution pH 2	Alkali solution pH 10
A-Aro 1	1	92.9	91.7	90.4	39.3	68.1
A-Aro 2	1.3	96.9	96.9	95.6	49.8	78.6
A-Aro 3	1.7	94.3	93.0	91.0	44.5	65.5
B-Aro 1	1	70.7	70.7	68.1	13.9	44.5
B-Aro 2	1.3	90.4	90.4	86.4	26.2	65.5
B-Aro 3	1.7	77.3	77.4	72.0	20.9	52.4
C-Aro 1	1	56.3	56.3	52.4	11.8	26.2
C-Aro 2	1.3	82.5	82.3	74.6	18.4	52.4
C-Aro 3	1.7	73.3	73.3	65.5	13.1	39.3

Table 6
Green strength of adhesives

No of days	Lap shear strength ($N/m^2 \times 10^5$)		
	A-Aro 2	B-Aro 2	C-Aro 2
1	6.5	5.2	5.2
2	13.1	15.7	18.3
3	26.2	36.7	39.3
4	44.5	51.1	55.0
5	68.1	76.0	78.6
6	78.6	87.7	81.2
7	94.7	90.4	82.5
10	97.0	90.4	82.5
15	98.2	89.1	82.5
30	96.9	90.4	82.5

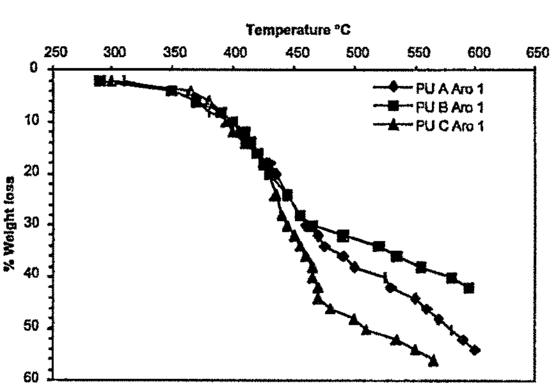


Fig. 3. Thermogram of PUs system A Aro 1, B Aro 1, and C Aro 1.

amines, aldehydes, CO, etc. [26,27], while the second stage which is not quite well distinct may be due to the polyol decomposition which occurred at ~450°C as shown in Fig. 3. Since polyols used in this study are based on castor oil, the main chain may result in the formation of 10-undecanoic acid and heptanal as evident by the thermal degradation of Ricinoleic acid [28], which is main constituent of castor oil. From the thermogram, decomposition behaviour was observed in all PU adhesive systems, it showed two-stage decomposition. The decomposition activation energy of these polymers was evaluated using the well-known Broido's method [29]. Initial decomposition temperature and activation energy of decompositions of the PU adhesives are shown in Table 7.

Table 7
Activation energy of polyurethane adhesives

System	IDT (°C)	Ea (kJ/mol)
A-Aro 1	290	71.3
B-Aro 1	300	79.4
C-Aro 1	310	94.0

4. Conclusion

Adhesives were prepared from three different polyols with different isocyanate adducts. Adhesives made from the polyol and aromatic isocyanate adduct, gave superior bonding strength for wood-to-wood specimens. The adhesives made from polyol A of higher hydroxyl value with an aromatic isocyanate adduct having a NCO/OH ratio 1.3 gave excellent lap shear strength compare to other homologous adhesive systems and was 10 times higher than with commercially available wood adhesives. PU adhesives synthesized from polyol A and aromatic isocyanate adduct shows good adhesion strength and chemical resistance as there is no ether linkages in the networks, while ether linkages in polyol B and C, is some what responsible for lower adhesion strength value and chemical resistance.

Acknowledgements

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References

[1] Kovacevic V, Smit I, Hace D, Suceska M, Mundri I, Bravar M. Int J Adhes Adhes 1993;13:126.
[2] Kovacevic V, Kljajie-Malinovic LJ, Smit I, Bravar M, Agic A, Cerovecki Z. In: Allen KW, editor. Adhesion, vol. 14. London: Elsevier Applied Science; 1990. p. 126.
[3] Kovacevic V, Smit I, Kljajie-Malinovic LJ, Suceska M, Bravar M. Angew Makromol Chem 1990;176/177:125.
[4] Agrawal RK, Drzal LT. J Adhes Sci Technol 1995;9:1381.
[5] Dreyfuss P, Larive DE. J Adhes 1989;27:105.
[6] Strobech C. Int J Adhes Adhes 1990;10:225.
[7] Krenceski MA, Johnson JF, Temin SC. J Macromol Sci Rev Macromol Chem 1986;26:143.
[8] Pizzi A. Wood adhesives chemistry and technology. New York: Marcel Dekker; 1983. p. 12.
[9] Charles VC. Hand book of adhesive bonding. New York: McGraw Hill; 1973. p. 175.
[10] White JT. Adhes Age 1981;7:19.
[11] Myres GE. Adhes Age 1988;10:31.
[12] Ebewela RO, River BH, Myres GE. Adhes Age 1993;12:23.
[13] Freeman GG, Krebich S. Forest Prod J 1968;18:39.
[14] Tranghton GE, Chow S. J Inst Wood Sci 1968;21:29.
[15] Dinwoodie JM. Inst Wood Sci 1978;8:59.
[16] Jia D, Liang X. J Polym Sci B: Polym Phys 1994;132:817.
[17] Vallat MF, Bessaha N. J Appl Polym Sci 2000;76:665.
[18] Ghatke ND, Phadke VB. J Appl Polym Sci 1967;11:629.
[19] Petrovic ZS, Fajinik DJ. J Appl Polym Sci 1984;29:1031.
[20] Athawale VD, Kolekar SL. Polym J 1998;30:873.
[21] Liucheng Z, Huilee D. J Appl Polym Sci 1997;64:1393.
[22] Xie Hong-Quan, Guo Jun-Shi. Int J Adhes Adhes 1997;17:223.
[23] Rajalingam P, Ganga R. Polym Int 1991;25:87.
[24] Cocks IV, Vanredew C. Laboratory hand book for oil and fat analysis. London: Academic Press; 1976.
[25] John N, Joseph R. J Appl Polym Sci 1998;68:1185.
[26] Jellinek HHG, Dankle SR. Degradation and stability of polymers. London: Elsevier Publication; 1983. p. 91.
[27] David DJ, Staley MP. Analytical chemistry of polyurethane, Part III (high polymers), vol. XVI. New York: Wiley Intersicence; 1974. p. 365.
[28] Saunders JH, Frisch KC. Polyurethane chemistry and technology, Part I, vol. XVI. New York: Interscience; 1963. p. 51.
[29] Broido A. J Polym Sci 1969;A 7:1761.

Polyol from castor oil and epoxy resin for PU Coatings

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Novel reactive polyols were synthesized via modification of castor oil, a renewable agricultural raw material with epoxy resin and triethylamine as a catalyst. This polyol was used for synthesis of polyurethane coating. Coating formulations were developed by reacting polyol with aromatic adduct, aliphatic adduct and castor oil based adduct in different NCO/OH ratio. All coating composition systems show good scratch resistance, better mechanical and chemical properties.

Majority of coating films exists in the form of three-dimensional polymer network produced by crosslinking of resins. Recently polyurethane has been developed as one of the most versatile resins. However, the demand of biodegradability stresses the use of renewable sources. Castor oil based polyurethane have been extensively studied as coatings and in network synthesis [1, 2]. Because of low reactivity of castor oil, focus has been directed to its derivatives. In view of this, a main constituent of castor oil i.e. ricinoleic acid which posses secondary hydroxyl functionality is frequenty utilized in the synthesis of polyurethanes [3]. Ricinoleic acid having free carboxyl group which s highly reactive, was selected in combination with epoxy resin to overcome disadvantages of epoxy coatings like brittleness, poor scratch resistance at higher temperature [4]. The present research of synthesizing novel polyol for polyurethane coating was carried out with the aim to have polyurethane of better mechanical and chemical properties compared to polyurethane of polyester polyol derived from different glycol's and ricinoleic acid as was done earlier by us [5].

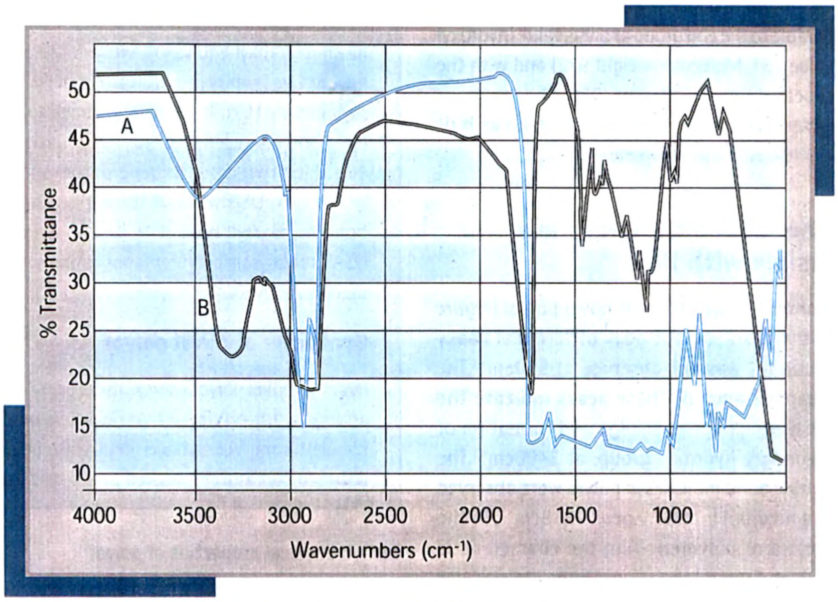

Figure 1: FTIR spectra of A: novol polyol and B: polyurethane (PU C1)

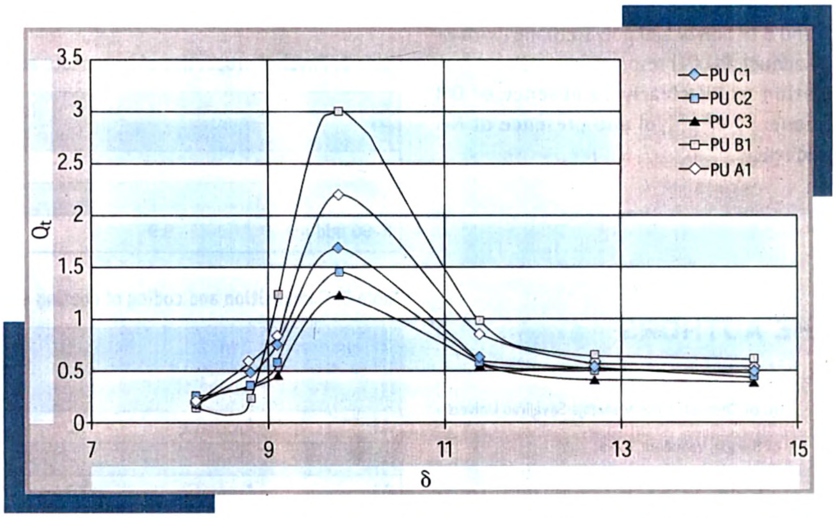

Figure 2: Plot of volume equilibrium of solvents (Q_t) versus solubility parameter of solvents (δ) with system A1, B1, C1, C2 and C3

Polyurethane with variations of NCO/OH ratio

Synthesis of polyurethane for coatings were carried out by reacting novel polyol with respective isocyanates (aromatic isocyanate, aliphatic isocyanate, R-60 isocyanate adducts) with or without catalyst at room temperature. The NCO/OH ratio variations were taken into account, as shown in *Table 3*. Then PU resin was diluted with suitable solvents to have viscosity for appropriate application of coating with brush on cleaned mild steel and tin panels. The coated panels were examined for impact resistance, scratch hardness, and pencil hardness, flexibility test, chemical resistance and adhesion test as per standard procedure.

Gel Permeation Chromatography shows a complete reaction

From GPC average molecular weight of polyol was found to be 963, which was very well comparable to the end group analysis value (hydroxyl value 231, Molecular weight 972) and with the expected theoretical value (936). The results indicate that the reaction of epoxy resin with ricinoleic acid was complete.

Chemical differences are visible with IR

From the IR spectrum of novel polyol (*Figure 1*) the characteristic peak of terminal epoxy group [6] was not observed at 920cm^{-1}.The disappearance of these peaks indicate the breakage of epoxy linkage and formation of secondary hydroxyl group, at 3400cm^{-1}.The double bond moieties in polyol were observed at a medium intensity peak 1635cm^{-1}. In the spectra of polymeric film the characteristic carbonyl stretching of urethane linkage was observed at 1735cm^{-1}, the absorption resulting from NH stretching and bending vibrations were observed at 3330cm^{-1} and 1560cm^{-1} respectively. IR spectra (*Figure 1*) are shown in A and B of polyol and polyurethane (with R-60 adduct, PU C1) respectively, indicate formation of PU clearly by absence of OH frequency of polyol and presence of NH frequency.

Experimental

Materials for inquiries

Castor oil (Jayant Oil Mills, Vadodara, India) was used after drying. Epoxy resin (DGEBA, Atul Industries, Valsad, India.) mol wt. 392, Triethylamine (Merck, USA), aromatic and alipahtic isocyanate adducts (Grand Polycoats, Padra, Vadodara, India) were used. The castor oil based polyol designated R60 in the study having hydroxyl equivalent weight 220 and having five hydroxyl groups per mole were supplied by Hardik Agencies, Ahmedabad, India and was used after drying in oven at 100°C for two days. Toluene diisocyanate (TDI Merck, USA)without further purification and dibutyltindilaurate (DBTDL, Merck, USA), a catalyst in polyurethane coating, were used as received.

Synthesis of novel polyol

Reactive novel polyol was synthesized by reacting castor oil derivative ricinoleic acid (2mole) having free carboxyl group with epoxy resin (1mole) in three necked round bottom flask equipped with nitrogen inlet and water condenser. 0.05mole of triethyl amine as a catalyst was added along with 100ml of dioxane in the flask. The reaction (*Scheme 1*) was continued at reflux temperature of dioxane for 2h. After completion of reaction dioxane was distilled out from the flask. At the end of reaction, a viscous liquid was collected in clean glass stoppered bottle. Physical properties of are shown in *Table 1*.

Preparation of R-60 adduct

1mole of dried R-60 resin was taken in a three necked round bottom flask, equipped with nitrogen inlet and mechanical stirrer. Whole assembly was kept in a thermostated water bath at 300°C. TDI (5mole) in 50ml. of toluene was added dropwise using dropping funnel and reaction mixture was stirred continuously for 5h. After completion of the reaction, the viscous liquid was collected in an airtight bottle. Physical properties of adducts are shown in *Table 2*.

Table 1: Physical properties of polyol

Polyol	Hydroxyl Value	Acid Value mg/KOH	Hydroxyl Equivalent Weight	Viscosity 30°C Brookfield Viscometer cp(5rpm)	Non volatile matter(%)
EpxR	231	2.3	243	13320	99.20

Table 2: Physical properties of isocyanate adducts

Adduct	Percent Free NCO content	Isocyanate equivalent weight	Specific gravity 30°C	Viscosity at 30°C by FC-B IV (s)
Aromatic adduct	12.5	336	1.02	210
Aliphatic adduct	16.5	255	1.05	175
R-60 adduct	9.9	425	1.35	325

Table 3: Composition and coding of coating system

Designation of coating system	Type of isocyanate adduct	RatioNCO/OH	Potlife at 30°C (min.)	Amount of polyol (g.)	Amount of isocyanate adduct (g.)
A1	Aromatic	1.0	240	24.3	33.6
A2	Aromatic	1.3	205	24.3	43.5
A3	Aromatic	1.7	150	24.3	57.12
B1	Aliphatic	1.0	360	24.3	25.5
B2	Aliphatic	1.3	390	24.3	33.15
B3	Aliphatic	1.7	420	24.3	43.35
C1	R-60	1.0	300	24.3	42.5
C2	R-60	1.3	255	24.3	55.25
C3	R-60	1.7	180	24.3	72.25
A1C	Aromatic	1.0	105	24.3	33.6
A2C	Aliphatic	1.0	210	24.3	25.5
A3C	R-60	1.0	135	24.3	42.5

Note: A1C, A2C, and A3C are catalyst system (DBTDL were added 0.05% w/w with their total composition

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Catalyst enhance drying characteristics

After application of polyurethane films the panels were kept in a vertical position for air-drying. Drying times were observed of all coated panel systems. Results indicate that catalyst increases the rate of crosslinking in all the cases as expected.

Higher NCO/OH ratio worsening flexibility

Flexibility of all the system panels was tested on tin panels by bending mendrel 1/8″ as per ASTM D622. Results are shown in *Table 4*, which indicates that system B of coated panels have good flexibility compared to coated panels with systems A and C. Because of more aliphatic nature of isocyanate adduct in system B, it provides flexible nature to the film. On the other hand system A coatings are more rigid due to aromatic nature of diisocyanate adduct. The results also indicate that the increase in NCO/OH ratios in systems A and C along with aromatic nature of isocyanate adduct increase the crosslinking density resulting into increase in rigidity as expected and hence flexibility decreases. Thus higher NCO/OH ratio gives poor results in flexibility test in all the systems.

Adhesion is extra ordinary

Adhesion test of coated materials was by crosshatch adhesion conducted according to ASTM D3359 method B to determine unacceptable adhesion. All systems show almost 100 % adhesion. This extra ordinary adhesion can be attributed to strong dipole-dipole interaction as well as H-bond formation possibility between the substrate and the adhesive coating which arises due to the presence of -NH, -CO and -O- groups in the systems. However in case of relative increase of NCO/OH ratio where there is high crosslinking, it becomes progressively more difficult for adhesive to interact with the substrates.

Higher density of crosslinking for good scratch, pencil hardness and chemical resistance

From the results in the *Table 4* it can be inferred that compare to systems A and B, system C has good hardness because of the combination of aromatic and aliphatic moieties in adduct, which provides higher degree of crosslinking and uniformity of network.

The results show that system A coated panel has good pencil hardness compared to systems B and C coated panels. As the NCO/OH ratio increases the pencil hardness also increases

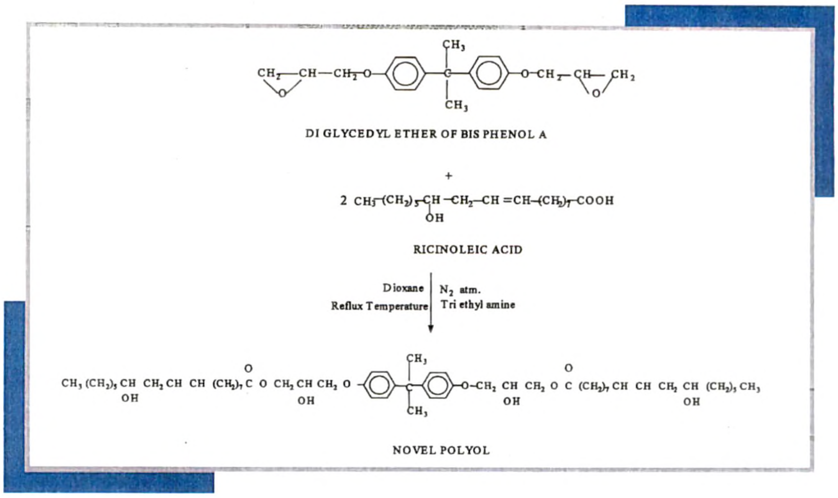

Table 4: Performance of coating properties

Compsition code	Adhesion crosshatch	Flexibility 1/8" bending mendrel	Impact resistance (lb. inch)	Scratch hardness (g.)	Pencil hardness
A1	P	P	200	3500	3H
A2	P	F	100	4000	3H
A3	F	F	150	4500	4H
B1	P	P	300	2000	1H
B2	P	P	350	2500	1H
B3	P	P	350	3500	1H
C1	P	P	350	4000	3H
C2	P	P	300	3500	3H
C3	F	F	200	3000	2H
A1C	P	P	200	3500	3H
A2C	P	P	300	2000	1H
A3C	P	P	350	4000	4H

P = Pass
F = Fail

Table 5: Chemical resistance of coated panels*

Coating compsition	Acid resistance 5% H_2SO_4	Alkali resistance 5% NaOH	Corrosion resistance 10% NaCl
A1	3	4	P
A2	4	5	P
A3	5	5	P
B1	2	3	P
B2	3	4	P
B3	4	5	P
C1	5	5	P
C2	5	6	P
C3	6	6	P
A1C	4	5	P
A2C	3	4	P
A3C	5	6	P

* 2 film partially cracked
3 loss of gloss
4 slight loss of gloss
5 protecting film unaffected
6 no efect
7 pass

Table 6 : Values of Vp, Qa, Mc, N and n of PUs.

System	Vp	Qa	Mc	N ×10^{-3}(mol/cm^3)	n ×10^{-4}(mol/g)
PU B1	0.3521	3.02	1305	0.782	3.83
PU A1	0.3870	2.18	1220	0.814	4.09
PU C1	0.4090	1.68	1047	0.952	4.77
PU C2	0.4485	1.44	662	1.500	7.55
PU C3	0.4875	1.23	553	1.830	9.04

in system A, B and C of coated panels. System of coated panels with catalyst show maximum hardness, because the catalyst increases the crosslink density compared to systems without using catalyst.

All the system panels were immersed in distilled water, 5% NaOH, 5% H_2SO_4 and 10% NaCl solution at room temperature. Results, shown in *Table 5*, indicate that all compositions of systems of dipped coated panels show no effect of water and also show good overall chemical resistance. However at higher NCO/OH ratio it shows better resistance even for acids, because it provides higher crosslinking density and allowing low permeation and diffusion of chemicals.

Many crosslinking points enhance swelling resistance

Swelling study of polyurethane systems A1, B1, C1 and C1, C2, C3 was carried out. The equilibrium degree of swelling (Q) which is reciprocal of volume fraction of polymer in swollen state (Vp), was calculated from the swelling data using the relation $Q=1/V_p$ and was plotted against d of various solvents. From the plot (*Figure 2*) dioxane (δ =9.8) gives the maximum value of Q for all the systems studied. The volume fraction of polymeric film of each system V_p in the swollen sample, molecular weight between crosslinks M_c (the average molecular weight between two crosslink points is a direct measure of crosslink density and was computed by well known Flory-Rehner equation), degree of crosslinking (n) and number of chains per unit volume (N) were also calculated by the respective equations reported earlier by us [7, 8].

The values of V_p, M_c, N and n for all samples studied in dioxane are summarised in *Table 6*. It can be seen from the table that V_p decreases with increase in chain length [7] of adduct used in the system. This means that aliphatic isocyanate adduct having long chain compared to aromatic isocyanate adduct and R-60 isocyanate adduct used in the system, so that the distance between two crosslink points increases with increase in chain length of adduct, the available free volume does also increase and hence Vp decreases. The increase in chain length increases the distance between two crosslink points resulting into less dense crosslinked structure and therefore Mc increases. In the case where NCO/OH ratio increases the distance between two crosslinks points decreases [8].The system B having aliphatic adducts gives maximum sorption of solvents in given systems. While the system C shows lower sorption compared to systems A and B, curing with R-60 adduct show lower sorption in curve, indicating that the chain length of adduct is shorter compared to other system using aromatic and aliphatic isocyanate adducts. Molecular weight between two crosslink points (M_c) of system C is lower compared to those of A and B indicating that the chain length of isocyanate adduct is highly crosslinked with polyol, so that sorption of solvents is very less in system C compared to A and B. As the NCO/OH ratio in system C increases from 1 to 1.3 to1.7 we find that higher ratio gives minimum sorption compared to lower ratio in all the systems. ■

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Result at a glance

All coating composition systems reported in this paper show
- good scratch resistance and
- good adhesion on substrate.

Use of catalyst enhances the mechanical properties of coating systems at the cost of adhesion.

The polyurethane systems containing aromatic isocyanate adduct show more brittleness and less impact strength than their aliphatic isocyante adduct.

Systems containing castor oil based adduct (R-60 isocyanate adduct) have
- good impact strength,
- good scratch resistance and
- excellent chemical and water resistance, compared to aromatic isocyante adduct.

Drying time of catalyst containing coating system is lower than one without catalyst.

Swelling studies infer that coating system containing R-60 isocyanate adduct have less sorption of solvent compared to system containing aliphatic and aromatic isocyanate adducts.

REFERENCES

[1] Saunders JH, Frisch KC. Polyurethane Chemistry and Technology, Interscience, New York, 1962.
[2] Patton TC, Ehrlich A, Smith M K. Rubber Age, 80 (1960), p 639.
[3] Saxena PK, Shrinivasan SR, Hrouz J, Ilarsky M. J Appl Polym Sci. 42 (1992),p 1343.
[4] Henry Lee, Neville K. Hand Book of Epoxy Resin, McGraw Hill Inc U.S.A. 1976,p23-2.
[5] Somani K, Parmar R, Kansara S, Patel N. Int. J Polym Mater (accepted).
[6] Haslam J, Willis HA, Squirrel DCM. Identification and Anlaysis of Plastic, Butterworth group, second edition, 1972, p526.
[7] Bhardwaj V, Somani K, Kansara S. J Macromol Sci. Pure and Appl. Chemistry 39, (2002), p 115.
[8] Ajithkumar S, Patel NK, Kansara SS. Polymers Gels and Networks 6 (1998), p 137.

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HIGH SOLIDS POLYURETHANE COATINGS FROM CASTOR-OIL-BASED POLYESTER-POLYOLS

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High solids polyurethane (PU) coating formulations were developed by reacting three different castor–oil–based polyester–polyols with aromatic as well as aliphatic isocyanate adducts in different NCO/OH ratios. Structure of polyurethane resins was confirmed by FTIR spectroscopy. The molecular weight between two crosslinks (Mc) and solubility parameter of the samples (polymer films) were determined by a swelling method. The polyurethane resins were coated on test panels and tested for their flexibility, scratch hardness, cross-hatch adhesion, impact, pencil hardness and solvent resistance as per standards. The effect of catalyst, structure of isocyanate and flexibility of polyols on the resulting polyurethanes was evaluated. Thermal stability of these polymers was determined by thermogravimetric analysis (TGA).

Keywords: high solid coatings, castor oil, polyurethane coating, polyester-polyol

INTRODUCTION

Over the last few years, reduction of organic solvents usage [1] has been a matter of great importance for paints and their application

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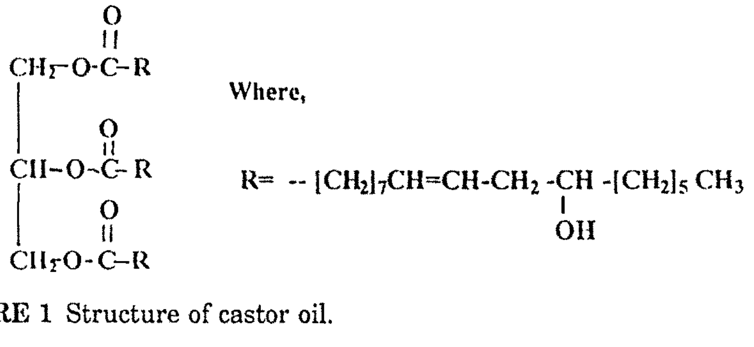
technologies because of the restrictions imposed by environmental pollution agencies and users all over the world. This has caused a shift in attention from conventional organic solvent–based coatings to water–borne powder coating, radiation–cured coating and high solids coatings. In recent years, high solids coatings are gaining importance to comply with keeping the environment clean. Among these, polyurethanes have good mechanical and chemical properties. Castor–oil–based polyurethane has been extensively studied as a coating and in network synthesis [2–5]. Varying a chain length of prepolymer with low viscosity and 100 percent solids content varies the crosslink density of network over a wide range. In general, coating with 70% or above solids can be considered as high solids coating [6]. Castor–oil–based polyols have great potential to be good reactive diluents.

In the present study, an attempt is made to prepare the high solids PU coatings from castor–oil–based polyols. Castor oil is a triglyceride of fatty acids, whose main constituent is ricinoleic acid, extracted from Ricinus Communis [7–9], and is frequently utilized as a polyol in the synthesis of polyurethanes [10]. Polyurethanes made from a variety of drying oils have been known for many years [11]. Low viscosity castor oil derivatives were developed to improve flexibility and impact strength. The structure of castor oil is shown in Figure 1.

EXPERIMENTAL

Materials and Methods

Ricinoleic acid received from Jayant Oil Mills, Vadodara, India, was used after vacuum drying. Ethylene glycol (EG), Diethylene glycol (DEG), Triethylene glycol (TEG) were received from Merck, USA and used as received. Dibutyl tin dilaurate (DBTDL) to be used as a catalyst was procured from Fluka and used without further purification. Aromatic and aliphatic isocyanate adducts were received from Grand Polycoats Co. Pvt. Ltd. Padra, Vadodara, and were characterized for



$$R = -[CH_2]_7CH{=}CH{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}[CH_2]_5CH_3$$

FIGURE 1 Structure of castor oil.

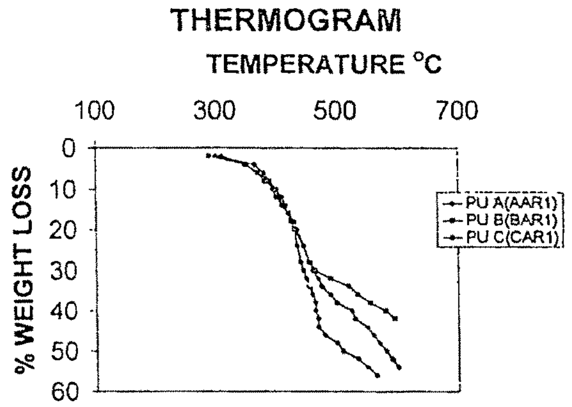


FIGURE 3 Thermogram of PU A (AAR1), PU B (BAR1), and PU C (CAR1).

Thermal Analysis

From TGA (in Figure 3) we can conclude that two stage degradations might have occurred, breaking of urethane link starts at ~260°C leading to the formation of CO_2, alcohols, amines, aldehydes, CO, etc. [14–15]. The second stage, which is not quite distinct, may be due to the polyol decomposition that occurred at ~450°C. Since polyols used in this study are based on castor oil, the main chain cleavage may result in the formation of 10-undecanoic acid and heptanal as evident by the thermal degradation of ricinoleic acid [16], which is the main constituent of castor oil. The same two-stage decomposition behavior was observed in all our polyurethanes. The activation energy of these polymers was evaluated using the well-known Broido's method. Initial Decomposition Temperature (IDT) and activation energy of polyurethanes are shown in Table 7.

CONCLUSIONS

High solids polyurethane coatings were made successfully from castor–oil–based polyols. Various polyurethane coating compositions with different ratios of NCO/OH, type of polyol, type and amount of

TABLE 7 Activation Energy of Polyurethane

System	IDT°C	Ea (KJ/mole)
PU A (AAR1)	290	71.32
PU B (BAR1)	300	79.40
PU C (CAR1)	310	94.0

Impact Resistance and Scratch Hardness

Impact resistance of dried film of all the systems was tested on mild-steel panels by a tabular impact tester. In this method, an indenter of 0.5 kg, was dropped from a certain height until the film cracked. The maximum height of instrument is 300 cm. The results of this test are shown in Table 4.

The results show that when the indenter hit panels having higher NCO/OH ratio, particularly from maximum height, some signs of crack and film detachment were observed. Comparison of the system containing aliphatic and aromatic isocyanate adducts, particularly at higher NCO/OH ratio (1 and 1.3), shows low impact strength, which may be due to the rigidity of the aromatic structure of the adduct.

Scratch hardness of dried films of all the systems was measured on panels with a mechanically operated "Sheen" scratch hardness. The results infer good scratch resistance. This may be due to high crosslink density.

Pencil Hardness

A coated panel was placed on a flat horizontal surface and a pencil was held at an angle 45° to the film. The pencil was pushed away from the operator in a 1/4″ stroke. This process was started with the hardest level pencil and was repeated with progressively softer pencils until the pencil did not cut the film. The pencil, which did not cut the film, denotes its hardness. The hardness of test formulations, measured at 27°C, is reported in Table 4.

The results indicate that irrespective of the type of glycol at given NCO/OH ratio, the aromatic system shows better pencil hardness compared to the aliphatic system, and improves as the NCO/OH ratio increases in the aromatic system. This may be due to increase in the rigidity provided by a more crosslinked structure.

Water and Chemical Resistance

All of the experimental polyurethane coating compositions showed no effect on the films when immersed in water for specified time period. It clearly reflects the characteristic water resistance property of the polyurethane coatings. The acid and alkali resistance of the polyurethane coatings was found to be good. However, coating compositions with higher NCO/OH ratio showed better acid and alkali resistance due to higher crosslink density. The results are shown in Table 5.

Mechanical Properties

Flexibility Test and Adhesion Test

Flexibilities of all the systems were tested on tin panels by bending 1/8″ mandrel by ASTM D 622. The results are shown in Table 4.

Adhesion of coated materials was tested by crosshatch, according to ASTM D 3359 method. The test coatings were cut through to the substrate using a sharp razor blade to give parallel lines 2 mm apart, forming a 10 × 10 block grid. The test surface was then brushed lightly to remove loose particles. Adhesive tape (Scotch brand 810 Magic Tape or 3 M adhesive tape) was pressed onto the scribed area and then pulled off rapidly at 180° angle within 60 seconds. The scribed area was inspected visually with an illuminated magnifer to determine percentage of coating removed.

Results show that all panels have almost 100% adhesion in all the systems, i.e. film was not removed from the coated panels. This indicates that the system has good adhesion properties.

TABLE 4 Adhesion, Scratch Hardness, Flexibility, Impact Resistance and Pencil Hardness of the Coating Films

Composition code	Adhesion (cross-hatch)	Flexibility 1/8″ bending mendrel	Scratch hardness gms.	Impact resistance lb. in.	Pencil hardness®
AAL1	P	P	1500	300	2H
AAL2	P	P	2000	100	2H
AAL3	P	F	2000	100	1H
AAR1	P	P	2500	200	3H
AAR2	P	F	3000	50	3H
AAR3	F	F	3500	50	4H
BAL1	P	P	2000	300	1H
BAL2	P	P	2000	200	1H
BAL3	P	F	2500	200	1H
BAR1	P	P	2500	200	2H
BAR2	P	P	3500	50	4H
BAR3	F	F	3500	50	5H
CAL1	P	P	2500	300	1H
CAL2	P	P	3000	200	1H
CAL3	P	P	3000	200	1H
CAR1	P	P	2500	200	2H
CAR2	P	P	3500	50	4H
CAR3	P	F	3500	50	5H

® 6H>5H>4H>3H>2H>1H>H>HB>1HB>2HB>3HB>4HB>5HB>6HB

TABLE 3 Composition and Physical Properties of Polyurethane Coatings

Designation of coating composition code	Type of isocyanate adduct	Amount of polyol gms.	Amount of isocyanate adduct gms.	Ratio NCO/OH	Viscosity® by FC B-IV secs. at 30°C	Pot life at 30°C hrs.	Drying properties		
							Surface drying min.	Tack free drying hrs.	Hard drying
AAL1	ALI	41.8	58.2	1	21	4.5	25	3	O/N
AAL2	ALI	35.6	64.4	1:3	27	4.5	35	3	O/N
AAL3	ALI	29.7	70.3	1:7	34	4.5	35	2.5	O/N
AAR1	ARO	35.2	64.8	1	31	4.0	20	2	O/N
AAR2	ARO	29.5	70.5	1:3	42	3.5	15	2	O/N
AAR3	ARO	24.3	75.7	1:7	57	3.0	15	2	O/N
BAL1	ALI	45.3	54.7	1	25	3.0	30	3	O/N
BAL2	ALI	38.9	61.1	1:3	38	6.0	30	2.5	O/N
BAL3	ALI	32.8	67.2	1:7	49	5.5	35	2.5	O/N
BAR1	ARO	38.6	61.4	1	41	5.5	20	2.5	O/N
BAR2	ARO	32.6	67.4	1:3	64	5.0	20	2	O/N
BAR3	ARO	27.0	73.0	1:7	73	4.5	15	2	O/N
CAL1	ALI	46.9	53.1	1	38	4.5	40	4	O/N
CAL2	ALI	40.5	59.5	1:3	50	7.0	45	4	O/N
CAL3	ALI	34.2	65.8	1:7	62	6.5	50	5	O/N
CAR1	ARO	46.9	53.1	1	42	6.0	15	2	O/N
CAR2	ARO	40.5	59.5	1:3	65	6.0	15	2	O/N
CAR3	ARO	34.2	65.8	1:7	79	5.5	10	2	O/N
AAL1$_c$	ALI	41.8	58.2	1	21	3.5	15	2.5	O/N

ALI–Aliphatic Isocyanate adduct
ARO–Aromatic Isocyanate adduct
AAL1c–The composition with 0.05% Dibutyl tin di laurate (DBTDL) catalyst
® 75% solids in xylene: MEK, 1:1 by weight., O/N Over Night

adducts, aliphatic isocyanate adducts, methyl ethyl ketone(MEK), and xylene as per the compositions shown in the Table 3. These coatings were applied on test panels and were then allowed to dry at room temperature for seven days to ensure complete curing.

Characterizations of Polyurethane Coatings

The polyurethane coatings were characterized for various physical properties such as viscosity, pot life and drying time as per BIS method [12]. The coating films were characterized for properties like adhesion, flexibility, hardness, impact resistance, chemical resistance and solvent resistance by standard procedures. The coatings were also characterized by IR spectroscopy. The films were characterized for their swelling behavior. Their thermal properties were studied by TGA.

RESULTS AND DISCUSSION

Viscosity and Pot Life

The viscosity data (Table 3) of the polyurethane coatings reveal that the viscosity of polyurethane coating compositions made from polyol A, B, and C, respectively, were quite low as compared to conventional polyurethane coatings having similar solids content. For a given NCO/OH ratio, the viscosity of the coating based on polyol A is lower than the remaining compositions based on polyols B and C. This could be attributed to the lower molecular weight of polyol A. Polyurethane coating composition with polyol A as well as the composition with catalyst dibutyl tin dilaurate (DBTDL) showed shorter pot lives compared to other compositions. This is a typical behavior of systems with higher number of functional groups.

Drying Properties

Times of surface dry, hard dry and tack free of various sets are reported in Table 3 as they give indications of drying time of the film after its application. The results show that polyol A dried faster than polyol C for a given isocyanate adduct and NCO/OH ratio. The coating compositions with aromatic isocyanate adduct as curing agent showed faster drying times, may be because of higher reactivity of their NCO groups with OH groups. The drying times of the coating films are also shortened by catalyst.

TABLE 1 Physical Properties of Isocyanate Adducts

Type of isocyanate adduct	Percent free isocyanate content	NCO equivalent weight	(%) Solid	Specific gravity 30°C	Viscosity 30°C by FC- B IV secs.
Aromatic	12.5	336	75	1.02	210
Aliphatic	16.5	255	75	1.05	175

their physical properties shown in Table 1. Solvents xylene, methyl ethyl ketone were received from Suvidhinath Laboratory, Vadodara, and used after distillation and dried with molecular sieves (4Å).

Preparation of Polyester–Polyols

Polyester–polyols were synthesized at 210–230°C in a round–bottom flask with thermocouple and nitrogen purge by dry process (fusion process). The polyester–polyols were synthesized by reacting ricinoleic acid with EG, DEG, and TEG, respectively. Conversion of the polyester–polyols was monitored by determining acid number with respect to time. The compositions and physical properties of polyols made as above are given in Table 2. Polyol A, Polyol B and Polyol C represent the polyester–polyol prepared reacting ricinoleic acid with EG, DEG, and TEG, respectively.

Preparation of Polyurethane Coatings

Various sets of polyurethane coatings were prepared from polyester–polyols by adding the required amount of aromatic isocyanate

TABLE 2 Compositions and Physical Properties of Castor–Oil–Based Polyester–Polyols

Designations of polyols	Hydroxyl value mg. KOH/gm	•Hydroxyl equivalent weight gm	Viscosity at 30°C FC B-IV secs.	Percentage non volatile matter (%NVM) @
Polyol A	306	183	124	99.1
Polyol B	265	210	137	99.5
Polyol C	249	225	168	99.30

• Hydroxyl equivalent weight = 56100/OH value

@ %age N.V.M.—Non-volatile matter, determined after keeping at 120°C for 2h under vacuum isocyanate adduct were studied for their physical and film performance properties. The study reveals that: (i) the presence of catalyst shortens the drying times of polyurethane coatings; (ii) lower amount of curing agent gives better flexibility and impact resistance, higher amount of curing agents gives better scratch hardness, chemical and water resistance; (iii) the coating films containing aliphatic isocyanate curing agents gave better flexibility and impact resistance than the coatings containing aromatic adduct.

From the study we can conclude that the high solids polyurethane coating composition with castor–oil–based polyols and Aliphatic Isocyanate adduct (NCO/OH 1.3) and the one with Aromatic Isocyanate Adduct (NCO/OH 1) gave optimum film performance.

REFERENCES

[1] Dekker, G. H. (1999). *Paintindia*, **49**(9), 117.

[2] Saunders, J. H. and Frisch, K. C. (1962). *Polyurethane Chemisrty and Technology*, Interscience, New York.

[3] Patton, T. C., Ehrlich, A. and Smith, M. K. (1960). *Rubber Age*, **80**, 639.

[4] Sperling, L. H., Thomas, D. A., Loreny, E. J. and Nagel, E. J. (1975). *J. Appl. Polym. Sci.*, **19**, 2225.

[5] Sperling, L. H. (1974). *Ed. Recent Advances in Polymer Blends, Crafts and Blocks*, Plenum, New York.

[6] Singh, Dhirendra (1993). *Paint India*, 49(9), 47.

[7] Othmer, Kirk (1979). *Encyclopedia of Chemical Technology*, 4th edition, vol. 5, John Wiley and Sons, Inc., New York.

[8] Naughton, F. C., Duneczky, F., Iwenson, C. R., Kroplinski, T. and Copperman, M. A. (1979). in Kirk-Othmer *Encyclopedia of Chemical Technology*, vol. 5, John Wiley and Sons, New York.

[9] Johnson, R. W. and Iritz, E. (1989). *Fatty Acids in Industries Process Properties, Derivatives and Applications*, Marcel Dekker, New York, p. 13.

[10] Saxena, P. K., Shrinivasan, S. R., Hrouz, J. and Ilarsky, M. (1992). *J. Appl. Polym. Sci.*, **42**, 1343.

[11] Schnider, W. J. and Gast, L. E. (1969). *J. American Oil Chem. Society*, 114.

[12] Indian Standard Specification: Methods of Sampling and Test for Resins for Paints: **IS 354**(1981).

[13] Flory, P. and Rehner, J. (1943) *J. Chem. Phy.*, **11**, 521.

[14] Jellinek, H. H. G., Dhankle, S. R. (1983). *Degradations and Stability of Polymer*, Vol. 1, Ch. 2, Elsevier, New York, p. 91.

[15] David, D J., Staley, H. B. (1974). *Analytical Chemistry of Polyurethanes*, Vol.XVI, Part III, High Polymers, p. 365.

[16] Saunders, J. H., Frisch, K. C. (1963). *Polyurethane Chemistry and Technology*, Part 1, Chemistry of High Polymers, Vol.XVI, Interscience Publications, Ch 2, p 51.