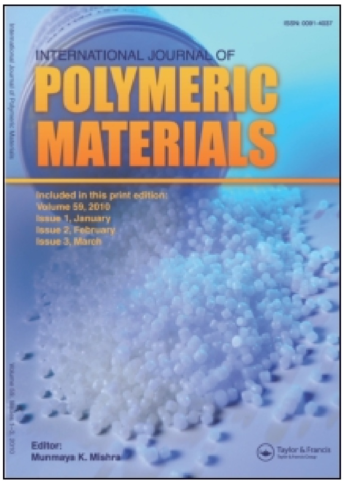

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HIGH SOLIDS POLYURETHANE COATINGS FROM CASTOR-OIL-BASED POLYESTER-POLYOLS

Keyur Somani[a]; S. Kansara[a]; R. Parmar[b]; N. Patel[c]
[a] Department of Chemistry, Vadodara, India [b] Department of Industrial Chemisrty, ISTAR, V.V.Nagar, India [c] Department of Chemistry, V.V.Nagar, India

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Keyur Somani
S. Kansara
Department of Chemistry, Maharaja Sayajirao University,
Vadodara, India

R. Parmar
Department of Industrial Chemisrty, ISTAR,
S.P. University, V.V.Nagar, India

N. Patel
Department of Chemistry, S.P. University, V.V.Nagar, India

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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Address correspondence to Keyur Somani, Department of Chemistry, Maharaja Sayajirao University, Vadodara-390 002, India. E-mail: sskansara@rediffmail.com

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

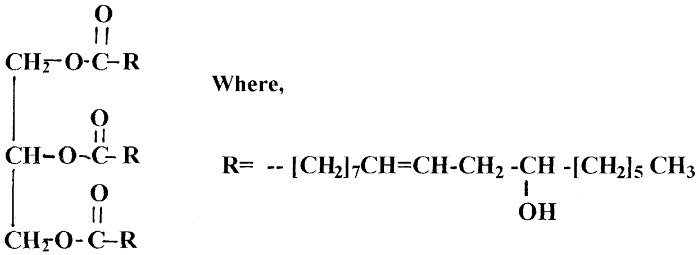

FIGURE 1 Structure of castor oil.

TABLE 1 Physical Properties of Isocyanate Adducts

Type of isocyanate adduct	Percent free isocyanate content	NCO equivalent weight	(%) Solid	Specific gravity 30℃	Viscosity 30℃ 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℃ 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℃ 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℃ for 2h under vacuum 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 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

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

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.

TABLE 5 Chemical Resistance and Corrosion Resistance of the Coating Films

Coating compositions code	Acid resistance 5% H_2SO_4 solution	Alkali resistance 5% NaOH solution	Corrosion resistance 10% NaCl solution
AAL1	2	4	P
AAL2	3	5	P
AAL3	5	3	P
AAR1	4	5	P
AAR2	5	2	P
AAR3	5	3	P
BAL1	1	2	P
BAL2	2	5	P
BAL3	3	5	P
BAR1	4	2	P
BAR2	4	3	P
BAR3	5	2	P
CAL1	1	4	P
CAL2	4	5	P
CAL3	4	5	P
CAR1	2	4	P
CAR2	4	5	P
CAR3	5	5	P

0–film completely removed
1–film cracked and partially removed
2–film partially cracked
3–loss of gloss
4–slight loss of gloss
5–film practically unaffected
P–pass
F–fail

Swelling Measurements

Swelling of polyurethane A (AAR1), B (BAR1) and C (CAR1) with NCO/OH ratio 1, aromatic adduct were studied. Films of each polymer network of known dimensions were cut and immersed in solvents with increasing order of solubility parameter δ from 8.2 to 14.5 $(\text{cal/cm}^3)^{1/2}$.

The solvents used were cyclohexane (8.2), xylene (8.8), ethyl acetate (9.12), dioxane (9.8), n-butanol (11.4), ethanol (12.7) and methanol (14.8). The swelling experiments yielded data regarding volume equilibrium, and degree of swelling (Q). The molecular weight between crosslink points was calculated. The swelling curve is shown in Figure 2.

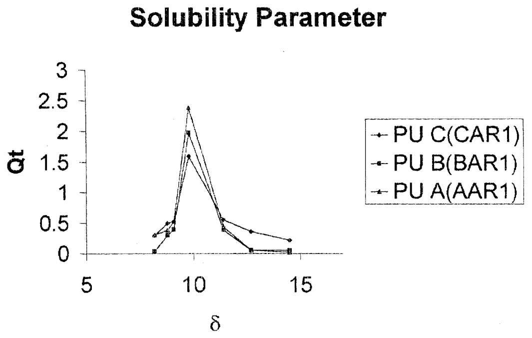

FIGURE 2 Plot of volume equilibrium of solvents (Q_t) vs. solubility parameter of solvents (δ).

The swelling equilibrium (Q), which is reciprocal to the volume fraction of polymeric film in swollen state (V_p), was calculated from the swelling data using the relation $Q = 1/Vp$ and was plotted against δ of various solvents.

The average molecular weight between two crosslink points, which is a direct measure of crosslink density, was measured from the well–known equation of Flory and Rehner [13], the Mc increases with increase in the chain length of polyol. For a given crosslink density, the sorption decreases with an increase in the chain length of polyol. Molecular weights of polyurethanes AAR1, BAR1, CAR1 are shown in Table 6.

IR Spectra

In the spectra of polymeric film, the characteristic carbonyl stretching of urethane linkage was observed at 1735 cm^{-1}. The absorption resulting from N-H stretching and bending vibrations was observed at 3330 cm^{-1} and 1560 cm^{-1} respectively. The double bond in the polyols moieties was observed as a medium intensity peak at 1635 cm^{-1}. IR spectra of polyol B and polyurethane B(BAR1) were submitted to the editor but are not reproduced here.

TABLE 6 Molecular Weight Between Two Crosslink Points of PU

Polyurethenes film	Molecular weight between two crosslinks points Mc
PU A(AAR1)	749
PU B(BAR1)	1124
PU C(CAR1)	2473

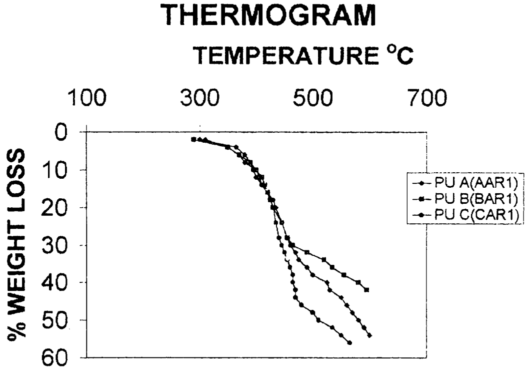

FIGURE 3 Thermogram of PU A (AAR1), PU B (BAR1), and PU C (CAR1).

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

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.

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