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Research Article

Studies on Polyurethane Coating Based on Modified Castor Oil, Commercial Acrylate Polyols and Polysiloxane

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Abstract: The polycondensation reaction of commercial acrylate polyols (AP), 2,4-Tolylene diisocyanate (TDI) and modified castor oil (MCO) [Castor oil-succinic anhydride-pena erythritol reaction product] at various proportions was carried out and afforded polyurethanes (PUs). To neutralize end –NCO groups, these PUs reacted with monocarbinol terminated polydimethyl siloxane (MTPS). The resultant PU coatings were applied on MS steel panels at room temperature. All the PU coatings were characterized by physical, chemical and mechanical properties.

Keywords: Polyurethane, castor oil; Acrylated polyols; Diisocyanate; Polysiloxanel; MS steel panel; Drying time and mechanical properties chemical resistance.

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1. Introduction

The plant oils received interest to develop eco-friendly polymeric materials like composites and coatings [1,2]. These oils were employed to develop polyurethane coatings as renewable resources [35].

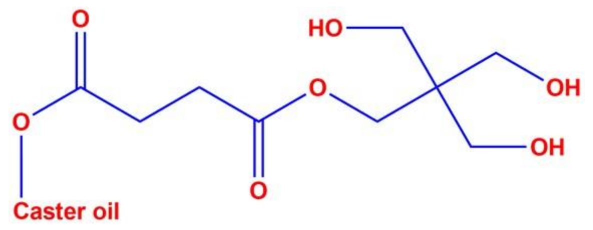
The oils were mostly, castor oil, soybean oil and linseed oils are important as starting material. More particularly the castor oil is trifunctional, i.e. presence of unsaturation, hydroxy and fatty ester groups in its molecular structure. So, it can be modified into several products. The review on the chemistry of castor oil suggested number of derivatization of castor oil into many industrial products [6]. Several scientists [7-12] developed the PU coatings from polyols based on various modifications of plant oils and some other additives to enhance the mechanical properties [7-24].

The PU coatings based on industrial polyols are mainly manufactured today. Some of polyols are based on acrylic, polyester and epoxy resins. They afford excellent properties of end products. The present author thought to introduce the branched polyols of castor oil into industrial polyols and polysiloxane for obtaining novel PU coatings. This may enhance the properties of PUs upto some extent. Thus the present paper comprises in extention of our previous work [25]. The PU formation by using aromatic diisocyanate i.e. 2,4-Tolylene diisocyanate is shown below.

2. Materials and Methods

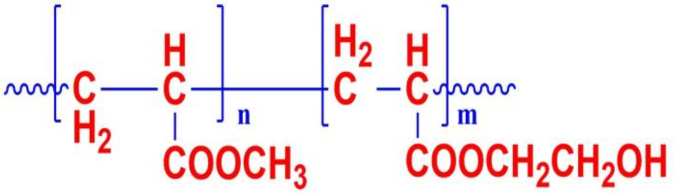
Modified castor oil (MCO) was prepared by reaction of castor oil with succinic anhydride / pentaerythritol followed by method reported in literature [7].

Its are:

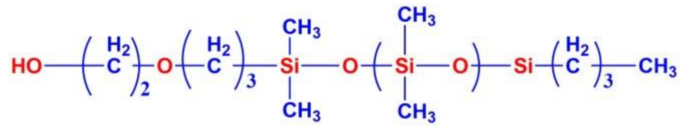
Specification of Modified castor oil (MCO)	
Mol. Wt.	2010 gm/mole
Hydroxy value	235 Mg KOH/gm
Viscosity at RT	235 MPas.
Molecular structure	

Following commercial acrylate polyols (AP) with their specification are procured from local market.

Table-1 Commercial acrylate polyols (AP)

Sr. No.	**Trade name**	**Solvent**	**Viscosity at RT Cps**	**Hydroxy value mg KOH/g**
A	Replakryl-927	Xylene	25-34	45-50
B	Replakryl-928	Xylene	17-27	50-55
C	Replakryl-929	Xylene/ Cellulose acetate	27-34	90-95
Their General structure				

2,4-Tolylene diisocyanate (TDI) was purchased as pure grade and used directly. All other chemicals used were of analytical grade. Monocarbinol terminated Polydimethyl Siloxane (MTDS) was obtained from nearest industry.

Specification of Monocarbinol terminated Polydimethyl Siloxane (MTDS)	
Product code	MCR-C18
Viscosity	60-140 cps
Mol. Wt.	5000 gm/mole
Density	0-97 gm/ml
Molecular structure	

All other chemicals used were of pure grade.

2.1. Preparation of polyurethane coatings

Various proportions (Table-I) of MCO : Polyoles were mixed in appropriate amount of butyl acetate solvent. Then in the next step the MCO: polyol and TDI (1:2 mole) were charged into 500 ml four necked round bottom flask arranged with a stirrer, thermometer, condenser with $CaCl_2$ guard tube and N_2 inlet gas, around 0.15% of DBTDL catalyst was added to mixture and warmed to 60-70°C for an hour with good mechanical stirring. The reaction progress was determining unreacted NCO group by dibutylamine back titration method [26].

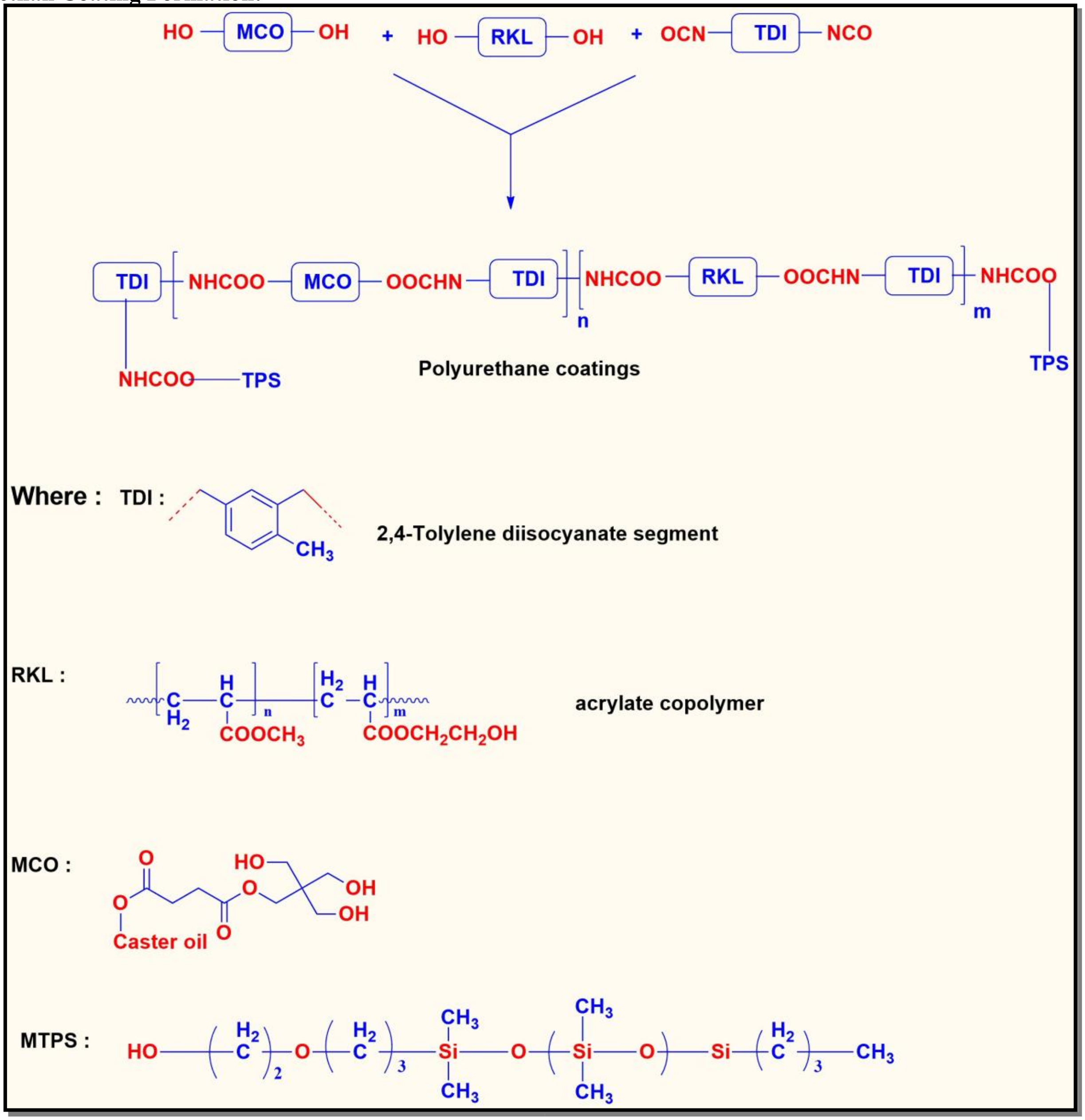
In the 2nd step MTDS (20% in butyl acetate) was added drop wise (at 60°C) and the reaction continued under stirring for further 1 hour at the 0.1 wt% NCO group, the temperature was raised to

80°C for 15 minute to expel residual NCO group. The reaction scheme is as follow,

Sample to be analysed was coated on to MS test panel of standard size (15 cm x 5 cm) as follow: (ASTM D4147-93 method)

An excess of prepared PU coatings sample was placed at the end of the MS steel panel and by taking a K-Bar rod (No. 5) applicator drawn across the substrate panel with uniform pressure and excess coating material pushed off through edge of panel. The panel allowed curing at room temperature for at least 24 hrs before any physical, chemical and mechanical testing.

Polyurethan Coating Formation:



2.2. Measurements

a) Infrared spectra of PUs were scanned on FTIR analyser.
b) The physical parameters like Non-volatile content (%), colour and viscosity of all uncured PUI coationg was measured by Ford cup B IV at 30°C ± 1°C in seconds.
c) Coating thickness and drying time were measured duly.
d) Following mechanical properties of all PUs coats were evaluated against ASTM standard mention.

Properties	**ASTM standard**
Flexibility [by conical mandrel(1/4")]	D522-939
Adhesion	D3395-95a
Scratch hardness	D3363-92
Impact resistance	D2794
Pencil hardness	D3363

Table-2: Composition of components for synthesis of polyurethane coatings

Composition of polyols (MCO : AP)	Total Hydroxy value per 100 g Polyols	Mole of -OH	TDI Mole	DBTDL % catalyst	Viscosity by Cup flow in seconds	Designation of coating sample
10:90	2800	0.05	0.06	15	130	TCA1
20:80	5100	0.092	0.11	15	138	TCA2
30:70	7500	0.134	0.15	15	150	TCA3
10:90	3000	0.0535	0.63	15	160	TCB1
20:80	5400	0.096	0.11	15	166	TCB2
30:70	7800	0.14	0.16	15	171	TCB3
10:90	3200	0.057	0.65	15	182	TCC1
20:80	6000	0.107	0.12	15	185	TCC2
30:70	8500	0.15	0.17	15	191	TCC3

Table-3: Mechanical properties of PU coatings*

Sample Code	Scratch hardness gms	Impact hardness lb/inch	Pencil hardness	Flexibility 1/8 mendrol	Cross hatch adhesion	DFT Microns (µ)
TCA1	1400	P	2H	P	P	19
TCA2	1600	P	4H	P	P	20
TCA3	2050	P	5H	P	P	21
TCB1	1500	P	3H	P	P	21
TCB2	1700	P	4H	P	P	21
TCB3	2100	P	5H	P	P	22
TCC1	1700	P	4H	P	P	23
TCC2	2000	P	4H	P	P	24
TCC3	2300	P	5H	P	P	24

P = Pass DFT : Dry film thickness

* (i) Non-volatile content in all coating in between 50 to 56 %.
(ii) Drying time for all coating in between 2 to 3 minutes.

Table-4: Chemical and corrosion resistivity of PU coatings

Sample Code	Acid resistance 5% HCl	Alkali resistance 5% NaOH	Corrosion resistance 5% NaCl	MEK Double Rab
TCA1	3	3	3	60
TCA2	4	4	3	70
TCA3	4	4	3	80
TCB1	3	3	3	70
TCB2	4	4	3	75
TCB3	4	4	4	85
TCC1	3	3	4	75
TCC2	4	4	4	80
TCC3	4	4	4	90

3. Results and Discussion

The obtained polyurethane coatings as per composition shown in Tables-2 and 3 were viscous brownish yellow liquids with viscosity 1250 to 4790 Cps. Their density, drying time and dry film thickness are also shown in Table-3. Drying time i.e. Set to touch and dry- hard are differ as depending upon the compositicy of polyols. The coating dry film thickness (DFT) was measured with Vernier Calipers. The values are in the range of 21 to 26□.

The IR spectra (not shown) of all the PUs coatings are almost identical. All the spectra comprise the bands due to MCO,AP and TDI segments. Only new bands appeared at 3421-3447 and 1721 due to formation of urethane linkage (NHCOO).

Adhesion test (cross hatch) achieves adherat strength of the PU coating film. A criss-cross pattern with five cuts in each direction was carried out. The adhesity tap was put on grid and take away over 180 °C angle. The grid area was measured. The results (Table-4) show that all the PU coating samples good adhesion to mild steel substrates.

Flexibility of all the coatings was tested on tin panels by bending 1/8" mandrel by ASTMD 934. The results are very good and shown in Table-4.

The impact resistance of all dried PU coating was tested on MS panels by a tubular impact tester. In whivh an indenter of ½ kg was dropped from fixed height until the film cracked. The results are shown in Table-4. The results indicate that all the coating systems have good impact resistance. The resultant scratch hardness of dried film of all PU coating (Table-4) also is excellent. The higher properties of MCO coating have higher value.

The coating hardness was estimated by a QHQ type pencil hardness apparatus. The pencil was first installed in the hardness tester, which was pushed through the coating at 45° to check marking was left on coating. The pulleys tighten by hand fingers and handle more at 5 cm/s speed. Initial with hardest 10H pencil were tested in order to decrease hard pencil. i.e.8H,5H,4H,3H,2H,1H and H. Each pencil was moved in unit direction coating the pencil tip did not scratch the surface of PU coatings. The results at present PU coating are shown in Table-4. The results indicate that all coatings have excellent Pencil hardness.

The chemical properties of all the produced PU coatings are presented in Table-3. The results of MEK rub test show excellent MEK resistance.

The chemical and corrosion resistance of all sets is very good. This may be attributed to high cross linking density between MCO and polyols with diisocyanate.

Thermogravimetric analysis of all the cured samples (taken from excess material at the time of coating on mild steel panel) is presented in Table 6. The interpretation of TG thermogram (not shown) and data reveals that the cured films are stable upto 230°C. The samples starts their degradation around 230-240°C and degrade rapid upto 500°C and final loss upto 90% around 600°C. The initial degradation is mainly due to the decarboxylation of urethane linkage (NHCOO → -CO_2). Then further stage of degradation might be due to Polyol decomposition that exist around 400 °C. The result shows that overall thermal stability of cured films is good. The presence of aromatic segment may be responsible for high performance at end coat.

Table-6: TGA analysis of PU cured products

Sample Code	**TG analysis of PU cured products**				
	Percentage wt. loss at Temperature T°C				
	230	**300**	**400**	**500**	**600**
TCA1	1.4	12	42	78	90
TCA2	1.2	10	39	75	87
TCA3	0.9	08	38	70	85
TCB1	1.2	11	40	76	85
TCB2	1.1	10	39	73	84
TCB3	0.9	08	36	67	90
TCC1	1.0	11	40	74	89
TCC2	1.0	09	38	70	89
TCC3	0.9	08	35	64	90

4. Conclusions

The novel polyurethane coats were prepared particularly by clubbing MCO and acrylate polyols. The produced polyurethane films have good physical, mechanical and chemical resistivity. The mechanical properties of all the PU coatings indicate that all the samples have better mechanical properties more particularly pencil hardness is excellent. The results also indicate that lower proportion of MCO impact on the properties of PU. Overall results show that MCO have very good effect on PU film formation as Mild steel. The high crosslinking density in the film formation may enhance the mechanical properties of PU films. The thermal properties at all the PU samples are also very good.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of Interest

The authors declare no conflict of interest.

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