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Preparation and properties of Polyurethane coating based on Modified castor oil, Commercial acrylate polyols and polysiloxane

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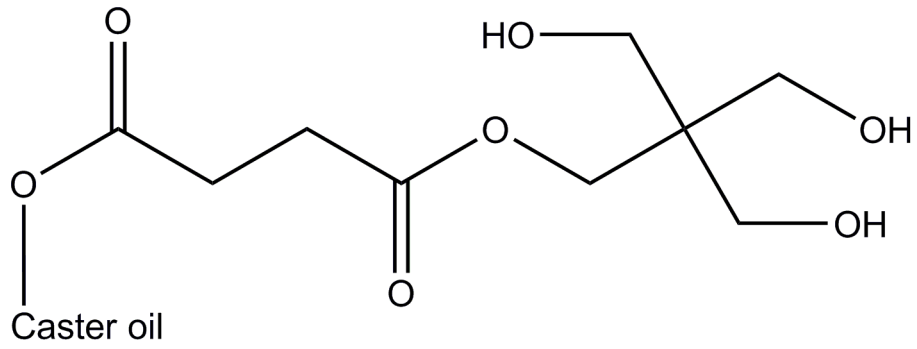
Abstract:
The polyurethanes (PUs) were prepared by polycondensation of modified castor oil (MCO)[Castor oil-succinic anhydride-penaerythritol reaction product], commercial acrylate polyols (AP) and Isophorone diisocyanate (IPDC) at various properties. The resultant PUs were then treated with monocarbinol terminated polydimethyl siloxane (MTPS) to neutralize –NCO groups. 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, Polysilazane, MS steel panel, Drying time, mechanical properties chemical resistance,.

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 [3-5].
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. Acharya [6] reviewed the chemistry of castor oil and its derivatization. The several scientists [7-12] developed the PU coatings from polyols based on various modification at plant oils and some other additives to enhance the mechanical properties [13-25].
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 obtaining novel PU coatings. This may enhance the properties of PUs upto some extent. Thus the present paper comprises the novel PU coating based on commercial acrylate polyols, polysiloxane and Isophorone diisocyanate. The PU formation is shown below,

Experimental:
Modified castor oil (MCO) was prepared by reaction of castor oil with succinic anhydride pentaerythritol followed by method reported in literature [7].
Its specification are: Mol. Wt.: 2010, Hydroxy value: Mg KOH/gm : 235, Viscosity at RT : 235 MPs.
Molecular structure of MCO



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 is

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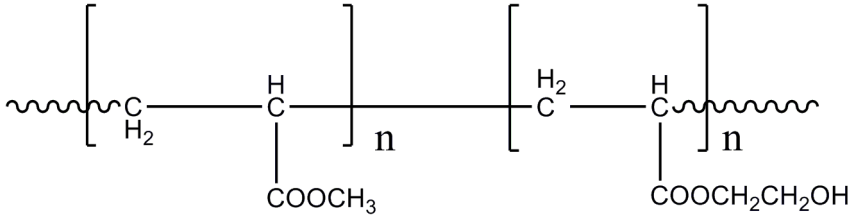
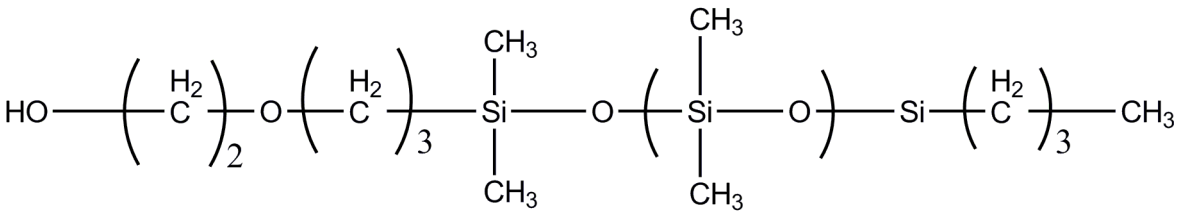


Isophorone diisocyanate (IPDI) was purchased as pure grade and used directly. Monocarbinol terminated Polydimethyl Siloxane (MTDS) was obtained from nearest industry. It's specification are :
Product code : MCR-C18
Viscosity : 60-140cps
Mol.Wt. : 5000
Density : 0-97
Molecular structure :



All other chemicals used were of analytical grade.

Preparation of polyurethane coatings:
Various proportions (Table-1) of MCO : Polyoles were mixed in appropriate amount of butyl acetate solvent. Then in the next step the MCO:polyol and IPDI (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 determine 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.

Measurements:
1. Infrared spectra of Pus were scanned on FTIR analyser.
2. The physical parameters like Non-volatile content (%), colour and viscosity [Brookfield viscometer RV-II in CPS] of all Pus were measured duly.
3. Coating thickness and drying time were measured duly.
4. 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	IDPC Mole	DBTDL % catalyst	Designation of coating sample
10 :90	2800	0.05	0.06	15	CA1
20:80	5100	0.092	0.11	15	CA2
30:70	7500	0.134	0.15	15	CA3
10:90	3000	0.0535	0.63	15	CB1
20:80	5400	0.096	0.11	15	CB2
30:70	7800	0.14	0.16	15	CB3
10:90	3200	0.057	0.65	15	CC1
20:80	6000	0.107	0.12	15	CC2
30:70	8500	0.15	0.17	15	CC3

Table-4: 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)
CA-1	1500	P	2H	P	P	21
CA-2	1700	P	4H	P	P	22
CA-3	2150	P	5H	P	P	23
CB-1	1600	P	3H	P	P	23
CB-2	1800	P	4H	P	P	23
CB-3	2200	P	5H	P	P	24
CC-1	1800	P	4H	P	P	25
CC-2	2100	P	4H	P	P	26
CC-3	2400	P	5H	P	P	26

P = Pass

Table-5: Chemical and corrosion resistivity of PU coatings

Sample Code	Acid resistance 5% HCl	Alkali resistance 5% NaOH	Corrosion resistance 5% NaCl	MEK Double Rub
CA-1	4	4	4	65
CA-2	5	5	4	75
CA-3	5	5	4	85
CB-1	4	4	4	75
CB-2	5	5	4	80
CB-3	5	5	5	90
CC-1	4	4	5	80
CC-2	5	5	5	85
CC-3	5	5	5	95

Results and discussion:

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

The IR spectra (not shown) of all the PUs coatings are almost identical. All the spectra comprise the bands due to MCO, AP and IDPC 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.

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Flexibility of all the coatings were 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 proportions 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 pulley thighted 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 uni 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.

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
CA-1	1.5	13	44	80	92
CA-2	1.3	11	42	76	90
CA-3	1.0	09	40	72	90
CB-1	1.3	12	43	78	90
CB-2	1.2	11	41	75	90
CB-3	1.0	09	38	70	92
CC-1	1.2	12	42	76	90
CC-2	1.1	10	40	73	90
CC-3	1.0	09	38	68	90

Conclusion:
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.

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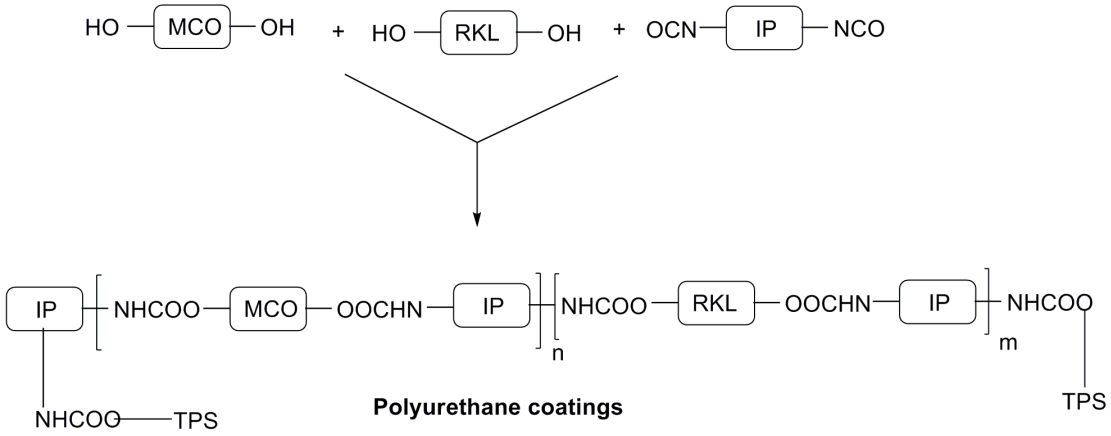
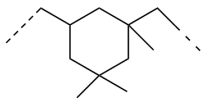
Polyurethan Coating Formation:

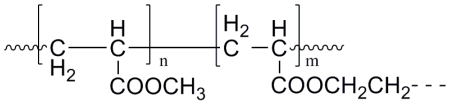


Where : **IP**



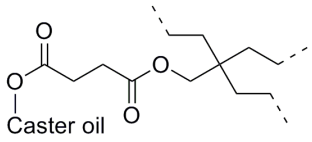
Isophron segment

RKL :

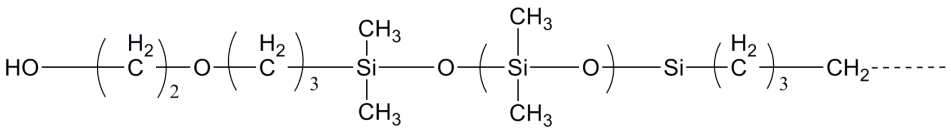


acrylate copolymer

MCO :



MTPS :



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