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A Comparative Study On The Properties Of Polypropylene Glycol And Castor Oil Based Polysiloxane-Polyurethanes

[1]Rasmika Patel*, [2] S. D. Bodara,
[1] [2] Department of Materials Science, Sardar Patel University, VallabhVidyanagar,
Anand-388120 Gujarat,India
[1]*rasmi29@gmail.com,[2]shraddhabodara1942@gmail.com

Abstract* — Silicon-based polyurethanes have a wide range of applications in many fields like automobiles, lubricants, adhesives, etc. due to their elastomeric properties. In this work, two different types of polyurethanes with different structures were synthesized: (i) polypropylene glycol-based polysiloxane-polyurethane and (ii) castor oil-based polysiloxane-polyurethane. The first one was synthesized by reacting polypropylene glycol (PPG), hydroxyl-terminated (polydimethylsiloxane) (PDMS) and different isocyanates such as isophoronediisocyanate (IPDI), Hexamethylenediisocyanate(HMDI) and Toluene diisocyanate(TDI) while for the other one instead of PPG, castor oil has been used. As the other two monomers are the same in both the polymers, variation in properties in these two polymers will be mainly due to the presence of PPG and castor oil-based moieties. Chemical and instrumental characterization techniques were used to determine the chemical and physical properties of both polyurethanes. For chemical characterization percentage of isocyanate, acid value and hydroxyl group have been carried out. Instrumental techniques have been used for the determination of functional groups (FTIR) and the average molecular weights of the polymers (GPC). The thermal properties were determined using a thermogravimetric analysis technique. These polyurethanes were coated on mild steel panels, silicon wafers and films were cast in the teflon mold. Scratch hardness, pencil hardness, and adhesion methods have been used for the determination of properties of coated panels, while chemical resistance properties of coatings and castings were found out using different chemical techniques. Properties of both the PUs have been compared. Silicon-based polyurethanes were mostly hydrophobic; therefore, it can be used where this type of property is required.

Keywords - *Castor oil; Poly propylene glycol; Polyether silicon urethane; Coatings*.

I. INTRODUCTION

Polyurethanes are currently one of the most multilateral materials having many applications in the field of foams, elastomers, coatings, castings, and biomaterials [4]. A myriad properties of polyurethanes can be obtained by varying the ratio of diisocyantes and polyols. However, polydimethylsiloxane**(PDMS)** is being recognized as having several unique properties such as high water resistance, good thermal stability, and mechanical strength [1, 3]. Due to its backbone composed of Si-O bond and methyl groups, many unique properties were arisen such as good hydrophobic property, bio-compatibility, good thermal stability, excellent water, chemical and oxidation resistance, great molecular flexibility, etc. [7]. The siloxane modified polyurethanes are synthesized by reacting siloxaneinto the chain of polyurethanes. These polymers have good water resistance and chemical resistance properties [2].

Thus, the present work motivated to synthesize castor oil and polypropylene glycol-based silicone polyurethanes by reacting different isocyanates with different polyols. Physical properties such as gel permeation chromatography, hydroxyl group estimation, drying properties and mechanical properties such as pencil hardness, scratch hardness, crosshatch, and flexibility have been found out. Functional groups and average molecular weight of polyurethanes have been determined using **FTIR** and **GPC** technique respectively.The thermal properties of polyurethanes have been determined by **TGA**.

II. EXPERIMENTAL

A. Materials

Castoroil,polypropyleneglycol[(PPG)m.w.=1000g/mole],polydimethylsiloxane,hydroxylterminated[(PDMS)m.w.=550g/mole],dibutyltindiluarate[(DBTDL)m.w.=631.56g/mole],isophorondiisocyanate[(IPDI)m.w. 222.22g/mole],hexamethylenediisocyanate(HMDI)[m.w.=168.2g/mole]andtoluenediisocyanate(TDI)[m.w.=174.2g/mole] were procured from Sigma Aldrich. Ethyl methyl ketone [(MEK)m.w.= 72.11g/mole] was obtained from Samir Tech-Chem Pvt. Ltd. Gujarat, India.

B. Polypropylene glycol based polysiloxane-polyurethanes

10 moles of PPG (1000g/mole) and 1 mole of PDMS (550g/mole) were charged into two necked flat bottom flask and added 5 ml MEK to reduce the viscosity of prepared mixtured. The reaction was carried out for 2-3 hrs at 80-90oC with stirring condition. After getting completely homogeneous phase. As per the OH groups 1.6 moles of different diisocyanates such as IPDI, HMDI and TDI were reacting with polysiloxanepolyols at 60-70^{o}C temperature with stirring condition. During this reaction another 5 ml of MEK as a solvent and DBTDL (0.001%) as a catalyst was added. This reaction was carried out until the percentage of NCO reached up to 2-3%.The percentage yield was 90%. The reaction scheme is shown in Figure 1.In this reaction the amount of PPG was taken higherthan the PDMS because after post curing of casted film silicone oil was released on the top surface of films.

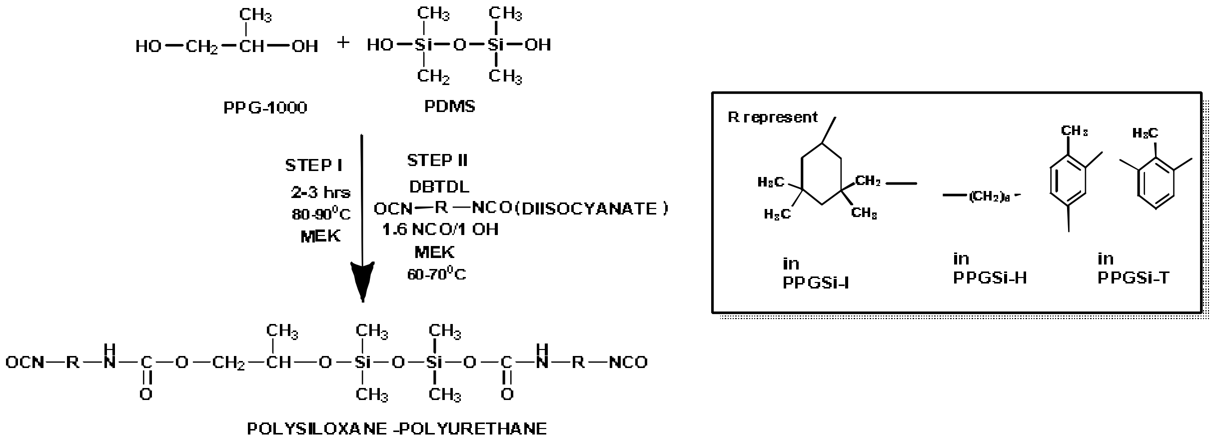

FIGURE: 1 Synthesis of PPG based poly siloxane - polyurethanes

C. Castor oil based polysiloxane-polyurethanes

10 moles of castor oil and 1 mole of PDMS as per the ratio of OH: PDMS (10:1) were taken into a two necked flat bottom flask. MEK was added as a solvent. This reaction was heated to 80 to 90°C for 3 hrs. under stirring. After getting completely homogeneous phase, further polysiloxanepolyols were reacted with different diisocyanates namely IPDI, HMDI and TDI with 1.8 moles to get polysiloxane-polyurethanes. MEK was added to reduce the viscosity of polysiloxanepolyols and DBTDL was used as a catalyst. Reaction was allowed to proceed until the percentage of NCO reached up to 2-3%. The percentage yield was 90%. The reaction scheme is shown in figure 2.In this reaction also same problem was occurred as like PPG based polysiloxane- polyurethanes. Because of that reason the amount of castor oil was taken higher than PDMS.

D. Characterizations

FTIR-ATR model alpha of Bruker, Germany was used to determining the functional groups in prepared silicon-based polyurethanes. The number average molecular weight and polydispersity index of polyurethanes were determined using Gel Permeation Chromatography (GPC) with Perkin Elmer instrument model series 200. Thermal gravimetric analysis was carried out to study the weight loss of cured polymer samples by the Perkin Elmer instrument TGA-7 thermal system.

E. Preparation of formulation for coating purposes

Polysiloxane-polyurethanes were coated on mild steel (M.S.) panels with the help of a film applicator for uniform coating. Before that mild steel panels have been cleaned and dried in the oven to remove dust particles. The polysiloxane- polyurethanes were mixed with the required amount of MEK solvent to reduce the viscosity and degassed under vacuum for a few minutes. These polyurethanes were applied on M.S. panels. For completion of setting, coated panels were allowed to dry at room temperature for a day and they were cured by keeping in an oven at 50-60^{o}C for 24 hrs.

III. RESULTS AND DISCUSSION

A. Physico-chemical properties of poly siloxane-polyurethanes

Table 1 shows the Physico-chemical properties of polysiloxane-polyurethanes. NCO to OH ratio used for preparing particular polymers is also given. Gel permeation chromatography has been used for the determination of number average molecular weight, weight average molecular weight and polydispersity index.

TABLE 1.Physico-chemical properties of polysiloxane- polyurethanes

Samples Code	OH/ NCO Ratio	Number Average Mol. Wt. $(\overline{Mn})$	Weight Average Mol. Wt. $(\overline{Mw})$	Poly Disper-sity Index
COSi-I	1:1.8	20377	5136	3.9
COSi-H	1:1.8	20975	6152	3.4
COSi-T	1:1.8	26392	8062	3.2
PPGSi-I	1:1.6	12583	7365	1.7
PPGSi-H	1:1.6	9538	5936	1.6
PPGSi-T	1:1.6	13616	6782	2.0

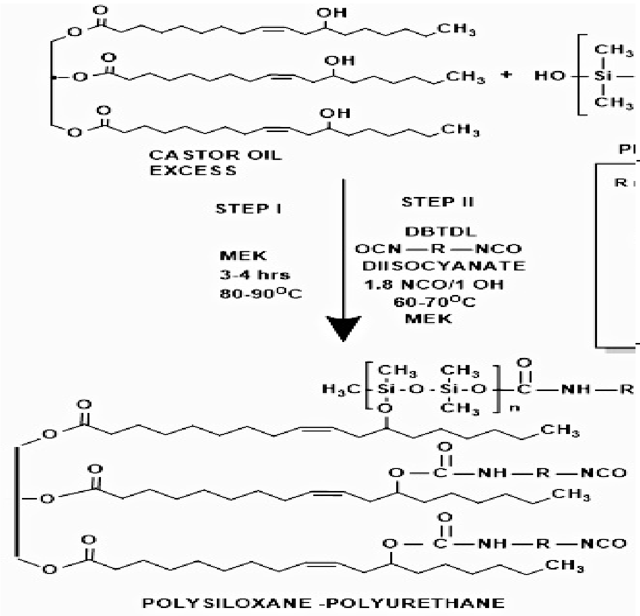

FIGURE: 2 Synthesis of CASTOR OIL based polysiloxane-polyurethanes

B. FTIR analysis

FTIR spectra of PPG based polysiloxane-polyurethanes were shown in fig1(a). This analysis has been done to determine functional groups present in polymers. The absorption bands of N-H, O-H and -O-C=O were measured in the range of 3340,1714 and 1698 cm^{-1} while -NH-C=O and O-C vibrational stretching frequencies of urethane linkage –NH-(C=O-)-O- were observed at 1090 cm^{-1}. Vibrations of –C-H bond have been seen at 2961-2854 cm^{-1}for further confirm the structure of PPG based polysiloxane-polyurethanes. In PPGSI-T PU vibrational frequency was observed at 1452cm^{-1}, which is shown the frequency of the benzene ring of TDI. The stretching frequencies in the range of 1100-1020 cm^{-1} shown the presence of the Si-O-Si bond of PDMS.

fig.1 (b) shows the FTIR spectra of castor oil-based polysiloxane- polyurethanes. FTIR analysis was done to determine functional groups present in the polymer. The stretching frequency around 3300-3350 cm^{-1}(N-H stretch) and 1700-1730 cm^{-1} (C=O stretch) in the spectrum of polyurethanes have been seen that the NCO group at 2270 cm^{-1} vibration has been disappeared. By that illustrate that the presence of NCO groups in polysiloxane-polyurethanes. The presence of siloxane in the polyurethane linkage has been observed at different vibrational and rocking frequencies at 1230 cm^{-1} (Si-CH3) and 800cm^{-1}(CH_3-Si) respectively. Strongbond stretching at 2900-2960 cm^{-1} shows the presence of alkanes (C=C) of fatty acids of castor oil. The vibrational frequency at 1450cm^{-1} which confirms the structure of TDI based polysiloxane-polyurethane. The vibrational stretching at 1600-1650 cm^{-1} which shows the frequency of –COO groups and at 1160 cm^{-1} stretching frequency of –C-O-C group further confirmed the structure.

C. Physical properties of coatings

Coatings surface properties such as pot life, surface drying, tack-free and hard drying of PPG based polysiloxane-polyurethanes and castor oil-based polysiloxane-polyurethanes coatings are shown in Table 2. It is seen that the castor oil-based polysiloxane-polyurethanes have taken less time for drying than the PPG based polysiloxane-polyurethanes due to the presence of some acids in castor oil.

TABLE 2.Coating performance of polysiloxane-polyurethanes

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Samples Code	**Pot life at room temperature (mins)**	**Drying properties**		
		Surface drying (mins)	**Tack free (mins)**	**Hard drying (mins)**
PPGSi-I	150	40	70	400
PPGSi-H	140	40	80	350
PPGSi-T	155	45	80	425
COSi-I	100	20	70	300
COSi-H	110	20	60	250
COSi-T	110	30	60	275

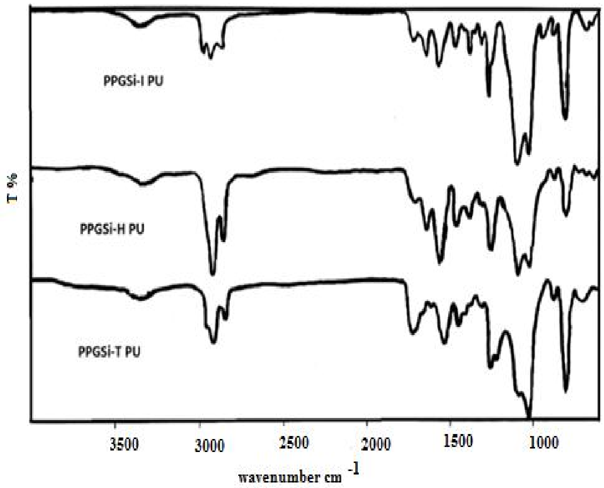

Fig. 1 (a). FTIR spectra of polypropylene glycol based polysiloxane- polyurethane

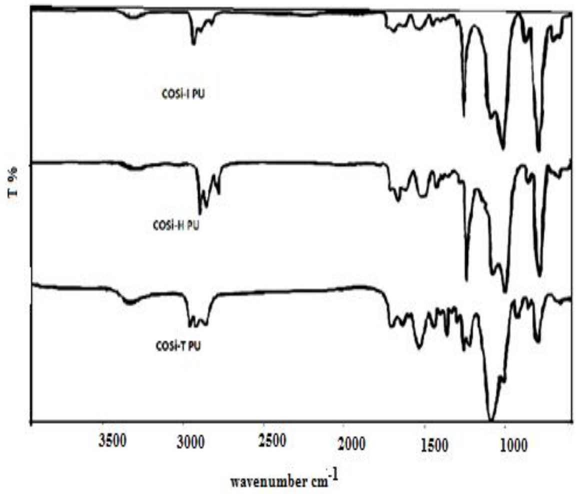

Fig. 1(b). FTIR spectra of castor oil based polysiloxane-polyurethanes

D. Thermal Stability of polysiloxane-polysurethanes

The thermal properties of the polymeric cured films were determined using thermogravimetric analysis. The thermo grams of polysiloxane-polyurethanes are shown in figreported in table 3. The determination of the cured polymeric samples was carried out in the temperature range of 50-450^{o}C. Polyether silicone polyurethanes were stable up to 280-300^{o}C. Determination of the cured (2)a and fig (2)b and the data of thermogram has beenpolymeric samples was shown good thermal stability and high char formation in castor oil-based polysiloxane-polyurethanes due to two steps degradation, by increasing NCO/OH ratio the char percentage and thermal stability increases due to the presence of polysiloxane and strong bonding between hydrogen bonds with urethanes moieties. For all the samples, 10% of weight loss occurs at 250-300^{o}C, this is due to the breakage urethane bonds, which converted in the form oxides, alcohols, amines, etc. Whereas, 30%of weight loss is seen in the range of 300-330 ^{o}C which is due to the decomposition of ether groups. At 330-350^{o}C, 50% of weight loss occurs due to the hard segments of polyurethane linkage. Thechar formation is started around 430 ^{o}C and the stable weight of cured samples was observed in the range of 450 °C in the thermo gram.

Table 3.Thermal analysis and char content of polysiloxane-polyurethanes

Samples Code	% weight loss			% char content at 450 °C
	10%	30%	50%	
COSi-I	280	317	342	7.124
COSi-H	270	314	342	9.933
COSi-T	255	301	343	12.173
PPGSi-I	269	319	335	5.32
PPGSi-H	259	315	328	9.933
PPGSi-T	284	326	342	5.341

E. Chemical resistance property of polysiloxane-polyurethanes

polyurethanes were observed every day under certain environmental conditions. The durability of polyurethanes has been observed for 120 days in 10% HCl, 10%acetic acid, and 10%NaOH and 10%NH_4OH which is shown in Table4. PPGSi-I has shown low stability in acids and bases compared to Castor oil based polysiloxane-polyurethanes. PPG based polysiloxane-polyurethanes shown reddish color in 10%HCl and fade color in 10% acetic acid, NaOH and NH_4OHafter 120 days. Castor oil based polysiloxane-polyurethanes has been shown good stability without any changes.

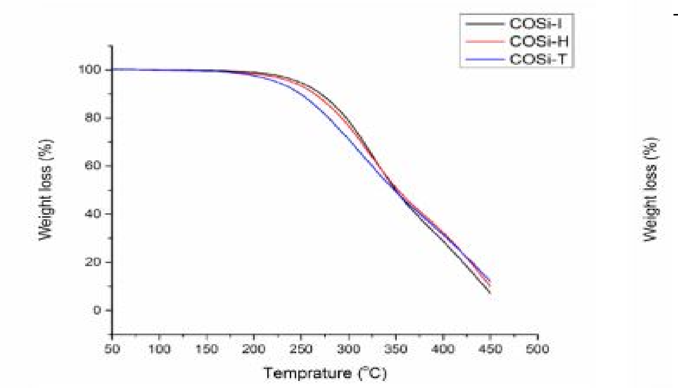

Fig.2 (a). TGA analysis of castor oil basedpolyesiloxane-poly polyurethanes

Fig.2 (b). TGA analysis ofPPG based polysiloxane-polyurethanes

F. Mechanical properties of polysiloxane-polyurethanes

Mechanical properties of coated panels were measured using pencil hardness, scratch hardness, cross hatch and flexibility test methods. Table 4 represents mechanical properties of coated panels. Castor oil based polysiloxane-polyurethanes coated panels have high scratch resistance property compare to PPG based polysiloxane-polyurethanes coated panels due to its good bonding and adhesion property. Pencil hardness is also good in castor oil based polysiloxane-polyurethanes. Flexibility test and adhesion test have been passed by castor oil based.

TABLE 4. Mechanical properties of polysiloxane-polyurethanes coatings

Samples Code	Pencil Hardness *	Scratch Hardness (gm)	Adhesion (cross-hatch)^a	Flexibility 1/8" Bending Mandrel
COSi-I	2H	2300	P	P
COSi-H	1H	2000	P	P
COSi-T	2H	2200	P	P
PPGSi-I	1H	2000	P	P
PPGSi-H	H	1900	P	P
PPGSi-T	1H	2200	P	P

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

CONCLUSION

In this study, we have tried to compare two different polysiloxane-polyurethanes. As per the results, we have concluded that castor oil based polysiloxane-polyurethanes show good thermal stability and good chemical resistance properties compared to PPG based polysiloxane-polyurethanes. Mechanical properties and physical properties of castor oil based polysiloxane-polyurethanes are higher than the PPG based polysiloxane-polyurethanes due to the good adhesion and bonding property.

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