

Hybrid polyurethane coating systems based on Renewable material

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ABSTRACT: Novel Biobased polyurethane coating containing composition was prepared from reactive polyol via modification of soyabean oil – a renewable agriculture raw material, The coating formulation was developed by reacting various composition of soyabean oil phosphate ester(SOPE) and different poly ethylene Glycols(200,400, 600 mol wt) as chain extender with aromatics and aliphatic isocyanate adducts in different NCO/OH ratios. The effect of stoichiometric on the properties of the resulting resin was investigated and the effect of varying NCO/OH ratio on the coating properties was also studied. Structure synthesized polyurethane were characterized by IR-spectral data. Physico-mechanical and weather resistance performance of the coated panels

Key Words: Polyurethane, Soyabean oil, renewable raw material, Physico- mechanical, weather resistance.

INTRODUCTION

Polyurethanes (PU) have found extensive applications in the coatings industry mainly because they exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance, and a wide range of mechanical strength. Because of these characteristics, PU coatings have emerged as coatings of choice for applications from industrial maintenance to automobile finishing to chemical resistant coatings. (1-2) Two-component polyurethane (2K-PU) systems are especially attractive since they offer flexibility in formulation which enables one to customize according to demanding end use requirements. Polyols are major components of PU coating systems and are often designed to suit the performance requirements of the intended applications. Polyesters and acrylics produce very tough polyurethane films under proper curing conditions and are among the most widely used polyols for high performance coatings. Polyether polyols are generally used in highly flexible systems such as sealants and other non coating applications.

In recent years, there has been renewed interest in developing materials and products based on bio-based

and renewable resources. The principal drivers for this, among others, include environmental, regulatory, and economic factors. A recent study indicates that soya-based polyols equal about 25% of the total environmental impact of the petroleum-based polyols and that the use of soya polyols will result in significant reductions in global warming smog formation, ecological toxicity, and fossil fuel depletion.(3) Preparation of polyols from vegetable oils has been extensively reported in the literature. (4-8).A variety of chemical modifications to vegetable oils have been studied to derive multiple hydroxyl-functional derivatives. Guo et al.(9)reported preparation of soya polyols by the hydrogenation of hydro formulated soyabean oil and studied the physical and mechanical properties of polyurethanes based on these soya polyols.

Petrovic and Javni(10) reported the use of soya polyols with PU prepolymers made from epoxidized soyabean oil and polymeric 4,4'-diphenylmethane diisocyanate to make coatings with good adhesion and hardness. Gerbase et al. (18-19) studied and reported different methods to functionalize vegetable oils in order to derive bio-renewable materials.

We have utilized epoxidized vegetable oils for deriving soya polyols using phosphoric acid as a modifying agent. Synthesis of soyabean oil phosphate ester polyol from epoxidized and partially epoxidized soyabean oil (ESBO) has been previously reported. The processes were developed to control oligomer formation and minimize hydrolysis of glyceride ester bonds in ESBO. Soyabean oil phosphate ester polyols (SOPEP) from ESBO with various epoxy values have been made and formulated in coatings. The film properties of the baking compositions based on these

polyols were studied for both solvent borne and waterborne systems (11). Low cost systems with good physical properties and excellent adhesion were reported.

In the present study, we derived soya polyols containing phosphate ester groups with varying OH contents from epoxidized soyabean using phosphoric acid as both catalyst and modifying agent. In the present work, a series of SOPE was synthesized from epoxidized soyabean oil. The film properties of 2K-PU coatings systems containing this polyol was studied.

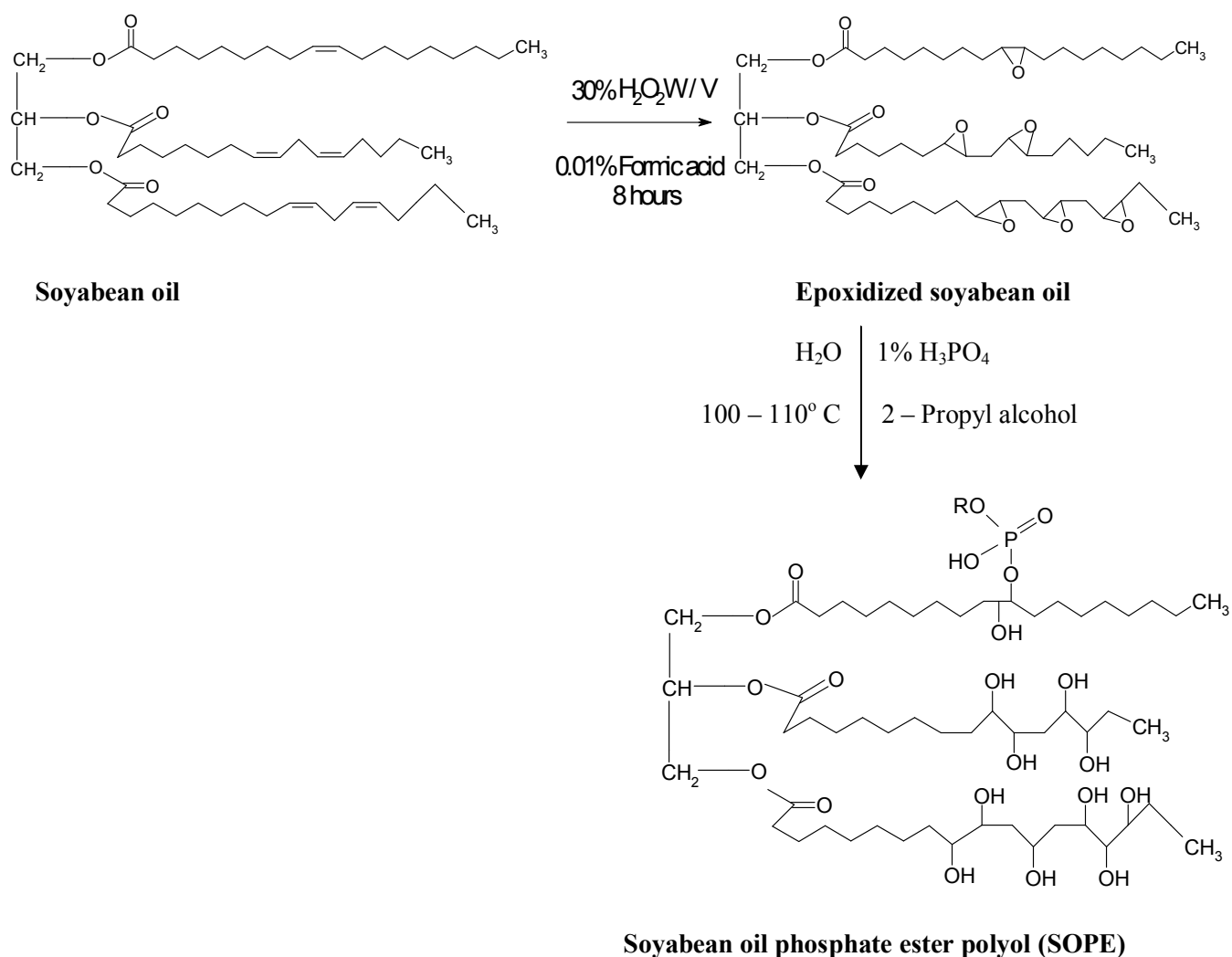


Figure: 1-Schematic Representation of Polyol Synthesis

EXPERIMENTAL

Materials:

Soybean oil was procured from local market, Polyethylene Glycols (200,400,600) mol wt. were supplied by Central Drug House, Delhi, India and had an average molecular weight (Mw of 200,400,600 gm/mol) respectively. Ortho phosphoric acid (85%), MEK, Xylene, and Ethyl Acetate were supplied by Astron Chemicals (Pvt) Ltd. Ahmedabad, India. Lithium hydroxide (Merck, USA) Aromatic Isocyanate adduct (Grand polycoats, Padra, Vadodara, India) was used. 2 – Propyl alcohol from (Aldrich, USA) was used as such.

Synthesis of Polyols:

For the synthesis of SOPEP, epoxidized Soybean oil (ESBO), (150.0 gm) and 2 – propyl alcohol (75 – 90% based on weight of ESBO) were charged into a 500 ml flask under agitation. Phosphoric acid (1% by weight) dissolved in distilled water (15.0 gm) was added to the flask from a dropping funnel at controlled rate of addition at 60-70° c. After complete addition reaction, mixture was stirred at 70-80° c for 4 hr. The progress of reaction was monitored by measuring epoxy value and acid value. After desired acid value obtained, the solvent was distilled off.

The acid catalyzed reaction of ESBO with water is believed to follow the reaction scheme shown in Figure 1. Under the experimental conditions used, there appears to be two competing reactions taking place simultaneously. The hydrolysis reaction, by nucleophilic attack of water on the cation atom of the epoxide group, produces a hydroxyl on the fatty acid backbone. The other competing reaction is oligomerization by an epoxy-epoxy or hydroxy-epoxy reaction with formation of an ether linkage. Soucek *et al.* conducted extensive research in this area and proposed a mechanism for oligomerization of cycloaliphatic epoxide compounds. (12-13) Due to the structural similarity of ESBO with cycloaliphatic epoxide, we believe that a similar reaction mechanism is probable. The lower viscosity of SOPEP IV (prepared with 4% phosphoric acid) was believed to be due to a higher degree of hydrolysis and lower degree of oligomerization, resulting in lower average molecular weight. Lower viscosity and lower hydroxyl content for SOPEP II could be attributed to a lower degree of oligomerization due to lower epoxy content (3.5% oxirane oxygen) of the ESBO.

Synthesis of SOPE / PEG 200,400 and 600 based Polyols :

The blending of low priced polymer with a higher performance polymer can provide a product that has good performance but is not too expensive. Such

mixtures generally require hydrogen bonding to provide a miscible polymer blend⁽¹⁰⁾. In present study 10 wt% of poly (ethylene glycol) (PEG 200,400 and 600) were incorporated in to base resin system SOPE

Solvent borne coating systems:

Commercial poly ethylenes Glycols (200,400, 600) and Aromatic and Aliphatic Isocyanate adduct were employed to test the effect of SOPEP, on coating properties. Based on the original recipe the SOPEP was mixed in various ratios from 20 to 80 % with the different PEGs. After mixing the entire ingredient Ethyl Acetate was added to adjust the viscosity to apply suitably with brush on the panels and were cured at room temperature.

Polyurethanes with different NCO/OH Ratios:

Synthesis of polyurethane was carried out by reacting novel polymeric blends with respective Isocyanate adduct. (Aromatic adduct and aliphatic adduct). without catalyst at room temperature. The physical properties of Isocyanate adducts are shown in the Table: 2. The NCO/OH ratio variation was taken in to the account. The PU resins were diluted with suitable solvent to have viscosity for appropriate application of coating with brush on cleaned mild steel panels. The coated panels were examined for Impact resistance, scratch hardness, pencil hardness flexibility tests, chemical resistance and adhesion test as per standard procedure.

Characterization methods:

Acid number A.N.(ASTM D 1639), Hydroxyl Number(OH# ASTM D 1957), Epoxy Value(E.V., ASTM D 1652), Pencil hardness (ASTM D 3363-92a), Cross hetch Adhesion(ASTM D 3359), Solvent resistance(ASTM D 5402), Impact resistance(ASTM D 2794-92). Viscosity was measured by Brook field viscometer at 25° c. Film thickness was measured by using Microtest Magnetic coating thickness gauge. Each panel had an average of three measurement to determine the thickness of panels.

Characterization of Polyols and polyurethanes by IR Spectroscopy

Figure 2 shows the IR spectra of SOPE with various PEGs. The most noticeable feature of the spectra is the increasing intensity of the peak at 1020 cm⁻¹ as a function of phosphate ester content.. Novel Polyols indicate the band at about 3400 cm⁻¹ which is due to – OH stretching. The strong and broad band indicates presence of the hydroxyl group associated to long chain and/or polymeric compound. The absorbance of O-H stretching of these polyols at different transition is due to either concentration effect or hydroxy number of polyols. It is very clear from the figure that there is

an increase in the intensity of above band which indicates that successful incorporation of PEGs, have taken place, which is further supported by increase in the hydroxyl content. The bands at about 1050 and 1350 cm^{-1} indicate the O-H banding of alcohol and C-O stretching of ester group respectively. The very strong band in the range of 1750-1735 cm^{-1} shows C=O stretching of aliphatic ester. The bands of C-H stretching and bending (deformation) in the $-\text{CH}_2$ group are observed at about 2962-2853 cm^{-1} and 1485-1445 cm^{-1} respectively.

The IR studies of different polyurethanes are shown in figure 3 and 4. The bands at about 3330 cm^{-1} and at about 1560-1650 cm^{-1} indicates the N-H stretching and N-H bending of urethane group. The bands observed in between 2962-2853 cm^{-1} indicates the C-H stretching and C-H bending of alkanes. The bands at 1220-1020 and 1410 cm^{-1} is the C-N vibration in urethane group. The band shown in between 1740-1690 cm^{-1} indicates clearly the formation of urethane group. The frequency at about the 870 cm^{-1} presents the substituted aromatic ring of TDI in aromatic adducts. In the higher NCO/OH ratio in polyurethane the some NCO group is present at about 2273 cm^{-1} . IR frequency around 1225 cm^{-1} is also clearly indicates C-O stretching of ether linkages in polyurethanes.

RESULT AND DISCUSSION

The results show that SOPEP can be successfully incorporated in to coating system. Generally all the polyols tested can provide acceptable properties. With SOPEP. As the only SOPEP in the coating. We obtained a coating with different properties. Mechanical and Chemical properties are shown in the Table: 3, 4, 5 and 6.

Higher NCO/OH ratio worsening flexibility:

Flexibility of all the system panels was tested on panels by bending menderal 1/8" as per ASTM D 622. Results are shown in Table: 3 and Table: 4 which indicates that the flexibility is good in all the systems. The results also indicates that increase in NCO/OH ratio in system SOPEP22 (80:20) SOPEP24 (80:20) with aromatic nature of Isocyanate adduct, increase the cross linking density resulting in to an increase in rigidity as expected and hence flexibility decreases.

Adhesion is extra ordinary:

Adhesion test of coated material was carried out by Cros -hatch adhesion conducted according to ASTM D 3359 Method B to determine adhesion. The phosphate ester group found to increase the adhesion to metal substrate by reaction with metal. Results show that adhesion was extraordinary in all the coating systems.

Higher density of cross linking for good Scratch, Pencil hardness and Chemical resistance:

The Impact resistance and Hardness increases with Increasing amount of SOPEP with aliphatic Isocyanate adducts compare to aromatic isocyanate adduct. An unexpected effect of incorporation of SOPEP was that the system cured at room temp faster, which may be due to higher functionality of SOPEP. With increasing NCO/OH ratio, except flexibility all the properties were improved. Since SOPEP gave the best overall performance, we investigated it in formulation with different SOPEP/PEG (200,400,600) ratios from 20-80%SOPEP as the resin Impact hardness increases with aliphatic isocyanate adduct with increasing NCO/OH ratio and with increasing chain length of PEG.

Scratch hardness increases with aromatic isocyanate adduct with increasing chain length of PEG. We investigated that the formulation with SOPE/PEG in the ratio of (60:40) gives the best overall performance with aromatic and aliphatic isocyanate adducts

CONCLUSION

Polyurethane can be synthesized from Soyabean oil, a sustainable resources which under goes cure at room temperature. SOPEPs can be employed as a hydroxyl component of a 2K-PU coating system with distinct advantages of low cost and lower VOC. Generally, hardness and solvent resistance are reduced by SOPEP systems; as compared to conventional polyester polyol-based systems have two useful functional groups Phosphate group for corrosion and adhesion improvement and Glycol group for cross linking. SOPEP investigated can be incorporated in to solvent borne coating with excellent adhesion, improved impact resistance. Soyabean oil phosphate ester polyol potentially offer the coatings industry a low cost route to tough durable, environmentally compliant high performance coatings

Table – 1: Physical properties of Polyols

Sr.No.	Properties	Polyol (SOPE)
1	Acid Value	2.1
2	Hydroxy Value	289.01
3	Hydroxy Equivalent Weight	196.84
4	Iodine Value	1.35
5	Viscosity @ 25 ⁰ C (10 rpm) cP	900 – 1000

Table – 2: Physical properties of Isocyanate Adducts

Adduct based On TMP	% Of Free NCO	Isocyanate equivalents	Specific gravity @ 30 ⁰ C	FC- viscosity @ 30 ⁰ C by FCBIV(s)
Aromatic	12.50	336	1.02	210
Aliphatic	16.50	255	1.05	175

Table-3: Polyurethanes from the mixture of SOPE and Polyethylene Glycols 200,400 and 600 with Aromatic Isocyanate Adducts

Different PU	Scratch Hardness (gms)	Impact Hardness lb inch	Pencil Hardness	Flexibility 1/8" mendrel	Cross- Hatch Adhesion (%)
SOPEP21					
20:80	1200	F	1 H	P	97
40:60	1600	P	2 H	P	98
60:40	1700	P	2 H	P	98
80:20	1300	F	2 H	P	96
SOPEP22					
20:80	1800	F	2 H	P	95
40:60	2300	F	2 H	P	96
60:40	2600	F	3 H	P	96
80:20	1900	F	2 H	P	95
SOPEP41					
20:80	1500	P	2 H	P	97
40:60	1800	F	2 H	P	98
60:40	2000	P	3 H	P	98
80:20	1700	F	3 H	P	98
SOPEP42					
20:80	2200	F	2 H	P	96
40:60	2300	F	3 H	P	97
60:40	2800	P	4 H	P	98
80:20	1800	F	3 H	P	98
SOPEP61					
20:80	1600	P	2 H	P	96
40:60	1900	P	4 H	P	97
60:40	2100	P	4 H	P	98
80:20	1700	F	3 H	P	97
SOPEP62					
20:80	2300	F	3 H	P	95
40:60	2400	P	4 H	P	97
60:40	2900	P	5 H	P	97
80:20	2000	F	3 H	P	98

*The first number after SOPEP represents the molecular weight of PEG and second number represents the NCO/OH ratio. **Pencil hardness** in decreasing order, 6H>5H>4H> 3H >2H>1H>H>HB>1HB>2HB>3HB>4HB>5HB>6HB, **Flexibility**: P = Pass, F = Fail.

Table-4: Polyurethanes from the mixture of SOPE and Polyethylene Glycols 200, 400 and 600 With Aliphatic Isocyanate Adducts.

Different PU	Scratch Hardness (gms)	Impact Hardness lb inch	Pencil Hardness	Flexibility 1/8" mendrel	Cross-Hatch Adhesion (%)
SOPEP21					
20:80	1000	F	1 H	P	97
40:60	1300	F	1 H	P	97
60:40	1500	P	2 H	P	98
80:20	1100	F	1 H	P	96
SOPEP22					
20:80	1600	F	2 H	P	97
40:60	2000	F	2 H	P	96
60:40	2400	P	3 H	P	97
80:20	1800	F	2 H	P	95
SOPEP41					
20:80	1400	P	1 H	P	98
40:60	1700	P	2 H	P	98
60:40	1900	P	2 H	P	98
80:20	1500	P	2 H	P	97
SOPEP42					
20:80	2000	P	2 H	P	96
40:60	2200	P	2 H	P	97
60:40	2600	P	3 H	P	97
80:20	1700	P	2 H	P	96
SOPEP61					
20:80	1500	P	2 H	P	96
40:60	1700	P	3 H	P	96
60:40	2000	P	4 H	P	96
80:20	1500	P	2 H	P	95
SOPEP62					
P20:80	2200	P	2 H	P	96
40:60	2300	P	3 H	P	97
60:40	2800	P	4 H	P	98
80:20	1900	P	2 H	P	96

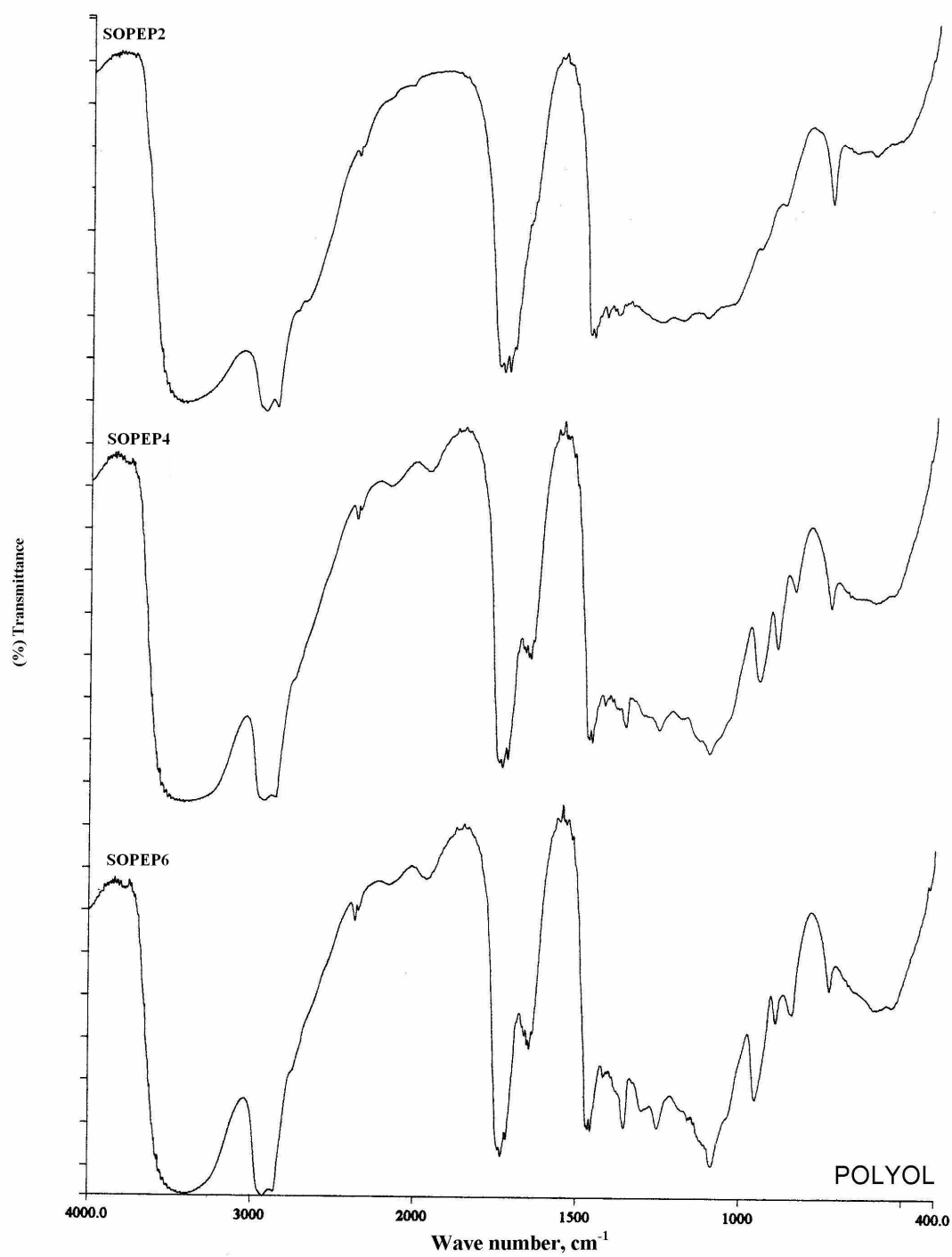
Table-5: Polyurethanes from the mixture of SOPE and Polyethylene Glycols 200,400 and 600 with Aromatic Isocyanate Adducts

Different PU	Acid resistance 5%Hcl	Alkali Resistance 5%NaOH	Corrosion Resistance 5%NaCl	MEK Double rub
SOPEP21				
20:80	2	2	P	>200
40:60	2	3	P	>200
60:40	4	3	P	>200
80:20	2	4	P	>200
SOPEP22				
20:80	2	3	P	>200
40:60	3	4	P	>200
60:40	4	5	P	>200
80:20	5	4	P	>200
SOPEP41				
20:80	2	3	P	>200

40:60	4	3	P	>200
60:40	3	4	P	>200
80:20	2	3	P	>200
SOPEP42				
20:80	3	3	P	>200
40:60	3	4	P	>200
60:40	4	5	P	>200
80:20	3	5	P	>200
SOPEP61				
20:80	3	3	P	>200
40:60	3	4	P	>200
60:40	3	5	P	>200
80:20	4	5	P	>200
SOPEP62				
20:80	3	3	P	>200
40:60	4	4	P	>200
60:40	4	4	P	>200
80:20	5	5	P	>200

Table-6: Polyurethanes from the mixture of SOPE and Polyethylene Glycol 200,400 and 600 with Aliphatic Isocyanate Adducts

Different PU	Acid resistance 5%Hcl	Alkali Resistance 5%NaOH	Corrosion Resistance 5%NaCl	MEK Double rub
SOPEP21				
20:80	2	3	P	>200
40:60	3	2	P	>200
60:40	4	4	P	>200
80:20	2	2	P	>200
SOPEP22				
20:80	3	3	P	>200
40:60	3	3	P	>200
60:40	4	5	P	>200
80:20	3	3	P	>200
SOPEP41				
20:80	2	3	P	>200
40:60	3	4	P	>200
60:40	2	4	P	>200
80:20	3	3	P	>200
SOPEP42				
P20:80	3	3	P	>200
40:60	3	4	P	>200
60:40	4	5	P	>200
80:20	3	3	P	>200
SOPEP61				
20:80	3	3	P	>200
40:60	3	4	P	>200
60:40	3	4	P	>200
80:20	4	5	P	>200
SOPEP62				
20:80	4	4	P	>200
40:60	3	4	P	>200
60:40	4	4	P	>200
80:20	5	5	P	>200

**Figure: 2 – IR Spectrum of Polyols**

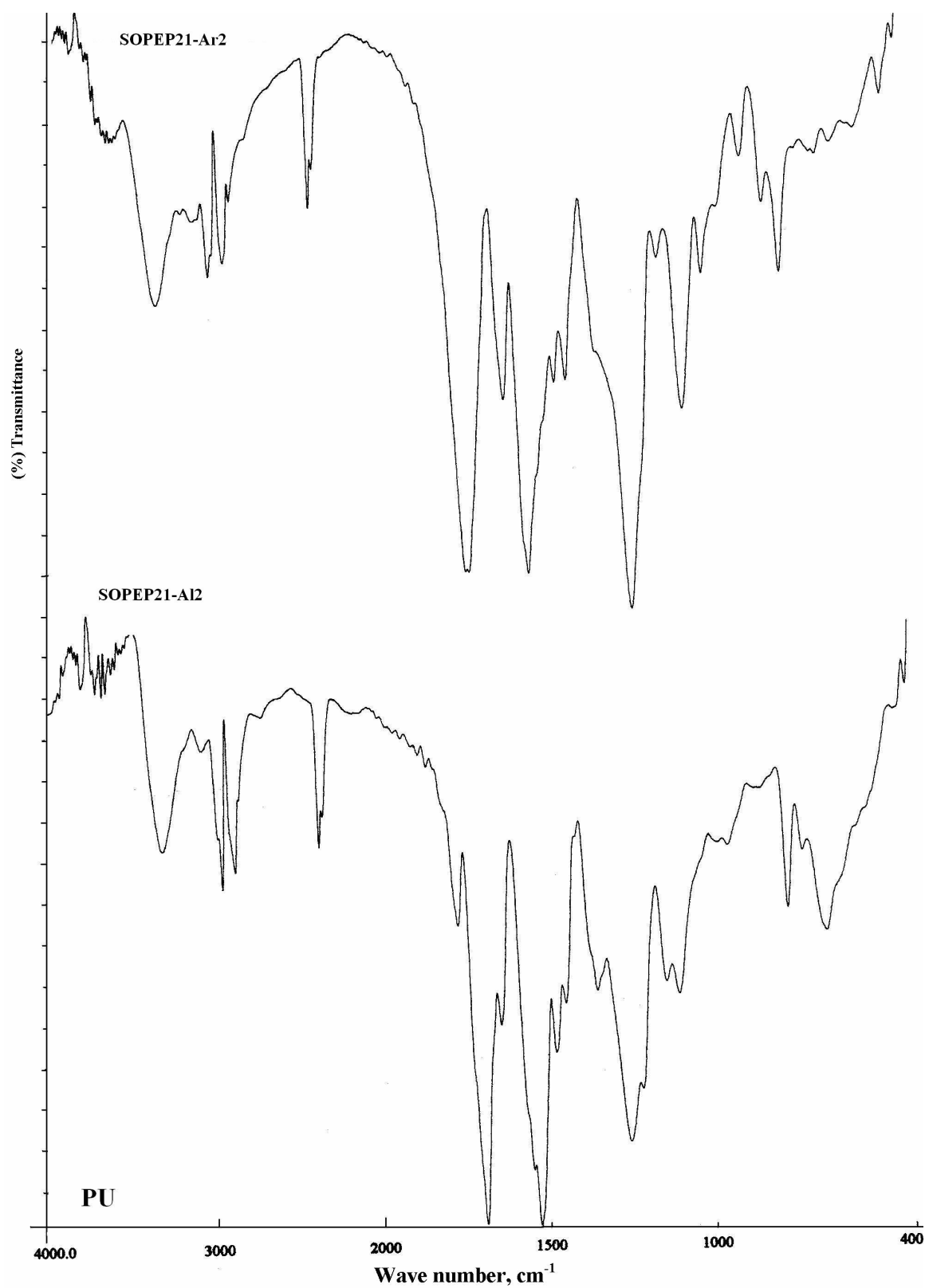


Figure: 3 – IR Spectrum of Polyurethane with Aromatic and Aliphatic adduct

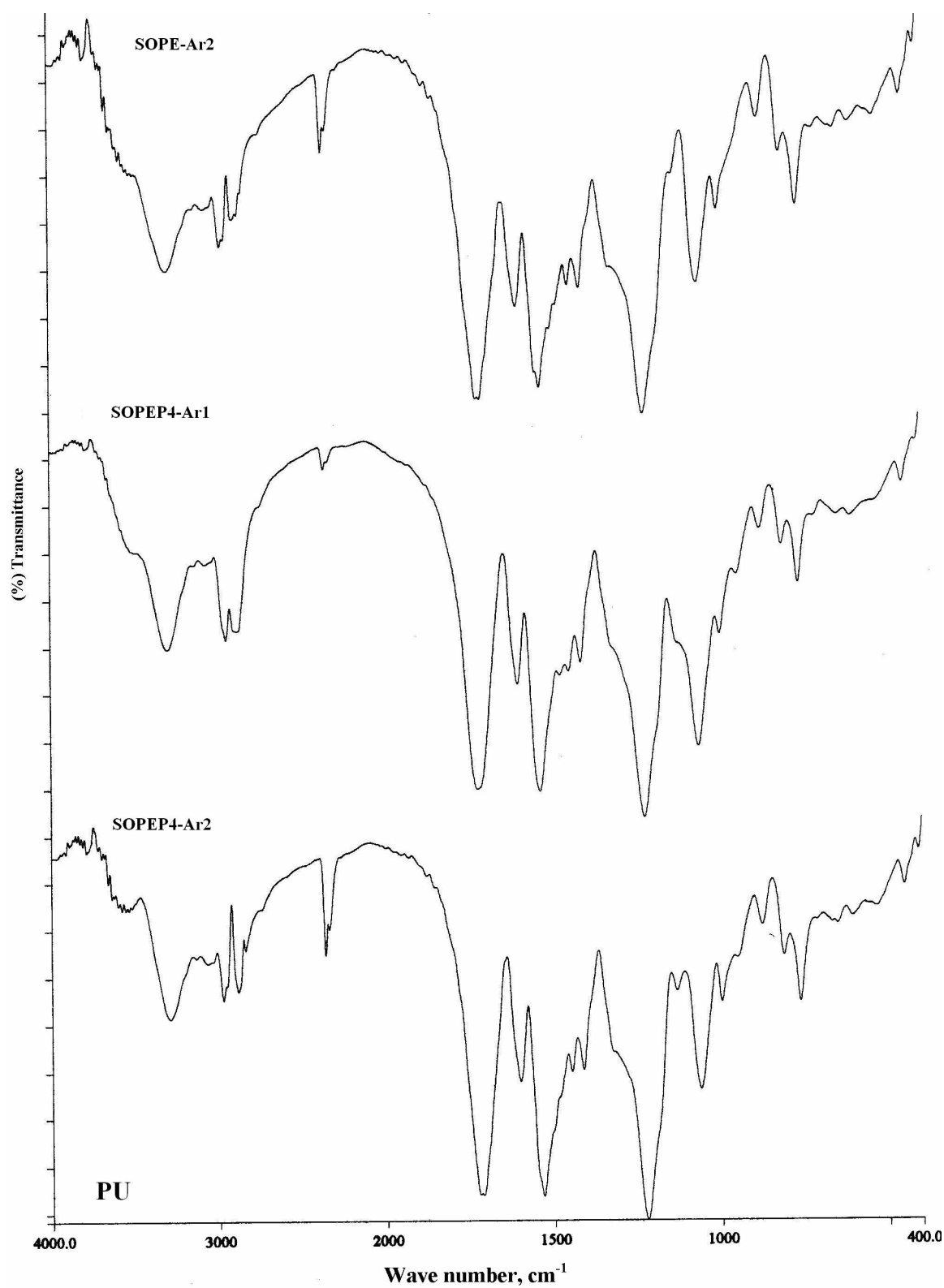


Figure: 4 – IR Spectrum of Polyurethanes with varying NCO/OH ratio

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