The Usage of Linseed Oil-Based Polyurethanes as a Rheological Modifier

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ABSTRACT: Some oil-based urethanes (urethane oils) were prepared from linseed oil, glycerol, and two types of diisocyanates, hexamethyle diisocyanate (HMDI) and 4,4′-diphenylmethane diisocyanate (MDI). These urethane oils were used as a rheological modifier in solvent-based coatings. For this purpose the mixture prepared from urethane oil and alkyd resin (AR-UO) was investigated in view of flow properties. Time dependence of AR-UO was investigated by using the hysteresis loop method. None of the samples showed thixotropic flow behavior. The flow type was decided after calculation of the ratio of viscosity at low shear rate to viscosity at high shear rate. The results showed that HMDI-based samples had the smallest viscosity ratio and increasing the amount of aromatic structure caused increasing shear thinning behavior. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1032–1035, 2005

Key words: coatings; polyurethanes; renewable sources; rheology; viscosity

INTRODUCTION

The popularity of polymers prepared from biological sources has grown significantly over the past decade because of environmental concerns. One of the most important biological sources is triglyceride oil that is obtained from plants. Oil-based polyurethanes (urethane oils) are produced by the reaction of isocyanate component(s) with hydroxyl containing oil derivatives. They are to a great extent biologically degradable polymers because of the oil part. Urethane oils (UOs) are used for decorative applications in the coating industry.[1,2]

When a coating is formulated, rheological properties that affect an application must be taken into consideration. A coating needs to have low viscosities at high shear rates that correspond to the application. On the other hand, to avoid settling and instability during storage and transport, it needs to have high viscosities at low shear rates. To provide this behavior, rheological additives are used in paint formulation.[3,4]

The aim of the present study is to synthesize and characterize some UOs for modifying paint flow. They are prepared from linseed oil, glycerol, and two kinds of diisocyanates. After determination of their solubility, they were added separately into soybean oil-based alkyd resin to prepare alkyd resin-urethane oil mixtures. The flow behaviors of the mixtures were determined and compared to each other.

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EXPERIMENTAL

Materials

Commercially purchased linseed oil was used as an oil component. The main characteristics of the oil were: refractive index (n_D^{20}), 1.4812; acid value, 1.1; saponification value, 197; iodine value, 166.8. Glycerine, hexamethyle diisocyanate (HMDI), and 4,4′- diphenylmethane diisocyanate (MDI) analytical grade from Merck were used. Solvents used were also from Merck. Soybean oil alkyd resin that had an oil length of 62 and an acid number 5 mg KOH/g was supplied by Sentapol AŞ.

Experimental set-up

The reactions were carried out in a 250 mL four-necked flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, and a condenser.

Preparation of urethane oil (UO)

The first step of the preparation of UO was the reaction of linseed oil and glycerol to prepare a partial glyceride mixture (PG).[2] For this purpose, linseed oil and glycerol (8.5% of the oil) were placed into the reaction flask and heated. When the temperature reached 218°C, $Ca(OH)_2$ (0.1% of the oil) was added as a catalyst. The temperature was set at 232°C and maintained for 45 min. The reaction was achieved under nitrogen atmosphere. After cooling the reaction mixture, it was mixed with diethyl ether and washed first with dilute hydrochloric acid and then with distilled water to remove the catalyst and free glycerol. The ethereal solution was then dried over Na_2SO_4 and the solvent was removed. The hydroxyl and acid values of PG were 126.3 mg KOH/g and 1.7 mg KOH/g, respectively.

PG and dry xylene were taken into the reaction flask and heated to 40–50°C, and an equivalent amount of isocyanate component was added slowly over a 30 min period. Lead naphthenate as a 24% solution in white spirit was added in the amount of 0.02% of the oil portion. The temperature was set at 90–95°C and maintained. The reaction was achieved under nitrogen atmosphere.

Preparation of alkyd resin-urethane oil mixture (AR-UO)

UO was added into the soybean oil-based alkyd resin at four ratios, 0.5, 2.5, 3.5, and 5%, and the mixture was heated with stirring at 200°C until it became clear. A solution of AR-UO of 60% by weight was prepared in white spirit.

Characterization

GPC chromatograms were obtained by using an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran as the eluent at a flow rate of 1 mL/min. Molecular weights were determined using polystyrene standards.

IR spectra were run on a Mattson 1000 spectrometer as films on sodium chloride discs.

Hydroxyl and acid values, and isocyanate content, were determined by using wet methods.[5]

Determination of solubility

The solubility of UOs in acetone, *n*-butanol, chloroform, *m*-cresol, formic acid, white sprit, and xylene was evaluated through visual examination at 25, 50, and 70°C. For this purpose, approximately 20 mg of polymer was added to 1 mL of selected solvent and kept in an ultrasonic bath for 15 min.

Determination of flow behavior

Rheological measurement was carried out with a Model Rheo Stress 1 Haake viscometer at 25°C.

The required amount of the sample was loaded into the cup. After immersing the rotor into the sample at a constant rate, the sample was allowed to remain at rest before starting the experiment.

Time dependence of AR-UO was investigated by using the hysteresis loop method.[6] In this method, shear rate increased first from zero to 100 s^{-1} at 60 s and then it decreased from 100 s^{-1} to zero in the same period.

The flow type was determined by calculation of viscosity in steady shear at two rates, 10 s^{-1} and 100 s^{-1}.[7] The ratio of viscosity at low shear rate to viscosity at high shear rate gave an idea that the fluid shows Newtonian or non-Newtonian type flow.

RESULTS AND DISCUSSION

Structure of polymers

Urethane oils (UOs) were synthesized in two or three steps, as shown in Scheme 1.

For the preparation of urethane oil (UO), linseed oil partial glyceride mixture (PG) was obtained by glycerolysis reaction, and the resulting ester mixture was converted to urethane oil by reacting with an equivalent amount of 4,4′- diphenylmethane diisocyanate (MDI) and/or hexamethyle diisocyanate (HMDI). For the preparation of UO from two kinds of diisocyanates, first HMDI was added into the PG. After consuming free isocyanate groups, MDI was added into the reaction mixture to combine the remaining hydroxyl groups. In the reaction mixture, the mol ratio of HMDI : MDI was set at 4 : 0, 3 : 1, and 2 : 2 for UO-40, UO-31, and UO-22, respectively. UO-13 and UO-04 which are the mol ratio of HMDI : MDI was 1 : 3 and 0 : 4 for UO-13 and UO-04, respectively, could not be obtained because gellation occurred.

The completion of the reaction between diisocyanate and PG, was controlled by IR measurements. In Figure 1(a, b), IR spectra of both the initial reaction mixture and the final product are given. The spectrum of the final product does not have an absorption peak at 2200cm^{-1}, which appears in the initial mixture assigned to the N=C=O group.

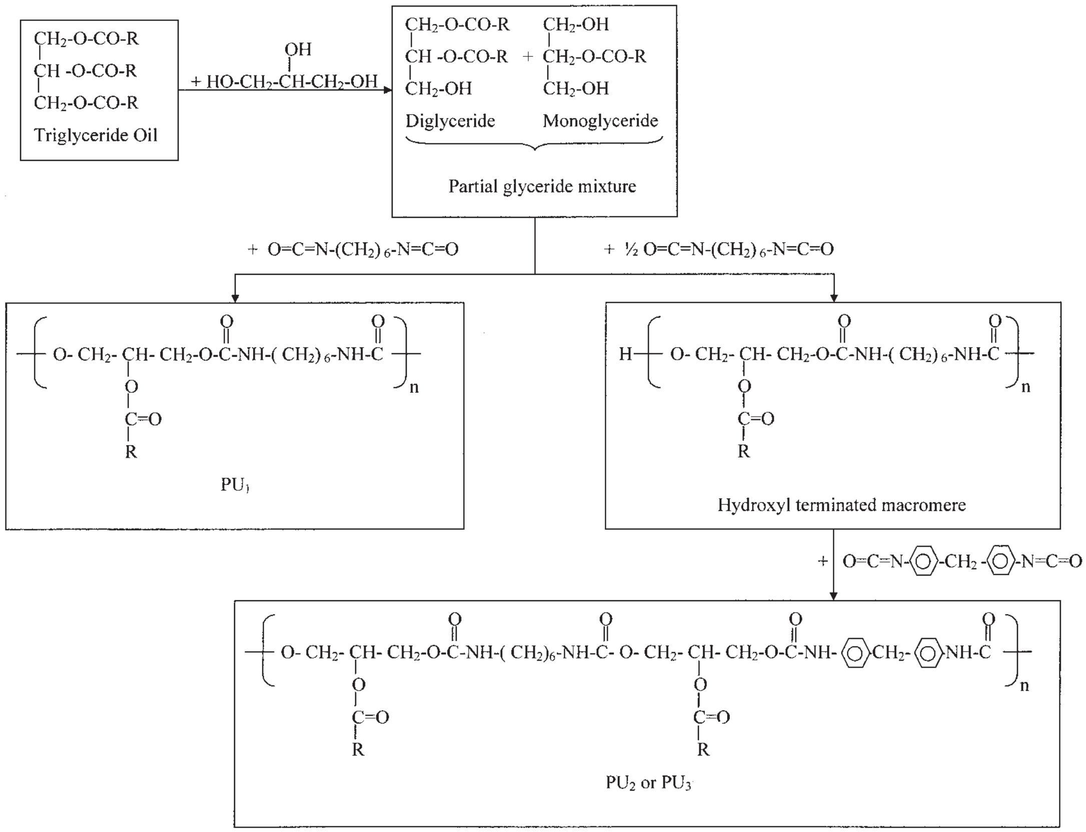
The molecular weights of UOs are given in Table I. The value of the polydispersity index (PDI) is acceptable for each polymer.

Solution characterization

Solubility test results are summarized in Table II. As shown from the table, *n*-butanol and formic acid did not dissolve the polymers. Xylene and white spirit are good solvents for all UOs.

Flow properties

To determine the effect of UO amount on flow properties of the binders, UO prepared was added at four different ratios, from 0.5 to 5%, into alkyd resin. Thus, alkyd resin-urethane oil mixtures (AR-UO) were obtained.



Scheme 1 Preparation of polyurethanes.

None of the mixtures showed thixotropic flow behavior because they did not give a hysteresis loop.

For each sample the values of viscosity at low shear rate (10 s^{-1}) and at high shear rate (100 s^{-1}), and the viscosity ratio are given in Table III. As shown, for the alkyd resin sample without adding UO, viscosity ratio was calculated at 1.12. This indicates that the alkyd resin did not show shear thinning or shear thickening flow behavior.

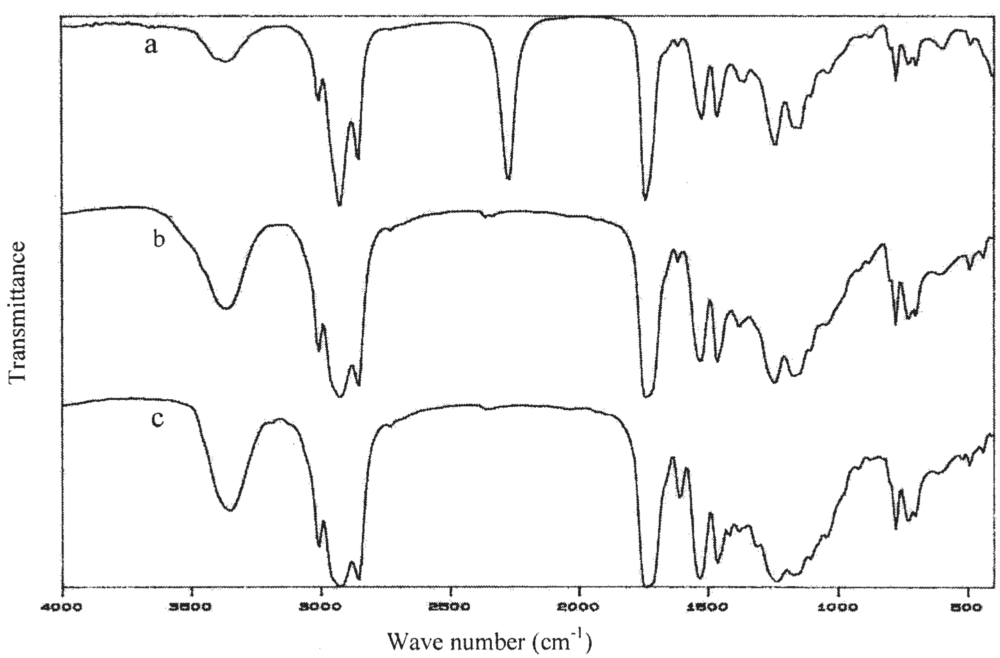


Figure 1 IR spectra of: (a) initial reaction mixture, (b) end of the reaction, and (c) PU_2.

TABLE I
The Mol Ratio of Diisocyanates in the Urethane Oil Preparation and Molecular Weights of UOs

Code	The mol ratio of HMDI/MDI	M_w	PDI
UO-40	4/0	2563	1.18
UO-31	3/1	6338	1.47
UO-22	2/2	8465	1.49
UO-13	1/3	←Gelation→	
UO-04	0/4	←Gelation→	

As shown from the same table, increasing the UO amount in the mixture caused an increase in the viscosity ratio, and the higher the UO amount is, the higher the viscosity is.

Polymer structure is another parameter affecting viscosity ratio. In this study, all polymers were prepared from the same PG. On the other hand, two types of diisocyanate were used for preparing UO with different ratios. UO-40 was the only sample prepared from HMDI, which is aliphatic diisocyanate. In comparison of the samples containing the same amount of UO, UO-40 had the smallest viscosity and viscosity ratio. Because an aliphatic chain gives the polymer flexible properties, the polymer, prepared from aliphatic isocyanate, can flow easier than the polymer containing an aromatic chain. UO-31 and UO-22 were synthesized from HMDI and MDI (an aromatic diisocyanate) with different ratios. UO-22 had more aromatic units in its structure. In comparison of the viscosity and viscosity ratio for the mixture having the same amount of UO (Table III), UO-22 gave higher values. Since an aromatic structure gives the polymer rigid properties, polymers having this type of units in their chains show higher viscosity.

Increasing the UO amount in AR-UO caused an increase in viscosity. As shown from Table III, at low shear rate, the UO amount was more effective on viscosity than at high shear rate because polymer chains are less oriented at low shear rates.

TABLE II
Solubility of UOs in Various Liquids

Solvent	Solubility of UO-40 25°C	UO-40 50°C	UO-40 70°C	UO-31 25°C	UO-31 50°C	UO-31 70°C	UO-22 25°C	UO-22 50°C	UO-22 70°C
Acetone	+	+	+	+	+	+	−	−	−
n-Butanol	−	−	−	−	−	−	−	−	−
Chloroform	+	+	+	−	+	+	−	+	+
m-Cresol	+	+	+	−	+	+	−	−	+
Formic acid	−	−	−	−	−	−	−	−	−
White spirit	+	+	+	+	+	+	+	+	+
Xylene	+	+	+	+	+	+	+	+	+

+: soluble, −: insoluble.

TABLE III
Viscosity and Viscosity Ratio for AR-UO

UO added into alkyd resin	Amount (%)	Viscosity (Pa.s) at: $\dot{\gamma} = 10\ s^{-1}$	$\dot{\gamma} = 100\ s^{-1}$	Viscosity ratio
UO-40	0.5	3.134	2.992	1.047
	2.5	4.550	4.324	1.052
	3.5	5.705	4.152	1.374
	5.0	6.813	4.500	1.514
UO-31	0.5	5.088	4.313	1.189
	2.5	5.345	3.870	1.381
	3.5	6.131	4.367	1.404
	5.0	7.113	4.405	1.615
UO-22	0.5	6.049	5.077	1.191
	2.5	7.453	5.374	1.387
	3.5	6.788	4.375	1.552
	5.0	11.530	5.764	2.000
without UO	0.0	1.661	1.485	1.120

CONCLUSIONS

Some of the oil-based polyurethanes (UOs) were prepared from linseed oil. Two types of diisocyanates, hexamethyle diisocyanate (HMDI) and 4,4′- diphenylmethane diisocyanate (MDI), were used. Xylene and white spirit were good solvents for all UOs.

To investigate the effect of polymer structure and polymer amount on flow properties of paint binders, UO-alkyd resin mixtures (AR-UO) were prepared and their flow properties were determined. UO was added into alkyd resin at four ratios, 0.5, 2.5, 3.5, and 5%. Time dependence of AR-UO was investigated by the hysteresis loop method. None of the samples showed thixotropic flow behavior. At the next step, the viscosity ratio was calculated for each mixture. In comparison of the samples with the same amount of UO, HMDI-based UO had the smallest viscosity ratio. Increasing MDI amount caused increasing viscosity ratio. These results showed that increasing the amount of aromatic structure caused increasing in shear thinning behavior.

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