Study of Film Properties of Some Urethane Oils

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In this study, sunflower oil-based urethane oils were obtained from three kinds of isocyanate components: toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI) and poly(1,4-butandiol) toluene 2,4–diisocyanate (PBTDI) terminated prepolymer. The polymers were prepared at four different ratios of isocyanate component/oil. Sunflower and linseed oil alkyd resin samples were also prepared as the comparative samples. The results suggest that the viscosity and the film properties of urethane oils depend on the amount and type of isocyanate component.

The increase in isocyanate content of the urethane oils caused high viscosity. In comparison with the samples having the same oil content, PBTDI-based samples showed the highest viscosity. Viscosity of the polymers can dramatically affect some film properties. For example, high polymer viscosity caused short drying time.

In comparision of alkali and water resistances of urethane oils with those of alkyd resins, better results were obtained depending on the structure of the urethane oils. On the other hand, alkyd resins and TDI–based polymers exhibited the best hardness properties.

INTRODUCTION

One of the most widely used type of organic coatings is urethane oil which is produced by the reaction of isocyanate with hydroxyl-containing oil derivatives. Urethane oils can be considered as an alkyd resin in which the phthalic anhydride is replaced by a diisocyanate. In the formulation of urethane oils, various oils have been used including, for example, linseed, sunflower, safflower, soybean, tall, and dehydrated castor oils.[1-12] Additionally, Erciyes et al. used *Ecballium elaterium* and *Prunus Mahaleb L.* seed oils in the formulation of urethane oils.[13] The other main component used in producing urethane oils is the isocyanate compound. This can be either aromatic or aliphatic. The choice of aromatic or aliphatic, however, is extremely important.[14] The films of aromatic isocyanates-based polyurethane can have good resistance to abrasion and some chemicals, but their surfaces break down in sunlight.[15] On the other hand, aliphatic isocyanate films have excellent resistance to ultraviolet light.

The aim of this study was to determine the effect of the amount and the type of isocyanate component on the film properties of the final products.

EXPERIMENTAL

Materials

Commercially purchased sunflower oil and linseed oil were used as oil components. *Table* 1 gives information on the main characteristics and fatty acid composition of these oils. In the study three types of isocyanate components were used. The chemical structures of the isocyanates are shown at the top of the next page.

Preperation of Urethane Oils

The first step of the process was the preparation of partial glycerides (PG) of sunflower oil which are formulated at four ratios of oil/glycerol. In the second step, the resulting ester mixture was converted to urethane oil by reacting with three types of isocyanate components—TDI, HMDI, and PBTDI. In the glycerolysis reaction, oil and glycerol were placed into the reaction flask and heated.

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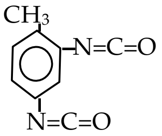
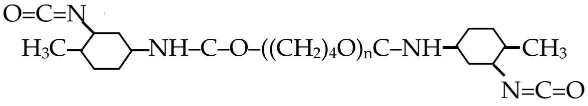
Compound	Code	Structure
Toluene diisocyanate (80% 2,4- and 20% 2,6 isomers, Merck)	TDI	
Hexamethylene diisocyanate (Merck)	HMDI	$O=C=N-(CH_2)_6-N=C=O$
Poly(1,4-butandiol) toluene 2,4- diisocyanate terminated prepolymer (9 wt % isocyanate, Aldrich)	PBTDI	

Chemical structures of the isocyanates used.

When the temperature reached 218°C, CaO was added in the amount of 0.1% of the oil portion as catalyst. The temperature then was at 230°C and reaction was continued at this temperature for 0.5 hr under nitrogen atmosphere. After cooling, the content of the reaction flask was dissolved in diethyl ether, washed with water, dried over sodium sulfate, and the solvent was removed. Hydroxyl value[16] and monoglyceride content[18] of the partial glycerides were determined. A wet method using acetic anhydride in pyridine was applied for determination of hydroxyl value.

At the last stage of the process, the partial glycerides mixture and dry xylene were taken into a 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 controlled by IR measurments and stopped when the peak at 2200 cm^{-1} disappeared.

The obtained reaction products were encoded for convenience according to partial glyceride and isocyanate compounds that are used in preparation. The samples were represented as PG[number]TDI, PG[number]HMDI, PG[number]PBTDI, for the TDI-, HMDI- and PBTDI-based samples, respectively. Numbers appearing in brackets shows that the product is prepared from partial glycerides with different hydroxyl values.

Table 1—Some Characteristics of the Triglyceride Oils Used in the Study[a]

Property	Sunflower Oil	Linseed Oil
Refractive index, n_D^{20}	1.4752	1.4812
Acid value	0.7	1.1
Saponification value	189.3	197.0
Iodine value[b]	122.0	166.8
Fatty acid composition (%)		
$C_{16:0}$	15.9	11.0
$C_{16:1}$	—	3.2
$C_{18:0}$	7.5	11.6
$C_{18:1}$	20.9	31.6
$C_{18:2}$	48.9	21.4
$C_{18:3}$	—	20.0
Other	6.8	1.2

(a) Reference 16.
(b) Reference 17.

Preparation of Alkyd Resin

As comparative samples, sunflower oil alkyd resin (SAR) and linseed oil alkyd resin (LAR) were prepared according to the following formulation.[19]

Ingredient	Part by Weight
Oil	2000
Glycerol	500
Lime	2
Phthalic anhydride	1400
Glycerol	80

The oil and glycerol were heated to 218°C in about 2 hr, then lime was added and the temperature was raised to 232°C. The temperature was held constant until a clear solution of a sample of the product diluted 1:3 in methyl alcohol was obtained. Phthalic anhydride and the second part of glycerol were added and the temperature maintained at 232°C for an additional 2 hr.

Determination of Viscosities and Film Properties

The viscosity of urethane oils was determined by using Brookfield RV/DV-II type rotational viscometer at 45°C.

Film properties such as drying time,[20] flexibility,[21] adhesion,[22] hardness,[23] water resistance,[24] alkali resistance,[24] and acid resistance[24] were determined. For this purpose, each sample was thinned with xylene to 40% solid content. Lead naphthenate (0.5%) and cobalt naphthenate (0.05%) as metal based on solid content were added. Driers were added 24 hr before the film application. In drying time and hardness determinations, a Bird film applicator with a 40 μm aperture was used for film application on glass plate. For the other tests, a dipping method was employed. For the flexibility, adhesion, and water resistance tests, tin plate panels were used as a substrate, while glass tubes were used for the alkali and acid resistance tests, as explained in the related standard methods.

Table 2—Initial Weight Ratio of Oil/Glycerine for Partial Glycerides and Some Properties of PG

Code	Oil/Glycerine	Hydroxyl Value	Monoglyceride Content (%)
PG1	25.0	71.6	8.4
PG2	12.5	126.3	13.9
PG3	11.1	141.5	21.8
PG4	7.7	170.3	26.7

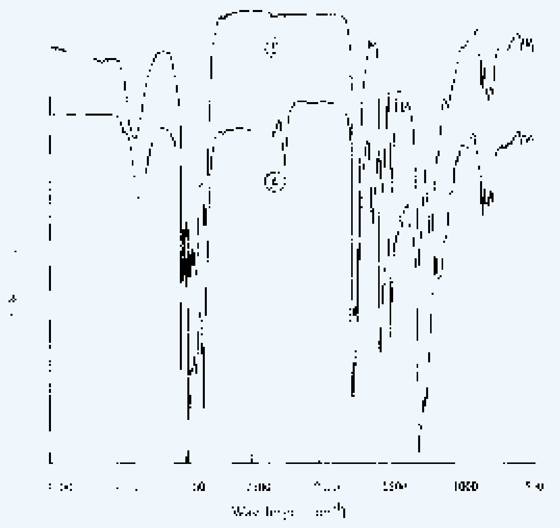


Figure 1—IR spectra of TDI-based reaction mixture after: (a) 2.5 hr and (b) 4 hr (final product).

RESULTS AND DISCUSSION

In this study, four types of partial glyceride mixture were prepared. The ratio of oil/glycerol in the initial mixture of the glycerolysis reaction, and hydroxyl value of the final product are given in *Table* 2. As expected, the hydroxyl value of PG increases with decreasing the ratio of oil/glycerine.

For the preparation of urethane oils, PG was reacted with three kinds of isocyanate compounds: TDI, HMDI, and PBTDI. IR spectra of both the reaction mixture of TDI based-urethane oil after 2.5 hr and the corresponding final product are shown in *Figure* 1. The spectra of the final product does not have an absorption peak at 2200 cm^{-1}, which appears in the initial mixture assigned to the N=C=O group.

The PG4PBTDI urethane oil based on PG4 and PBTDI gelled during the reaction because of the high hydroxyl value of PG4 and the high molecular weight of PBTDI.

Sunflower and linseed oil-based alkyd resin samples were also prepared as comparative samples. The ratio of oil/glycerol in the initial mixture was taken as 3.4 .

Table 3—Molecular Weight Data of the Polymers

Code	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n / \overline{M}_w$
PG1TDI	2276	3645	1.60
PG2TDI	3104	5432	1.75
PG3TDI	3170	5928	1.87
PG4TDI	3429	6927	2.02
PG1HMDI	2288	3846	1.68
PG2HMDI	2845	5519	1.94
PG3HMDI	3118	6236	2.00
PG4HMDI	3360	6787	2.02
PG1PBTDI	7236	15919	2.20
PG2PBTDI	10471	33612	3.21
PG3PBTDI	15500	57660	3.72
PG4PBTDI	←	Gelation	→
LAR	4651	27673	5.95

The number and average molecular weights ($\overline{M}_n$ and $\overline{M}_w$, respectively), and polydispersity index (PDI) which is the ratio of $\overline{M}_n / \overline{M}_w$ were measured by gel permeation choromatography (GPC). The results are shown in *Table* 3.

Viscosities of urethane oils and alkyd resins versus shear rate are plotted in *Figure* 2. As shown, the viscosity of the same isocyanate-based product increased with a decrease in the ratio of oil/glycerol of the initial mixture. This can be explained with the molecular weight of the products. Decreasing the ratio increases the concentration of hydroxyl groups of PG samples, resulting in increased amount of urethane groups in the polymer chain. This causes the high molecular weight. Additionally, the viscosities of the same partial glyceride-based polymers are different from each other because of the molecular weights and structure of isocyanate components used. If the ratio of oil/glycerol in the initial mixtures of alkyd resins and urethane oils are compared with each other, it can be seen that the initial mixture of alkyd resins has the smallest oil/glycerol ratio (*Table* 2). For this reason it should be expected that the resins produced from these mixtures have the highest viscosity. As shown in *Figure* 2, the viscosities of alkyd resins are very close to PG2PBTDI, and lower than the viscosities of PG4TDI and PG3PBTDI. This result can be explained by the difference between the procedures of the preparation of alkyd resins and urethane oils. As shown in *Table* 4, PDI of the alkyd resin sample is the highest value because of reaction conditions such as temperature. Urethane oils are produced at 90-95°C whereas the reaction temperature of alkyd resin is at 220°C. In literature, the same trend is evident in the case of model and conventional alkyd preparation.[25,26] Kangas et al. studied the synthesis of binders for higher-solids coatings. They synthesized model alkyd resin by esterifying phthalic anhydride, triols, and fatty acid with dicyclohexylcarbodiimide (DCC) at 25°C in pyridine medium. In their study, reference alkyds were prepared by conventional esterification of the same formulations at 220°C. Model alkyds generally had lower PDI than their conventional counterparts. The results indicated that the mild-temperature process is irreversible and is essentially free of side reactions.

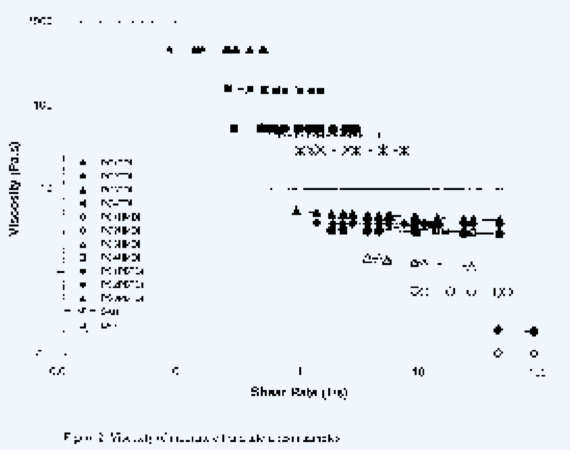


Figure 2—Viscosity of urethane oil and alkyd resin samples.

Table 4—Some Film Properties of the Products

Code	Flexibility[a]	Adhesion[b]	Hardness	Acid Resistance[c]
PG1TDI	2 mm	5B	2	nc[d]
PG2TDI	2 mm	5B	14	nc
PG3TDI	2 mm	5B	18	nc
PG4TDI	2 mm	5B	26	nc
PG1HMDI	2 mm	5B	0	nc
PG2HMDI	2 mm	5B	0	nc
PG3HMDI	2 mm	5B	0	nc
PG4HMDI	2 mm	4B	0	nc
PG1PBTDI	2 mm	5B	0	nc
PG2PBTDI	2 mm	4B	0	nc
PG3PBTDI	2 mm	4B	0	nc
PG4PBT	◀—— Gelation ——▶			
SAR	2 mm	5B	9	nc
LAR	2 mm	5B	10	nc

(a) The diameter of cylinder which caused no crack on the film.[21]
(b) Test method B was applied.[22]
(c) The test was carried out at 25°C with 9% H_2SO_4 solution.[24]
(d) Legend : nc—no change

In *Figure* 3, drying times of the final products were plotted against hydroxyl value. As shown, while the hydroxyl value of the PG increases, drying time decreases. However, comparing the drying times of the same partial glyceride-based polymers, all products prepared from HMDI exhibit the longest drying time. This can be explained with the viscosity of the polymer and the mechanism of drying. The drying is a chemical change involving oxidation and polymerization. Reactions with atmospheric oxygen in the drying film brings about polymerization and crosslinking through the fatty acids.[27] During the drying reaction, the viscosity of the polymer increases with time. It should be emphasized that drying time depends on the original polymer viscosity. High initial viscosity causes short drying time, and low polymer viscosity causes long drying time.

The effect of hydroxyl value and type of isocyanate component used on the alkali resistance can be seen from *Figure* 4. In this graph, alkali resistance is given as the failure time of the polymer films. As shown, all products prepared from PG1, which has the lowest hydroxyl value, showed the worst results. For TDI- and PBTDI-based products, hydroxyl value of PG increases, the failure time of the polymer film increases. Additionally, for PBTDI-based products, the resistance is better than TDI-based products. These results can be explained with the molecular weight of the polymers and the stearic hindrance potential of the isocyanate component of the polymer. If the polymer's molecular weight is low, alkali molecules can diffuse easily into polymer molecules, and the film damage time becomes short. In literature the same trends have been noted.[26] Kangas et al. observed that some film properties, such as solvent, acid, base and water resistance, of conventional and model alkyds improve as the fraction of molecular weight increases. In contrast to TDI- and PBTDI-based polymers, for all HMDI-based polymers the failure time was almost constant. This result indicates that the alkali resistance is related to the structure of the isocyanate used. It is well known that polyurethane films based on aromatic isocyanates can have good resistance to solvents and a number of chemicals.[14]

In the comparison of water resistance, high molecular weight TDI-based polymers gave the best results (*Figure* 5), because the time required for whitening to disappear is the shortest. HMDI-based polymers gave the worst results. The water resistance of PG2PBTDI and PG3PBTDI was better than HMDI-based product and worse than TDI-based product as compared the same PG-based products. This result can also be interpreted with the structure of the isocyanate molecules and the molecular weight of the polymers.

Other film properties, such as acid resistance, adhesion, flexibility, and hardness are shown in *Table* 4. As shown, flexibility, adhesion, and acid resistance for all the products are very close to each other. On the other hand, alkyd resins and TDI-based polymers exhibit the best hardness properties, because of the structure of the compound used in their preparation. It is well known that TDI and phthalic anhydride are used for applications requiring rigidity.[15] For TDI-based products, increasing of the amount of the benzene ring in the molecule causes an increase in the hardness properties. On the other hand, increasing the aliphatic groups results in softer coatings.

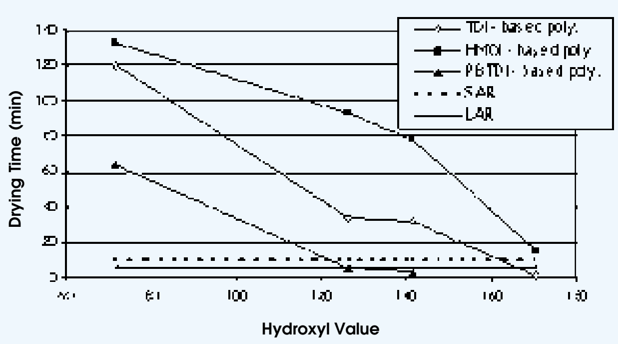


Figure 3—Effect of hydroxyl value of PG on drying time.

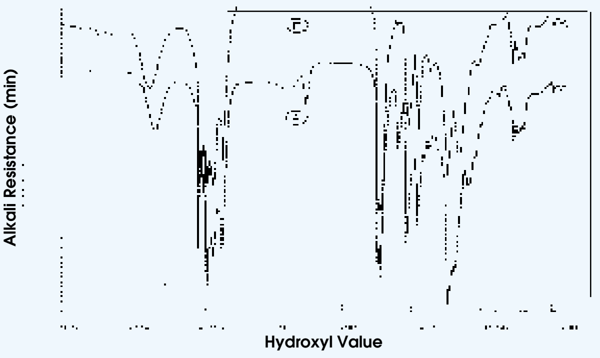


Figure 4—Effect of hydroxyl value of PG on alkali resistance.

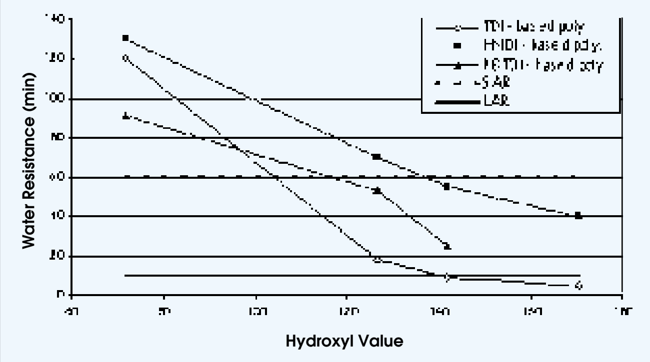


Figure 5—Effect of hydroxyl value of PG on water resistance.

For this reason, the films of HMDI and PBTDI- based products are softer (*Table* 4).

CONCLUSIONS

In this study, the effects of the amount and the type of isocyanate component on the film properties of urethane oils were determined. The results were compared with those of alkyd resins based on linseed and sunflower oils. The following conclusion may be drawn from the above discussion:

(1) The viscosity of the same isocyanate-based product increased with increasing the hydroxyl value of the partial glyceride mixture. Additionally, the viscosity of the same partial glyceride-based polymers is different from one other depending on the molecular weights and structure of isocyanate components used.

(2) With greater amounts of isocyanate components, the shorter drying time was achieved.

(3) Polymers prepared from TDI or PBTDI, and PG2, PG3, and PG4 showed the best alkali resistance.

(4) Polymers based on aromatic isocyanates had good water resistance.

(5) Among the isocyanate-based polymer, TDI-based polymers exhibited the best hardness properties.

(6) Flexibility, adhesion, and acid resistance for all products are very close to each other.

(7) The overall picture emerging from the viscosity data and the film properties is that as an alternative for alkyd resin samples, the three urethane oils prepared in this study, TDI-based polymer (PG4TDI) and TDI terminated prepolymer-based polymers (PG2PBTDI and PG3PBTDI) can be used as a binder. Because polymers gave the best results, it is also possible to formulate a new higher solids coatings from these polymers after investigating the viscosities of polymer solutions.

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