

Action of Hydrocarbon and Ester Plasticizer in Urethane Elastomer for Sealing Purposes

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ABSTRACT: A comparison of the effects of two types of modifiers, anthracene oil (hydrocarbon) and dioctyl phthalate (ester), on physical and mechanical properties of urethane elastomers prepared from polyetherols (propylene oxide derivatives of various functionalities and MW) and TDI was performed. The aim of the study was to assess their suitability as binders in permanently elastic urethane sealants for use in construction. The urethane elastomers under investigation were synthesized by a prepolymer method. The modifiers, added to the reactive mixture before curing, were found to be fully compatible with the urethane elastomers and did not interfere with the curing process. The usable range of application for both modifiers was found to be up to 40 phr. Over this range the modified urethane elastomers are viscoelastic liquids. The hydrocarbon modifier does enhance the hydrophobic properties of urethane elastomer, at a lower degree of crosslinking. It was found that modified urethane elastomers may be good binders for sealants, although their long-term sealing properties must be confirmed under field conditions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 523–529, 2001

Key words: urethane; elastomer; plasticizer; mechanical properties

INTRODUCTION

Urethane elastomers represent a type of polymers that are suitable as sealants in various applications, including heavy-duty service in buildings, highways, runways, and aircraft parking places in the airports. The requirements for the sealant in such applications are very high and difficult to meet: the sealant must retain good adhesion to concrete, high elasticity, weathering resistance, and resistance to fuels, lubricants, and deicing agents over long periods of time; the sealant is

subjected to cyclic dimensional changes as a result of temperature changes and the shrinkage and expansion of the sealed structure; and the required period of service is normally 8–10 years.^{1–3}

There are two main classes of urethane sealants: one- and two-component types. The one-component sealants comprise urethane prepolymers terminated with isocyanate groups, which crosslink *in situ* by reaction with surrounding moisture (mainly from the air). Although they are easy to apply, even by the inexperienced user, they are generally subject to long curing times because the crosslinking reaction is diffusion controlled and are thus used mainly for minor sealing tasks.³

The two-component urethane sealants are more difficult to use because they must be prop-

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Table I Polyetherols

Description	Molecular Weight	Hydroxyl No.	Equivalent Weight
Polyoxypropylene triol T1	3600	48.0	1166
Polyoxypropylene triol T2	560	240	1038
Polyoxypropylene diol D	2000	60.0	180

erly metered and mixed, and their pot time is limited to several minutes. However, they are characterized by shorter cure times, which may be easily controlled by variation of the amount of catalyst used. When used with a mechanical application device they allow for quick and economical sealing operation. Moreover, they generally have a longer shelf life than that of the one-component types.

Urethane elastomers are of either polyester or polyether type. The main difference is in the oligomeric compound used as the building block of the urethane polymer. Polyetherols are used more frequently for sealants because they have lower viscosity, higher reactivity, and give polymers with higher weathering resistance than that of polyesters. The latter usually produce polymers with a higher modulus, which is disadvantageous in sealing applications.

The use of urethane elastomers as sealing compounds, without modification, is rare. Urethane sealants are customarily modified by the addition of plasticizers, fillers, and adhesion promoters.⁴⁻⁸ Obviously the proper choice of chemical building blocks for the urethane elastomer is of primary importance.

In previous studies^{9,10} the performance of two-component cold-cured polyether urethane as the potential sealing material was studied in terms of chemical block and crosslinking density variation, and plasticization by some hydrocarbon plasticizers. It was found that the polyoxyethylene/polyoxypropylene adduct-based urethane elastomers modified either by anthracene oil or by

naphthene plasticizer have promising properties for this application.

In this study a comparison of both hydrocarbon and ester-type plasticizers as modifiers for polyether polyurethane elastomers for sealing purposes was conducted. The effect of these two types of plasticizers was investigated in polyether elastomers on the basis of polypropylene oxide adducts. The synthesized elastomers were a linear elastomer, obtained from polypropylene oxide adduct diol, and two crosslinked elastomers, obtained from two different polypropylene oxide adduct triols of varying molecular weights. The two plasticizers chosen for comparison were anthracene oil (hydrocarbon plasticizer) and dioctyl phthalate (ester-type plasticizer).

Both plasticizers differ in chemical character and polarity. The nonpolar anthracene oil is expected to be located in the hydrocarbon blocks of the elastomers, and the polar phthalate in the vicinity of polar urethane groups. Therefore, their water-repelling action, migration ability, and extractability may also differ.

EXPERIMENTAL

Prior to elastomer synthesis all polyols (Rokita Chemical Factory, Poland) and plasticizers (Blachownia Chemical Factory and Boryszew Chemical Factory, Poland) were vacuum-dehydrated to achieve a moisture content of less than 0.05%. The TDI isocyanate (Zachem Chemical Factory, Bydgoszcz, Poland) was used as received. The ma-

Table II Characteristics of Plasticizers

Compound	Solubility Parameter	Boiling Temperature (°C)	Density (g/cm ³)
Dioctyl phthalate (DOP)	9.06	230	0.985
Anthracene oil (AO)	8.8	>350	1.11

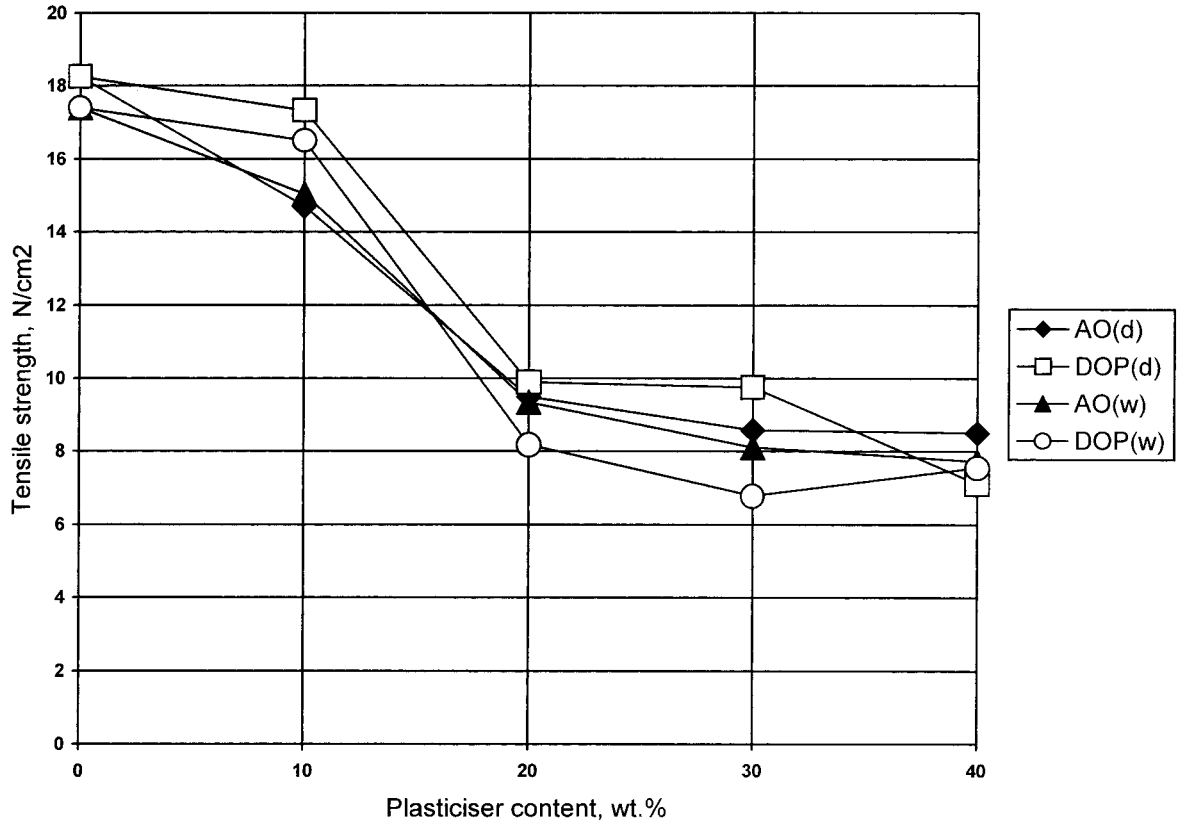


Figure 1 Tensile strength of elastomers cured with T1 polytriol. AO, anthracene oil; DOP, dioctyl phthalate; d, dry; w, wet.

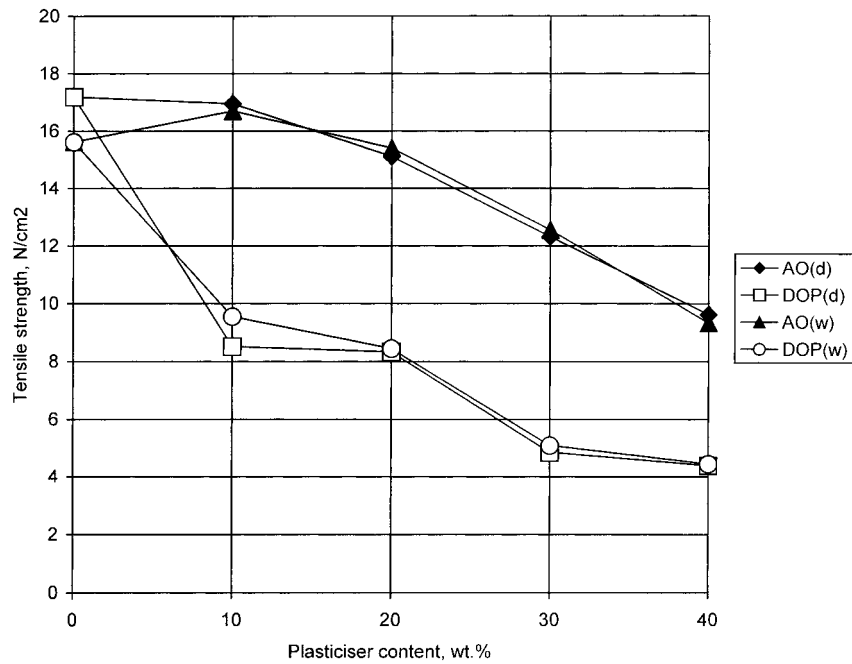


Figure 2 Tensile strength of elastomers cured with D polydiol. (Abbreviations as in Fig. 1.)

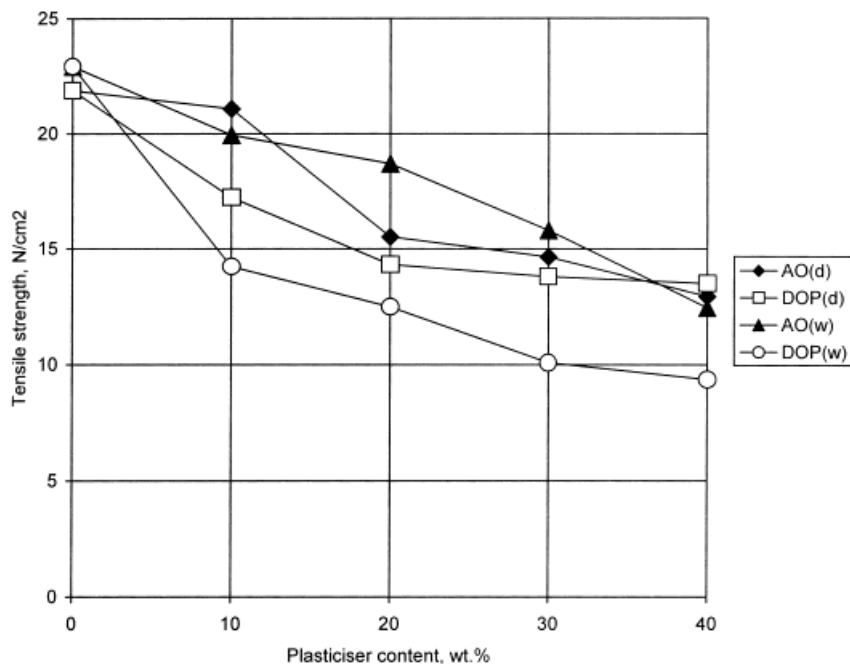


Figure 3 Tensile strength of elastomers cured with T2 polytriol. (Abbreviations as in Fig. 1.)

materials are listed in Tables I and II. The equivalent molecular weight of polyols was calculated on the basis of the OH number determination by

titration according to the Polish Standard PN-86/C-04837. The densities were taken from the manufacturer's specifications.

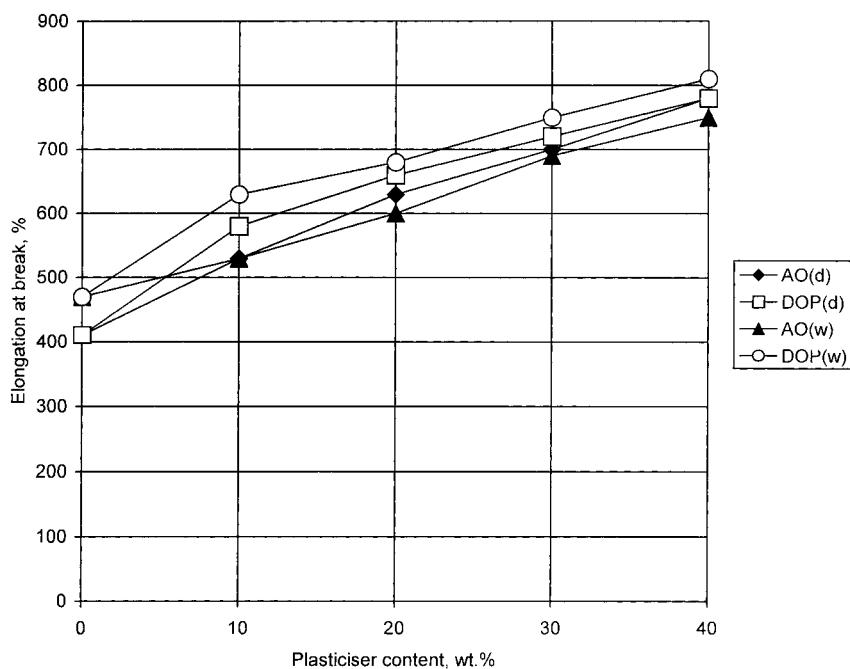


Figure 4 Elongation at break of elastomers cured with T1 polytriol. (Abbreviations as in Fig. 1.)

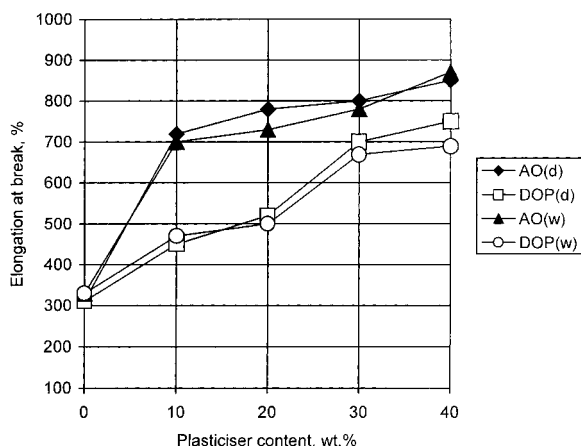


Figure 5 Elongation at break of elastomers cured with D polydiol. (Abbreviations as in Fig. 1.)

Synthesis

The elastomers were prepared by a prepolymer technique. The prepolymer from TDI and polyoxypropylene diol was synthesized at 80°C in a glass vessel equipped with a mechanical stirrer. The molar ratio of NCO to OH groups was 2.1 : 1. The reaction was carried out for 3 h under a dry nitrogen blanket. The resulting prepolymer (yellow viscous liquid) was stabilized with 0.1 wt % of benzoyl chloride, both to prevent runaway reactions and to improve its stability.

The isocyanate group content in the prepolymer was determined by titration with dibutylamine (automatic Mettler–Toledo titrator). The value was 3.38 wt %, compared to 3.57 wt % obtained from calculation.

Preparation of the Modified Elastomer

The elastomeric compositions of the prepolymer sample (usually 50 g) were prepared by thorough mixing at room temperature with a stoichiometric amount of polytriol. To this mixture the required amount (previously calculated) of the modifier (0–60 wt %) was added. Then 0.5 wt % of mercury phenyl oleate was added (urethane cure catalyst). The mixture was degassed in a vacuum chamber for 5 min and then poured into molds and allowed to cure for at least 1 week at room temperature.

The obtained specimens were used for determination of mechanical and physical properties of the resulting elastomers. They were dog-bone shaped, 115 × ~3 mm (length × thickness), according to the Polish Standard PN-81/C-89034.

Specimen samples were immersed in water at room temperature to study their water absorption after immersion (for 1, 7, and 30 days) and their retention of mechanical properties.

The tensile strength, elongation at break, and Shore hardness of the resulting elastomers were determined. The elongation at break and tensile strength were determined on an FU1000e (TIRA, Germany) universal testing machine. The elongation rate was 500 mm/min. The results were calculated as the number average of three samples of each composition. Water absorption was tested on standard dog-bone-shaped specimens, which were immersed in distilled water for 1, 7, and 30 days. The absorption was determined gravimetrically and calculated in wt %.

RESULTS AND DISCUSSION

General

The modified elastomers were rubbery, soft (<40° Sh A hardness), transparent, and tacky with a plasticizer content over 50 wt % (100 phr). The composition with AO was dark brown. No plasticizer sweatout was observed in the concentration region under investigation, which is not surprising in that the solubility parameters of both plasticizers lie in the vicinity of that of polyether polyurethane ($\delta = 9.3$).²

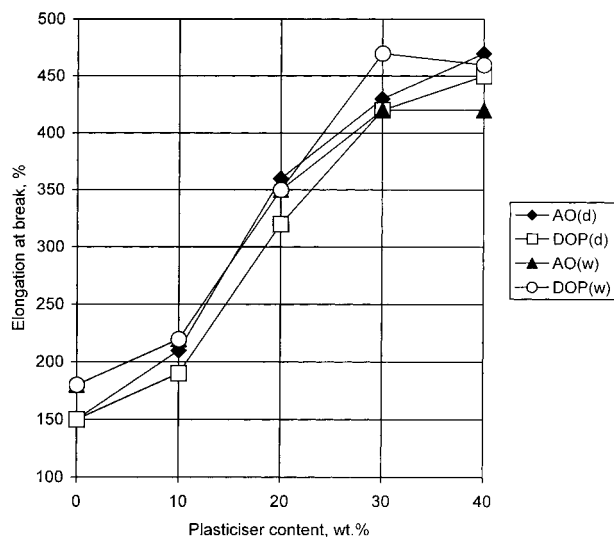


Figure 6 Elongation at break of elastomers cured with T2 polytriol. (Abbreviations as in Fig. 1.)

Table III Water Absorption of the Modified Elastomers

Curing Agent	Plasticizer Content, (wt %)	Water Absorption (wt %)					
		AO			DOP		
		1 day	7 days	30 days	1 day	7 days	30 days
T1	0	1.08	1.14	1.78	1.08	1.14	1.78
	10	0.15	0.34	0.57	1.15	1.24	2.45
	20	0.15	0.22	0.42	1.02	1.07	1.77
	30	0.06	0.16	0.23	0.93	1.21	1.34
	40	0.02	0.07	0.18	0.91	1.11	1.28
T2	0	2.25	2.72	3.13	2.25	2.72	3.13
	10	1.18	1.36	2.04	2.51	2.57	2.98
	20	1.11	1.32	1.57	1.35	1.50	2.50
	30	1.02	1.15	1.46	1.08	1.35	2.19
	40	0.98	1.14	1.26	1.02	1.25	2.02
D	0	2.08	2.12	2.15	2.08	2.12	2.15
	10	1.35	1.49	1.99	2.03	2.10	2.15
	20	1.29	1.32	1.77	1.45	1.58	1.88
	30	0.91	1.12	1.65	1.57	1.82	1.89
	40	0.88	1.06	1.34	1.45	1.55	1.40

Elastomers cured with D were almost linear (there were no crosslinks via polyetherol linkages, although some crosslinking via unintended allofanate groups was possible), a result that was established by a solubility test in DMF. The average distances between the network knots in the polytriol-cured elastomers were about 2250 u for T1 and about 550 u for T2. These distances were calculated from the structural reactants and the resulting polymer.

Mechanical Properties

The mechanical properties of the unmodified (reference) and modified elastomers are illustrated in Figures 1–6.

The crosslink density has some effect on tensile strength. The elastomer with the shortest inter-knot distance (also with the shortest distance between urethane groups) has a tensile strength value about 40% more than that of the two remaining unmodified species, with similar distance between urethane groups. The values for slightly crosslinked T1 and linear D elastomer are very close, which suggests that the hydrogen bonds between polar urethane groups primarily contribute to the overall strength of the elastomers. Therefore, their solvation by plasticizer should result in elastomer weakening and decrease of internal strength. Of the two plasticizers

chosen for evaluation the hydrocarbon derivative AO was supposed to interact with aromatic moieties of isocyanate and, to some extent, with the hydrocarbon (isopropyl) skeleton of polyether, whereas the more polar DOP should interact with urethane linkages.

Both plasticizers exert significant effects on elastomer properties. An increase in plasticizer concentration results in a sharp decrease of tensile strength and a considerable increase of elongation at break. Unexpectedly, the linear elastomer behaves similarly to the crosslinked elastomers. As expected, the elasticity of T2 elastomers with the highest crosslink density is lower than that of D and T1 elastomers. The plasticizing efficiency of the two plasticizers under investigation appears to be similar.

The high values of elongation at break and low tensile strength are promisingly advantageous in sealant application, for which, contrary to construction adhesives, low values of tensile strength are required. Moreover, immersion in water for 30 days does not result in a significant decrease of mechanical properties.

Water Absorption

Water absorption data are presented in Table III. Water absorption of unplasticized reference elastomers depends on the contribution of polar ure-

thane groups and, to some extent, on the crosslinking density. The effect of the plasticizers under investigation is diverse. The water absorption decreases as the plasticizer content increases, but this effect is more significant in the case of AO.

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