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A novel approach to recycling of polyurethanes: chemical degradation of flexible polyurethane foams by triethyl phosphate

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Abstract

It was established that flexible polyurethane foams based on polyester or polyether polyol and toluene diisocyanate can be converted quantitatively into liquid form by treatment with triethyl phosphate $(C_2H_5O)_3P(O)$. Structures of the degraded products were studied by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The degraded products are phosphorus containing oligourethanes. The likely mechanism is presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyurethanes; Chemical recycling; Triethyl phosphate

1. Introduction

Recycling of polymer waste materials and used polymers is one of the suitable ways for the conservation of natural resources and for the reduction of environmental stress. The chemical degradation of polyurethanes—rigid, flexible or polyurethane elastomers involves well-known methods of hydrolysis [1,2], glycolysis [3–6] and aminolysis [7–9].

The primary aim of these studies is to develop an unique, highly efficient method for converting polyurethane waste materials and used polyurethanes into reusable products by treatment with esters of phosphoric or phosphonic acids. The products formed could be used in the preparation of polymers, including polyurethanes, with reduced flammability, improved adhesion, improved resistance against UV irradiation.

Hereby we report on the chemical degradation of flexible polyurethane foams based on toluene diisocyanate and polyester polyol or polyether polyol by treatment with triethyl phosphate.

2. Experimental

2.1. Materials

Flexible polyester polyurethane foam based on polyester polyol Varalux HL, TDI-T-80, H_2O, Sn-octoate, B-Y (amino catalyst), Sil. stab. BF-2370 and flexible polyether polyurethane foam based on polyether polyol, TDI-T-80, H_2O, Sn-octoate, B-Y (amino catalyst), Sil. stab. BF-2370, Bayer AG, Germany. Triethyl phosphate, commercially available product (Aldrich).

2.2. Measurements

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker apparatus, 500 MHz, in $CDCl_3$ solvent. The viscosity was measured on a Brookfield LV viscometer. Phosphorus content was determined on a Specol spectrophotometer at 420 nm.

2.3. Degradation of flexible polyurethane foam by triethyl phosphate

120 g of flexible polyester polyurethane foam cut into small pieces 3–5 mm large and 364 g of triethyl phosphate were placed in a three-necked flask equipped with a stirrer, thermometer and reflux condenser. The degradation proceeded at 190°C. Then the temperature was lowered to 60°C, the unreacted triethyl phosphate was removed under vacuum (0.1 mmHg) and reused. Experiments on the chemical degradation of flexible polyester polyurethane foam were performed with heating for 1, 2 and 3 h. The results from the degradation are presented in Table 1.

The same procedure was used for the degradation of flexible polyether polyurethane foam by triethyl phosphate.

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Table 1
Conditions for the chemical degradation of flexible polyester polyurethane foam (PU) by triethyl phosphate (TEP)

PU (g)	TEP (g)	Duration of degradation (h)	Reacted TEP (g)	Unreacted TEP[a] (g)	Degree of degradation (%)	Yield of degraded product (g)	Content of phosphorus (%)
120	361	1 (3[b])	90	271	100	207	7.17
120	363	2 (3)	94	269	100	210	7.60
120	361	3 (3)	97	265	100	211	8.24

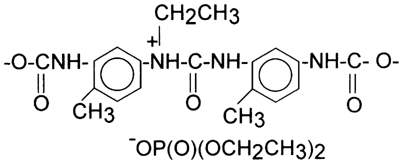
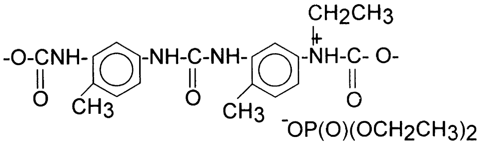
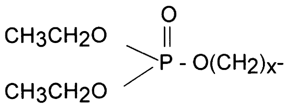
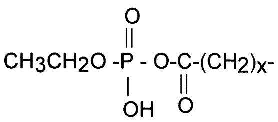
[a] Unreacted triethyl phosphate was removed by vacuum distillation and reused for degradation.
[b] Time for the addition of PU.

Table 2
Conditions for the chemical degradation of flexible polyether polyurethane foam (PU) by triethyl phosphate (TEP)

PU (g)	TEP (g)	Duration of degradation (h)	Reacted TEP (g)	Unreacted TEP[a] (g)	Degree of degradation (%)	Yield of degraded product (g)	Upper layer (g)	Lower layer (g)	Solid product (g)	Content of phosphorus (%)	
										Upper layer	Lower layer
120	364	2 (3[b])	96	268	100	211	Homogeneous product			7.18	
120	363	3 (3)	123	240	100	238	132	106	5	5.25	5.55
120	364	4 (3)	118	246	100	231	120	111	5	4.87	5.31

[a] Unreacted triethyl phosphate was removed by vacuum distillation and reused for degradation.
[b] Time for the addition of PU.

Table 3
Phosphorus containing products from the chemical degradation of flexible polyester polyurethane foam by triethyl phosphate

N	Structure	^{31}P NMR, δ (ppm), J (Hz)	Content (%)
1	 	-0.20, quintet $^3J(P,H) = 7.23$	82.0
2		0.17, septet $^3J(P,H) = 7.78$	14.0
3	 $CH_3CH_2O-\underset{OH}{\underset{\vert}{\overset{O}{\overset{\Vert}{P}}}}-O-\underset{O}{\underset{\Vert}{C}}-(CH_2)_x-$	0.53,t $^3J(P,H) = 7.73$	4.0

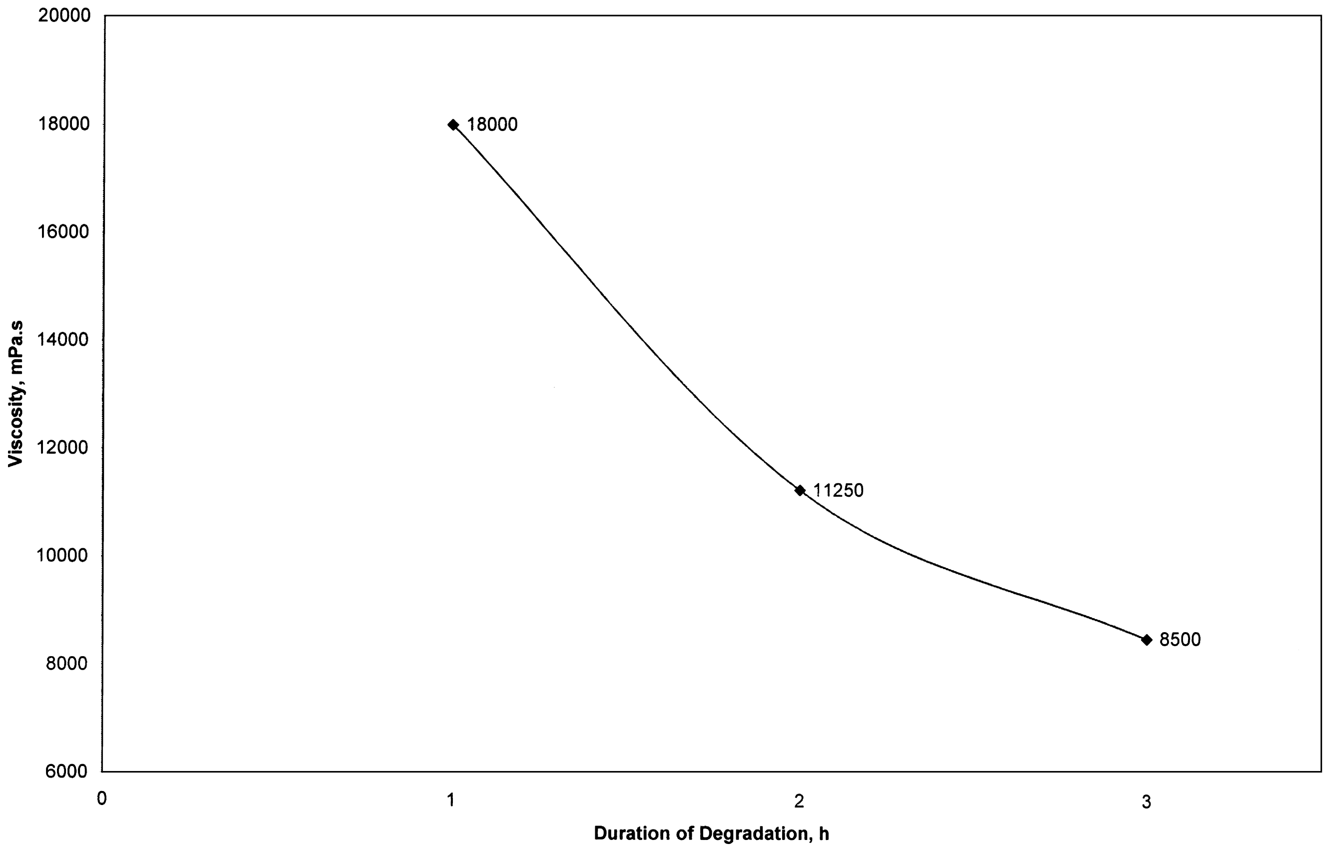


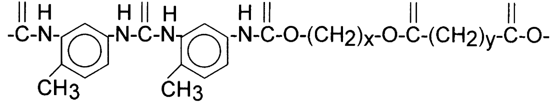
Fig. 1. Viscosity vs. duration of degradation of flexible polyester polyurethane foam by triethyl phosphate.

Experiments were performed with heating for 2, 3 and 4 h (Table 2).

3. Results and discussion

3.1. Degradation of flexible polyester polyurethane foam

Flexible polyurethane foam based on toluene diisocyanate and polyester polyol with the following repeating unit was converted into liquid form by treatment with triethyl phosphate at 190°C.



^{31}P {H} NMR spectrum of degraded flexible polyurethane foam shows signals at −0.20, 0.17 and 0.53 ppm. The signal at −0.20 ppm with the highest intensity represents a quintet with $^3J(P, H) = 7.23$ Hz and can be assigned to the phosphorus atom in the structure **1** (Table 3).

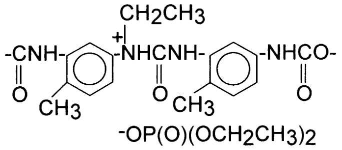
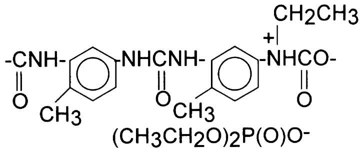
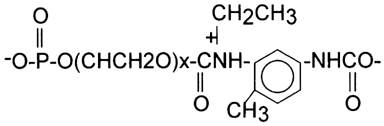
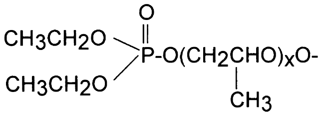
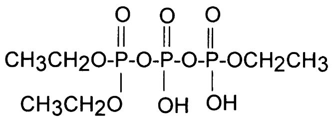
The signal at 0.17 ppm represents a septet with $^3J(P, H) = 7.78$ Hz and can be assigned to the phosphorus atom in the structure **2** (Table 3). The signal at 0.53 ppm represents a triplet with $^3J(P, H) = 7.73$ Hz and can be assigned to the phosphorus atom in the structure **3** (Table 3). The signals at: 1.41 ppm, (triplet) which can be assigned to $^+NCH_2CH_3$ protons, at 1.31 ppm, (triplet) is due to $C(O)OCH_2CH_3$ protons, at 3.82 ppm, (quartet) for $^+NCH_2CH_3$ and at 0.95 ppm, (triplet) for $^-OP(O)OCH_2CH_3$. All these signals in the ^1H NMR spectrum confirm the formation of the above-mentioned structures. Data from the ^{13}C NMR spectroscopy (Table 4) support the formation of the structures **1**, **2** and **3**.

The viscosity of the degraded products decreases with the increase in the duration of degradation (Fig. 1).

Table 4
^{13}C NMR data of the degraded products

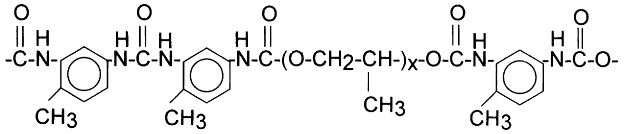
Type of carbon atom	δ (ppm)	Type of carbon atom	δ (ppm)
$^+N–CH_2CH_3$	8.15	$^+N–CH_2CH_3$	52.96
$^-O–P(O)OCH_2CH_3$	11.07	$C(O)OCH_2CH_3$	62.82
$C(O)OCH_2CH_3$	14.92	$^-OP(O)OCH_2CH_3$	62.86
$C_6H_3–CH_3$	16.37	$O–P(O)OCH_2CH_3$	64.23
$O–P(O)OCH_2CH_3$	16.48	$C(O)OCH_2CH_2–$	69.49
$C(O)CH_2CH_2–$	24.16	$OC(O)NH–$	154.17
$C(O)OCH_2CH_2–$	34.06	$NHC(O)NH–$	154.64
$C(O)CH_2–CH_2–$	34.26	$–C(O)–OCH_2–CH_2–$	173.47

Table 5
Phosphorus containing products from the chemical degradation of flexible polyester polyurethane foam by triethyl phosphate

N	Structure	^{31}P NMR, δ (ppm) J (Hz)	Content (%)	
			Upper layer	Lower layer
4		− 0.20, quintet $^3J(P,H) = 7.42$	61.5	74.2
5		− 0.55, q $^3J(P,H) = 7.3$	21.2	2.6
6		0.24, t $^3J(P,H) = 7.8$	5.1	3.3
7		0.55, t $^3J(P,H) = 8.0$	2.6	3.5
8		m, −11.16–12.28	9.6	16.3

3.2. Degradation of flexible polyether polyurethane foam

Flexible polyurethane foam based on toluene diisocyanate and polyether polyol with the following repeating unit was converted into liquid form by treatment with triethyl phosphate at 190°C.



In contrast to the flexible polyester polyurethane foam the degradation of flexible polyether polyurethane foam by triethyl phosphate results in the formation of two liquid layers and one solid product after 3 and 4 h of heating (Table 2). Interestingly after 2 h of heating the reaction mixture is homogeneous.

3.2.1. Study on the upper layer

The data from the ^{31}P NMR spectroscopy are summarized in Table 5. The $^{31}P\{H\}$ NMR spectrum of the degraded product obtained after 4 h of heating reveals signals at 0.55, 0.24, −0.20, −0.55, and at −11.16 to −12.28 ppm. The signal at −0.20 ppm, with highest intensity, represents a quintet with $^3J(P,H) = 7.42$ Hz and can be assigned to the phosphorus atom in the structure **4**. The triplet at 0.55 ppm with $^3J(P,H) = 8.0$ Hz can be assigned to the phosphorus atom in the structure **7**. The signal at 0.24 ppm with $^3J(P,H) = 7.8$ Hz is due to the phosphorus atom in the structure **6**. The quartet at −0.55 ppm with $^3J(P,H) = 7.3$ Hz can be assigned to the phosphorus atom in the structure **5**. Signals at −11.16 to −12.28 ppm in $^{31}P\{H\}$ NMR spectrum represent two doublets and one triplet. Obviously there is an interaction between the different phosphorus nuclei. In ^{31}P NMR spectrum there is one quintet at −11.27 ppm with $^3J(P,H) = 7.8$ Hz which is characteristic for $P–OCH_2CH_3$ spin–spin interaction. The other part of the spectrum is too complicated to be assigned to a particular type of phosphorus atom. On the basis of these results we could assume **8** as the most likely structure. Data from ^1H and ^{13}C NMR spectroscopy confirm the formation of the above-mentioned structures during the degradation of flexible polyether polyurethane foam.

3.2.2. Study on the lower layer

The study on the lower layer by ^{31}P, ^1H and ^{13}C NMR spectroscopy showed that the lower layer consists of the

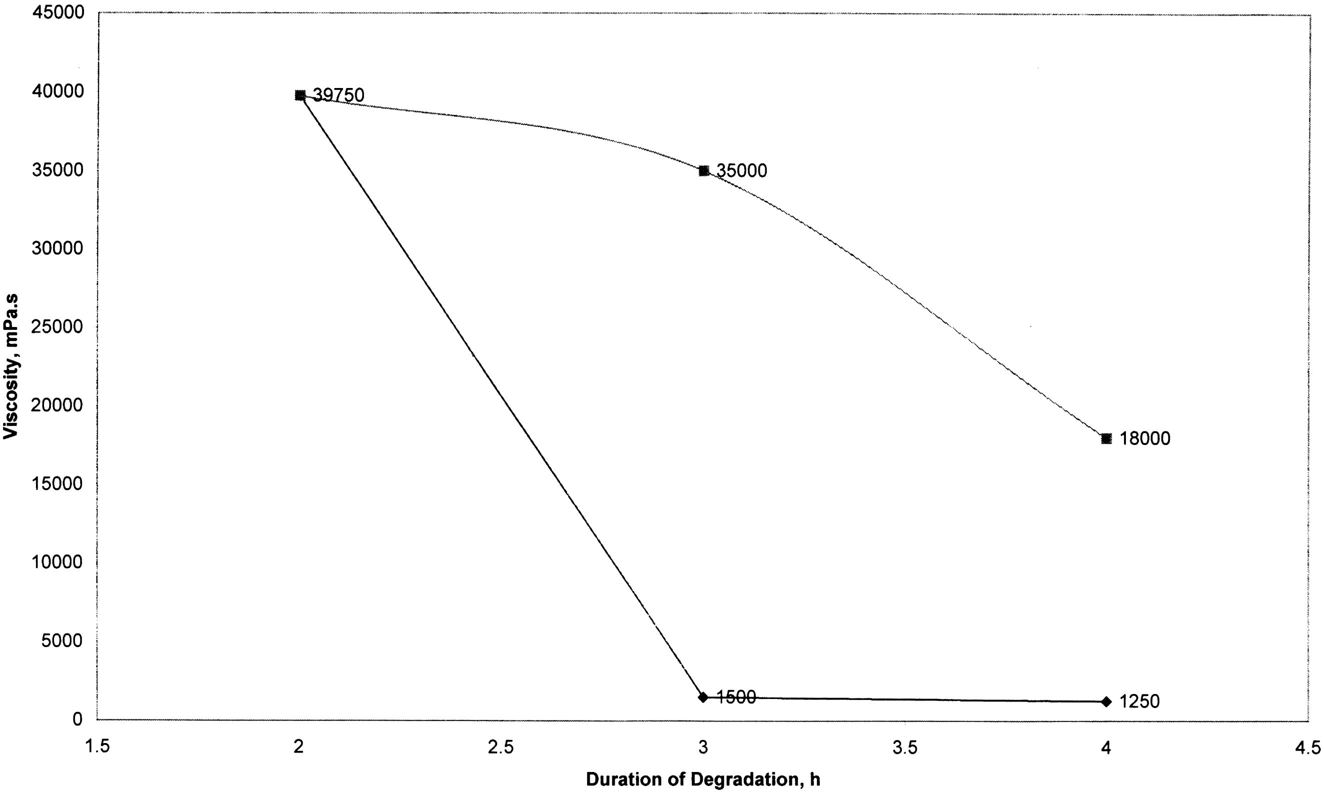


Fig. 2. Viscosity vs. duration of degradation of flexible polyether polyurethane foam by triethyl phosphate: ◆—upper layer; ■—lower layer.

same structures as the upper layer. The only difference is the composition of the mixture (Table 5).

The viscosity of the upper layer decreases with the increase in the duration of degradation (Fig. 2) and after 4 h of heating the viscosity is 1250 mPa.s while the viscosity is 18 000 mPa.s after the same degradation period.

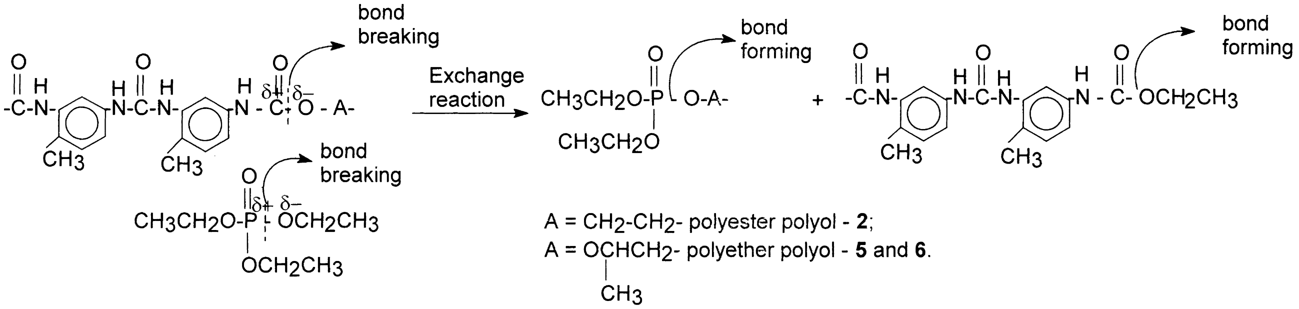
3.3. Mechanism of the degradation of flexible polyurethane foam by triethyl phosphate

The results obtained show that the degradation of polyurethane by triethyl phosphate includes two simultaneous reactions: an exchange reaction with the participation of the urethane group and the ethoxy group of phosphoric acid (Scheme 1) resulting in the breakdown of the polymer chain; and the alkylation of urethane group by triethyl phosphate (Scheme 2).

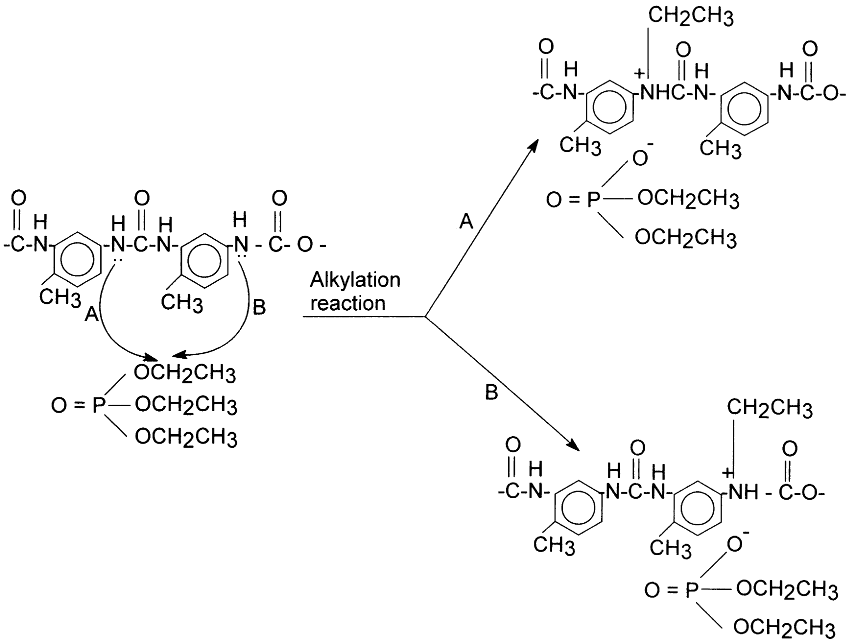
The formation of the above-mentioned structures during the degradation of flexible polyurethane foam is the result of: (i) an exchange reaction between the urethane group and the ester group of phosphoric acid; and (ii) an alkylation of urethane or urea groups by triethyl phosphate. This was proved by model reaction between urethane (ethyl carbamate) and dimethyl phosphonate [10].

4. Conclusion

It has been shown that flexible polyurethane foams can be converted quantitatively into liquid form by an exchange



Scheme 1.



Scheme 2.

reaction between the urethane group and ethoxy groups of phosphoric acid triethyl ester. The degraded products are phosphorus containing oligourethanes.

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