

# Smart Polymer Recycling: Synthesis of Novel Rigid Polyurethanes Using Phosphorus-Containing Oligomers Formed by Controlled Degradation of Microporous Polyurethane Elastomer

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**ABSTRACT:** This article describes a new approach for the recycling of microporous polyurethane elastomers by Tris(1-methyl-2-chloroethyl) phosphate-induced degradation. The phosphorus-containing degradation products formed are transformed into reactive intermediates by reaction with propylene oxide and are used for the preparation of rigid polyurethane foams. These new phospho-

rus-containing materials have higher density and better mechanical properties compared to the standard rigid polyurethane foams. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 302–308, 2007

**Key words:** degradation; flame-retardance; foams; polyurethanes; recycling

## INTRODUCTION

Polymer recycling is an important tool to improve the efficiency of energy consumption and to minimize the environmental impact of plastics. Despite the obvious progress in plastics waste reuse, the simple addition of ground waste-polymer to a “virgin” resin still lacks the necessary economic attractiveness. That is why the chemical transformation of polymer waste that could afford new monomers or polymer building blocks with new properties is such a viable alternative. The chemical degradation of polyurethanes, rigid, flexible, or polyurethane elastomers, involves well-known methods of hydrolysis,<sup>1</sup> glycolysis,<sup>2–4</sup> and aminolysis.<sup>5–8</sup> The degradation of microporous polyurethane elastomers has also been accomplished by treatment with mono-, di-, and triethanolamine,<sup>9</sup> and ethylene glycol,<sup>10</sup> as well as by catalytic glycolysis with 1,4-butanediol.<sup>11</sup>

Recently, we have reported on a highly efficient method for polymer recycling based on the degradation induced by esters of phosphonic or phosphoric acids. This strategy was used to transform polycarbonate,<sup>12</sup> poly(ethylene terephthalate),<sup>13</sup> and polyamide-6<sup>14</sup> into useful polymer additives. Polyurethanes

could also be depolymerized by the same reactive organophosphorous compounds.<sup>15–20</sup> The phosphorus-containing oligourethanes are logical application targets as fire retardants since phosphorus containing oligomers are widely used for the improvement of the polymers’ flame resistance.<sup>21–24</sup> The simple mixing of the fire retardant with the polymer matrix, however, is often burdened by phase separation and the diffusion to the surface eventually eliminates the fire suppressing additive. Therefore, the development of reactive organophosphorous agents that could be chemically incorporated into the polymers designated for fire protection would be highly beneficial. In this study, we aim to show that the products from the controlled degradation of a microporous polyurethane elastomer induced by Tris(1-methyl-2-chloroethyl) phosphate could be used successfully for the preparation of rigid polyurethane foams. The influence of these new fragments on the mechanical and thermal properties of the newly synthesized rigid polyurethane foams is investigated as well.

## EXPERIMENTAL

### Materials

The pure rigid polyurethane foam formulation “Resifoam AL 634/10” was supplied by Resina Chemie, Holland. It was based on Resinol AL 634 as the polyol component (hydroxyl number 407 mg KOH/g) and

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TABLE I  
Composition of the Reaction Mixture Obtained After Degradation Of Microporous Polyurethane Elastomer with Tris(1-methyl-2-chloroethyl) Phosphate

Compound	g	%
$\begin{array}{c} \text{O} \\ \parallel \\ \text{ClCH}_2\text{CH}(\text{CH}_3)\text{O}-\text{P}-\text{O}(\text{CH}_2)_4\text{OC}-\text{(CH}_2)_4\text{-CO}(\text{CH}_2)_4\text{-O-} \\   \qquad \qquad \qquad \parallel \qquad \qquad \qquad \parallel \\ \text{ClCH}_2\text{CH}(\text{CH}_3)\text{O} \qquad \qquad \qquad \text{O} \qquad \qquad \qquad \text{O} \end{array}$	45.6	51.6
$\begin{array}{c} \text{O} \\ \parallel \\ \text{ClCH}_2\text{CH}(\text{CH}_3)\text{O} \diagdown \text{P} \diagup \\ \text{ClCH}_2\text{CH}(\text{CH}_3)\text{O} \diagup \text{P} \diagdown \text{OH} \end{array}$	10.0	11.4
$\begin{array}{c} \text{O} \qquad \qquad \qquad \text{O} \\ \parallel \qquad \qquad \qquad \parallel \\ \text{ClCH}_2\text{CH}(\text{CH}_3)\text{O} \diagdown \text{P} \text{---} \text{OCH}_2\text{CHO} \text{---} \text{P} \diagup \\ \text{ClCH}_2\text{CH}(\text{CH}_3)\text{O} \diagup \qquad \qquad \qquad   \qquad \qquad \qquad \diagdown \qquad \qquad \qquad \diagup \\ \qquad \qquad \qquad \text{CH}_3 \qquad \qquad \qquad \text{OCH}(\text{CH}_3)\text{CH}_2\text{Cl} \qquad \qquad \qquad \text{OCH}(\text{CH}_3)\text{CH}_2\text{Cl} \end{array}$	30.7	34.8
$[\text{ClCH}_2\text{CH}(\text{CH}_3)\text{O}]_3\text{P} = \text{O}$	1.9	2.2

Urestyl 10 (4,4'-diphenylmethane diisocyanate) as the isocyanate reagent. Tris(1-methyl-2-chloroethyl) phosphate, TMCEP, a commercially available product from BASF AG (Ludwigshafen, Germany) was used as received. Propylene oxide (99+%, Aldrich) was distilled prior to use.

### Degradation procedure

The degradation was based on a previously published method<sup>20</sup> that was modified for the polyurethane at hand. The microporous polyurethane (40 g) was cut into small 3–5 mm pieces and was placed in a three-necked flask equipped with a reflux condenser, thermometer, and stirrer. TMCEP (120 g) was added and the temperature was increased to 180°C and kept at that level for 8 h under stirring. The system was cooled to 130–150°C and the unreacted TMCEP was removed under vacuum (0.16–0.18 mm Hg). 1-Chloro-2-propanol (3.78 g, 0.04 mol) and 1,2-dichloropropane (6.4 g, 0.056 mol) were also collected under liquid nitrogen. The reaction product is a liquid with viscosity 36,000 mPa s. Yield: 88.2 g. The composition and structure of the reaction products are presented in Table I and Scheme 1. They are soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , THF, DMF, and DMSO.

### Treatment of degraded microporous polyurethane elastomer with propylene oxide

Into a four-necked flask, equipped with a reflux condenser, thermometer, stirrer, and a dropping funnel was placed in a 65.5 g degraded microporous polyur-

ethane elastomer. Propylene oxide (7 g) was placed into the dropping funnel at 90°C and was added within 20 min to the reaction mixture with a simultaneous increase in the reaction temperature to 100°C. At that temperature, the reaction mixture was stirred for 4 h. Finally, the reaction product was subjected to a dynamic vacuum (18 mm Hg, 80°C). Yield: 71.2 g. The composition of the final reaction mixture is given in Table II.

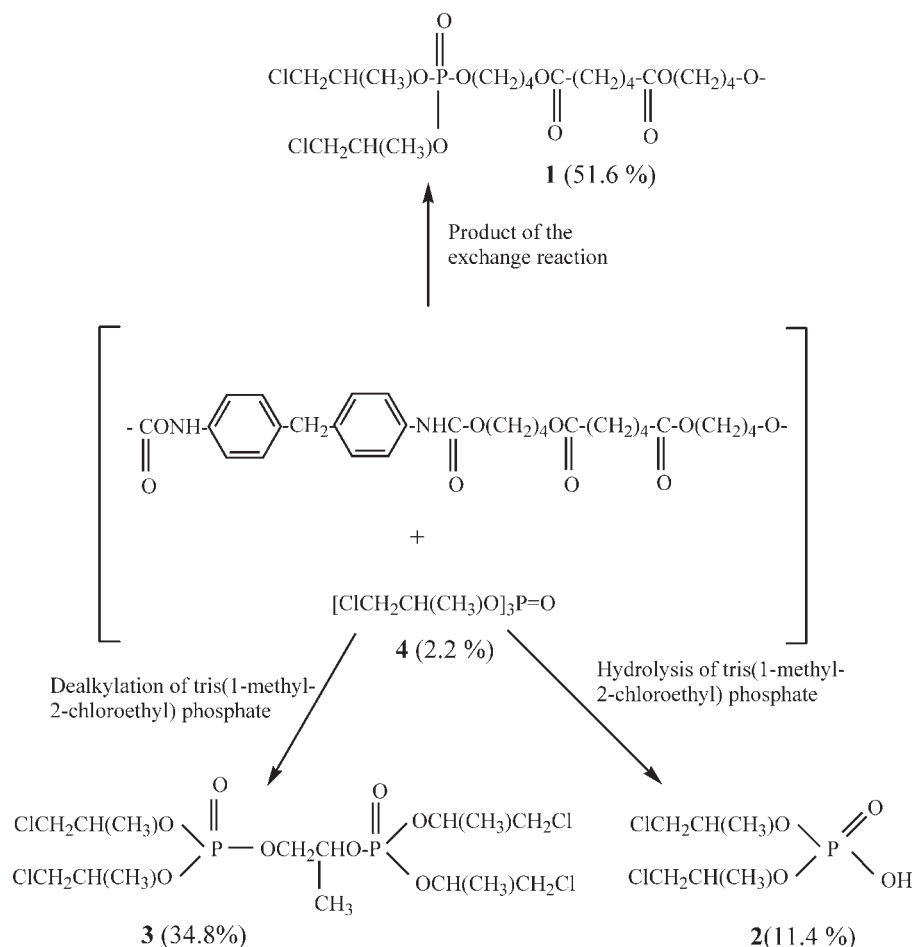
### Preparation of rigid polyurethane foams

The rigid polyurethane foam (F-1) was prepared by mixing Resinol AL 634 and Urestyl 10 at a weight ratio 1 : 1.47 (isocyanate index = 110). After intensive stirring, the mixture was poured into a container with dimensions 180/130/130 mm. The formulation prescription for the rigid polyurethane foams that incorporate degradation products (DP) in 5 wt % (F-2), 10 wt % (F-30), and 15 wt % (F-4) is given in Table III.

### Measurements

#### Nuclear magnetic resonance

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature on a Bruker Avance spectrometer (300 MHz) using tetramethylsilane as an internal standard and  $\text{CDCl}_3$  as the solvent.  $^{31}\text{P}$  NMR spectra were recorded on the same instrument in  $\text{CDCl}_3$  with chemical shifts reported in parts per million relative to external 85%  $\text{H}_3\text{PO}_4$ .



**Scheme 1** Interactions of microporous polyurethane elastomers with Tris(1-methyl-2-chloroethyl) phosphate.

#### Acid number

The acid number was calculated by the titration of sample with potassium hydroxide in the presence of phenolphthalein.

#### Viscosity

The viscosity was measured on a Brookfield LV viscometer.

#### Mechanical properties

The study of the mechanical properties of the rigid polyurethane foams was carried out on a "TIRA TEST 2300 in. (Germany) testing machine with plotting the force-displacement curves. The bending strength and the flexural modulus were determined by a three-point scheme with a centered loading and a displacement rate of 10 mm/min (ISO1209). The specimen size was 20/25/120 mm and the distance between the points of support was equal to 100 mm. Five specimens from each polyurethane foam were tested and the results were averaged. The compressive

strength and the compressive modulus of elasticity were tested at 5 mm/min displacement rate of the compression plate (ISO 844). Overall, six specimens from each polyurethane foam were tested, three were loaded along the parallel of foaming, and the other three were loaded on a perpendicular direction of the foaming. The specimens were  $50 \times 50 \times 50 \text{ mm}^3$  in size. The results of each series were averaged.

#### Dimensional stability

The dimensional stability was examined using a specimen with dimensions  $100 \pm 1 \times 50 \pm 1 \times 25 \pm 1 \text{ mm}^3$ .

#### Thermal analysis

The thermal stability of the foams was examined by thermal gravimetric analysis (TGA) using a derivatograph C (MOM, Hungary) at a  $10^\circ\text{C}/\text{min}$  heating rate. The nitrogen flow rate was 17 L/h over a 20 mg sample.

TABLE II  
Composition of the Reaction Mixture After Treatment with Propylene Oxide

Compound	g <sup>a</sup>	% <sup>a</sup>
	33.9	47.6
	13.1	18.4
	22.8	32.0
$[ClCH_2CH(CH_3)O]_3P=O$	1.4	2.0

<sup>a</sup> 65.5 g degradation mixture, obtained after the reaction with Tris(1-methyl-2-chloroethyl), phosphate, is treated with propylene oxide.

#### Resistance to combustion

The resistance to combustion of the rigid polyurethane foams was studied by the limiting oxygen index (LOI). The LOI was determined by the van Krevelen equation.<sup>25</sup>

### RESULTS AND DISCUSSION

Tris(1-methyl-2-chloroethyl) phosphate, TMCEP, was chosen as the degrading agent because this ester of the phosphoric acid is widely used as a flame retardant for rigid polyurethane foams. The treatment of the microporous polyurethane elastomer with TMCEP at 180°C results in the formation of a homogeneous mixture, which consists of products 1, 2, 3, and 4 (Table I, Scheme 1).

The assignments of the chemical shifts of P, C, and H atoms in the DP are based on the data published by van Wazer and coworkers,<sup>26</sup> Penczek and Pretula,<sup>27</sup> Ignatious,<sup>28</sup> and Troev.<sup>29</sup> For example, the signal at -3.10 ppm in the <sup>31</sup>P NMR spectrum and the one at -2.67 ppm, which represent quintets with <sup>3</sup>J(P,H) = 7.6 Hz, can be assigned to the phosphorus atom of the product 3 surrounded by OCH(CH<sub>3</sub>) groups and of the unreacted Tris(1-methyl-2-chloroethyl) phosphate, respectively. The signal at -2.06 ppm, which represents a quintet with <sup>3</sup>J(P,H) = 7.1 Hz, can be attributed to the phosphorus atoms bonded with OCH<sub>2</sub>- group in products 3 and 1. The signal at -2.06 ppm can be assigned to the phosphorus atom of the product 2 as well. The multiplet at

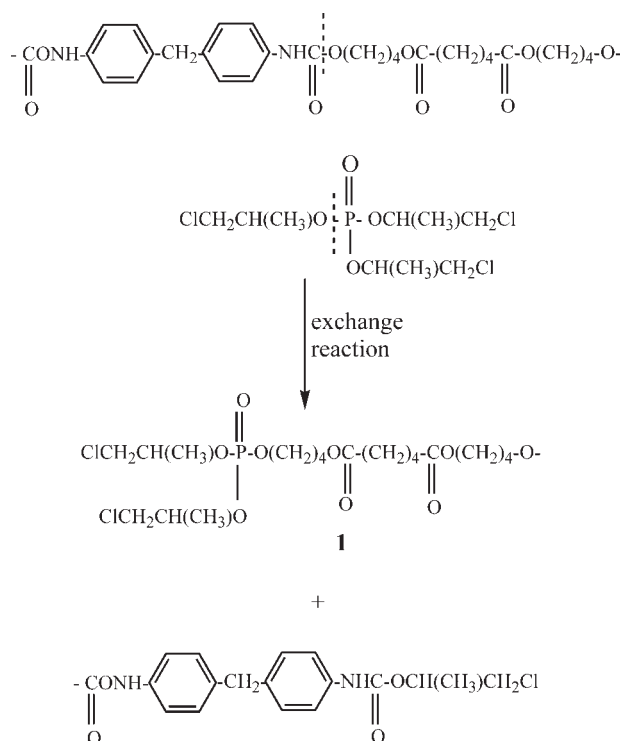
4.01–4.10 ppm in the <sup>1</sup>H NMR spectrum of the DP is characteristic for P—OCH<sub>2</sub>— protons. Such protons are present in products 3 and 1. The signal at 64.27 ppm in the <sup>13</sup>C{H} NMR spectrum, which is a doublet with <sup>3</sup>J(P,H) = 6.3 Hz, can be assigned to POCH<sub>2</sub>- carbon atoms in products 3 and 1.

Product 1 is formed as the result from the exchange reaction between 1-methyl-2-chloroethoxy groups of Tris(1-methyl-2-chloroethyl) phosphate and urethane groups (Scheme 2).

This exchange reaction results in breaking down the main polymer chain of the microporous polyurethane elastomer and leads to the formation of oligomers. The

TABLE III  
Characteristic Data and Properties of Rigid Polyurethane Foams

Characteristic data	F1	F2	F3	F4
Resinol AL 634 (g)	62.5	62.5	62.5	62.5
Urestyl 10 (g)	92.0	92.0	92.0	92.0
Degraded product (DP)				
g	0.0	8.1	17.2	27.3
wt (%)	0.0	5.0	10.0	15.0
Isocyanate index	110	108.3	106.4	104.3
P (%)	0.73	1.01	1.33	1.63
Cl (%)	2.48	3.17	3.96	4.83
Reaction time at 20°C cup test				
Cream time (s)	28.0	24.0	30.0	60.0
Gel time (s)	91.4	118.3	140.0	167.4
Tack free time (s)	111.4	143.3	175.1	227.4
Density (kg/m <sup>3</sup> )	33.5	37.5	40.9	46.9
Closed cell (%)	97.2	96.8	96.5	96.0
LOI × 100	25.9	25.0	25.9	25.8

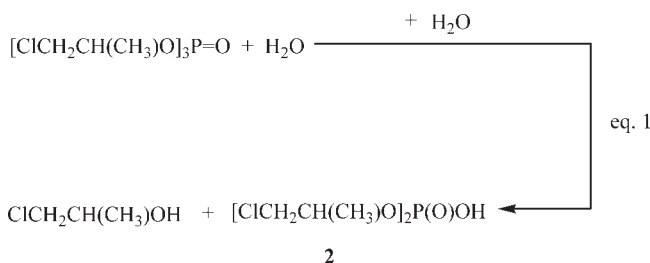


**Scheme 2** Exchange reaction between urethane group and alkoxy group of Tris(1-methyl-2-chloroethyl)phosphate.

content of the phosphorus fragment in the product **1** is calculated on the base of integral intensity of the phosphorus atoms in the  $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the reaction mixture.

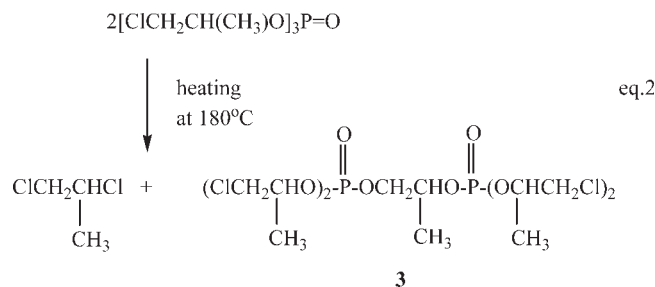
It is established that the TMCEP-induced degradation of the microporous polyurethane elastomer is accompanied by the formation of 1-chloro-2-propanol and 1,2-dichloropropane. Both compounds are removed from the reaction mixture by distillation and liquid nitrogen trapping. The structure of both compounds was identified by  $^1\text{H}$  NMR spectroscopy. Their formation is discussed below.

1-Chloro-2-propanol (3.78 g, 0.04 mol) is possibly formed as a result of TMCEP hydrolysis because of the traces of moisture present in the microporous polyurethane elastomer [eq.(1)]



The content of **2** (11.4%) was calculated on the basis of the amount of 1-chloro-2-propanol evolved.

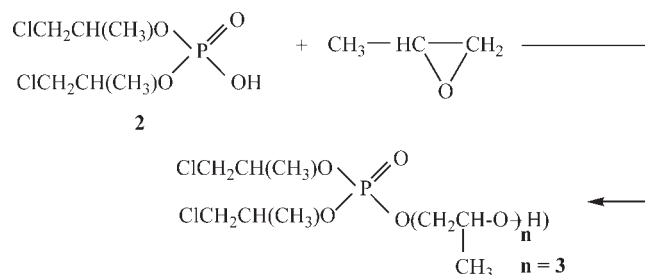
Dealkylation of TMCEP results in the formation of 1,2-dichloropropane (6.4 g, 0.056 mol) and compound **3** [eq. (2)].<sup>30</sup>



The content of **3** (m.w. = 542 Da) is 34.8% as calculated on the basis of the amount of 1,2-dichloropropane evolved.

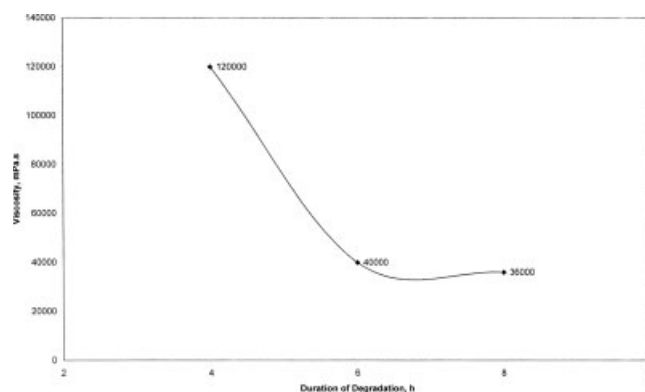
The experimental results show that (i) the duration of the degradation process at temperatures lower than  $180^\circ\text{C}$  is too long—10–12 h; (ii) the viscosity of the reaction mixture decreases with increasing of the reaction time (Fig. 1). Lowest viscosity was obtained when the reaction mixture was heated for 8 h.

The degradation mixture has an acid number of 89-mg KOH/g because of the presence of the product **2**. The treatment with propylene oxide reduces this acid number to 4.5 mg KOH/g as the result from the following reaction:

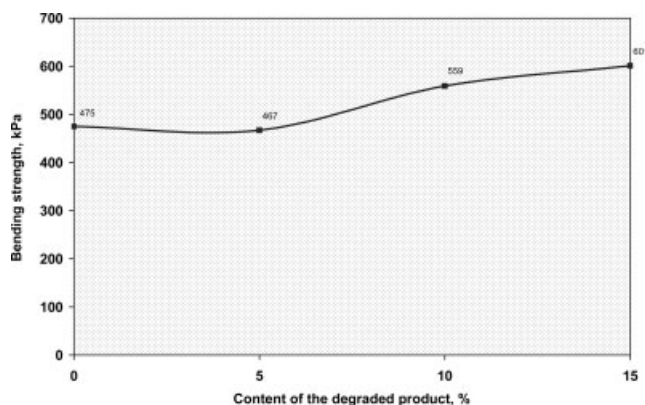


The reaction mixture has hydroxyl number of 74.9 mg KOH/g. The propylene oxide treatment also lowers the viscosity of the degradation mixture from 36,000 to 3200 mPa.

The degradation mixture obtained after treatment with propylene oxide (Table II) contains 5.75% P and



**Figure 1** Changes in the viscosity during the degradation of microporous polyurethane elastomer by Tris(1-methyl-2-chloroethyl) phosphate.

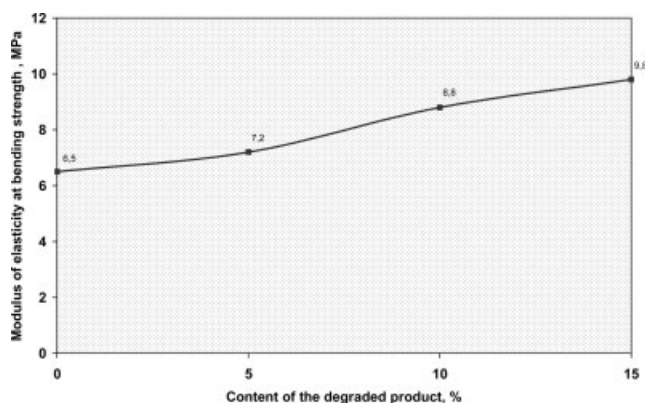


**Figure 2** Influence of the content of degraded product on the bending strength.

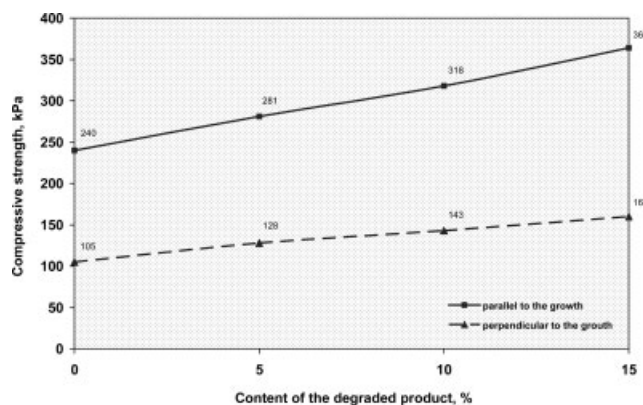
14.0% CI and is further used for the preparation of rigid polyurethane foams.

The mixture is incorporated into the rigid polyurethane foam compositions in quantities up to 15 wt % (Table III). The results from the study on the reactivity of the new compositions show that the cream time, gel time, and tack free time increase when compared with the standard system (Table III). The density of the new rigid polyurethane foams increases with increasing the amount of the DP (Table III).

The percentage of the closed cells is slightly influenced by the amount of the DP incorporated (Table III). The presence of DP in the rigid polyurethane compositions favorably affects their mechanical properties as well. The bending strength (Fig. 2) increases when 10 and 15 wt % of DP are used for the polyurethane formulation. The relative increase is 17.7% and 26.5%, respectively. The maximum value of the modulus of elasticity increases 50% at bending strength (Fig. 3). The compressive strength at 10% relative deformation, parallel and perpendicular to the growth, also increases and depends on the amount of DP added (Fig. 4). For a sample containing 15 wt % of DP, the compressive strength at 10% relative deformation parallel to the growth and perpendicular to



**Figure 3** Influence of the content of degradation products on the modulus of elasticity at bending strength.

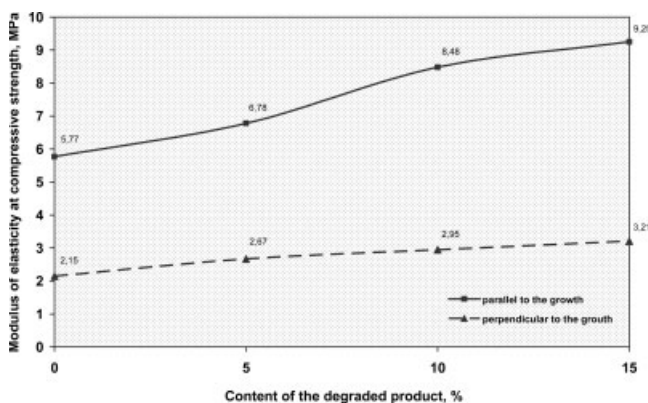


**Figure 4** Effect of the content of degradation products on compressive strength.

the growth increases with 51 and 52%, respectively. It should be noted that the presence of DP in the polyurethane foams leads to substantial improving of the modulus of elasticity at compressive strength (Fig. 5). The compressive modulus of elasticity parallel to the growth increases from 6.78 MPa for a sample containing 5 wt % of DP to 9.25 MPa for sample with 15 wt % of DP. The same relationship exists for the compressive modulus of elasticity perpendicular to the growth as well (Fig. 5). The results obtained show that DP can be used successfully for the preparation of rigid polyurethanes with improved exploitation characteristics (high density and good mechanical properties).

A study on the dimensional stability of the foams (Table IV) shows that the dimensional stability of the DP containing foams (F-2, F-3, and F-4) at  $-20^{\circ}\text{C}$  is identical to the standard system (F-1). At  $100^{\circ}\text{C}$ , however, the dimensional stability of F-2, F-3, and F-4 foams is lower compared with the standard system.

The thermal degradation of the rigid polyurethane foams was analyzed by TGA (Table V). The TGA analyses are carried out under  $\text{N}_2$  atmosphere because organophosphorus compounds considered to be active as flame retardants must be initially trans-



**Figure 5** Dependence of the modulus of elasticity at compressive strength on the content of degradation products.

**TABLE IV**  
Properties of Rigid Polyurethane Foams

Dimensional stability (%)	F-1	F-2	F-3	F-4
24 h, -20°C				
Length (%)	0.0	0.3	-0.15	-0.10
Width (%)	0.5	0.8	-0.30	0.30
Thickness (%)	0.4	0.2	-0.60	0.0
Volume (%)	0.9	1.3	-1.05	0.20
24 h, 100°C				
Length (%)	-0.35	-0.70	1.70	-1.40
Width (%)	-0.70	0.20	-0.7	3.40
Thickness (%)	0.0	0.20	1.80	3.40
Volume (%)	-1.10	-0.30	2.80	5.4

formed into inorganic phosphates. The oxidation of the organophosphorus compounds is facilitated by the oxygen in the air and takes place above 600°C, producing smaller residue amounts than those produced under N<sub>2</sub> atmosphere at 850°C. The TGA data show that the standard foam (F-1) and the DP modified foams (F-2, F-3, and F-4) start to decompose at 155–160°C. The fast degradation region is in the temperature interval 250–260°C for all samples. The maximum rate of degradation is at 320°C for F-1, F-2, and F-3, and at 286°C for F-4. The results obtained reveal that there is no significant difference in the thermal stability of the standard foam and new foams. The char residue (CR) at 850°C is 21.2% for the standard sample, whereas it is 18.3% for F-2 and 20.9% for F-3 and F-4.

van Krevelen has demonstrated that there is a significant correlation between the CR in weight percentage and the LOI.<sup>25,31</sup> This linear relationship can be presented by the following equation:

$$\text{LOI} \times 100 = 17.5 + 0.4 \text{ CR}$$

where CR is the char residue in weight percentage at 850°C from the TGA measurement. This equation has been already used successfully for the calculation of the LOI of the phosphorus-containing epoxy resins.<sup>28</sup> The LOI of the standard system Resifoam 634/10, which contains 25 wt % of Tris(1-methyl-2-chloroethyl) phosphate as the flame retardant is 25.9 (Table III). Notably, the same values are also calculated for F-3 and F-4, but with lower DP content, 10 and 15 wt %, respectively. For F-2, the LOI is 25.0 even with 5 wt % of DP.

## CONCLUSIONS

We have found that phosphorus- and hydroxyl-containing oligourethanes produced via chemical degradation of microporous polyurethane elastomer by Tris(1-methyl-2-chloroethyl) phosphate and subsequent propylene oxide treatment could be used successfully for the preparation of a new rigid polyurethane foams. The new rigid foams have higher den-

**TABLE V**  
Thermal Stability of Polyurethane Foams

Materials	Temperature (°C) at characteristic weight loss (%)						Residue at 850°C (%)
	5	10	20	30	40	50	
F-1	235	272	305	320	339	365	21.2
F-2	226	259	294	314	329	355	18.3
F-3	226	261	290	302	320	358	20.9
F-4	226	252	281	295	320	357	20.9

sity and better mechanical properties compared to the standard rigid polyurethane foam. Their thermal stability is comparable to commercial products containing higher amounts of flame retardants.

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