

Influence of phosphorus content and of increase of cyclic structures content in crosslinked cellular urethane copolymers upon their physical properties*

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Received 23 May 1975

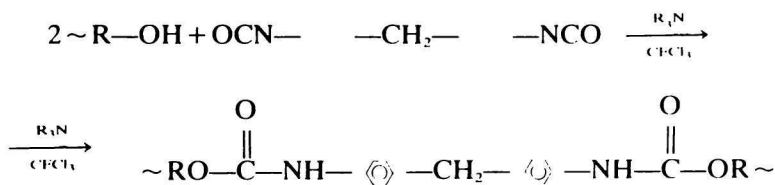
The influence of polyhydroxy compounds containing at least one P—C bond as well as that of polyhydroxy compounds containing cyclic structures upon the flammability, thermal resistance, and thermomechanical properties of cellular copolyurethanes has been investigated. The minimum of flammability was reached at the phosphorus content 1.85% in urethane copolymer containing no chlorine and at 0.7—0.85% P in copolymers obtained from organo-phosphorus compounds containing chlorine and phosphorus in a molar ratio from 2 to 6. In TGA experiments, from cellular copolyurethanes containing phosphorus and chlorine a much larger amount of residue remained at 400°C, than from urethanes containing phosphorus alone. The thermomechanical properties of cellular copolymers did not deteriorate up to the 30% content of any organo-phosphorus compound used in experiments in mixtures with polyetherols. An increase of crosslinking density of phosphorus containing urethane copolymers as well as additional inserting from 2 to 6% of aromatic or saccharose rings caused the decrease of flammability of polyurethanes.

Изучалось влияние полигидроксильных веществ, содержащих минимально одну связь P—C или циклические структуры, на горючесть, температуроустойчивость и термомеханические свойства целлюлярных сополимеров. Минимальная горючесть достиглась при содержании фосфора 1.85% в уретановом сополимере несодержащем хлор и при 0,7—0,85% P в сополимерах полученных из фосфорорганических веществ содержащих хлор и фосфор при молярном отношении от 2 до 6. На основе ТГА измерений было установлено, что при 400°C намного высший остаток из целлюлярных сополиуретанов содержащих фосфор и хлор, чем из уретанов содержащих только фосфор. Термомеханические свойства целлюлярных сополимеров не ухудшились до 30% содержания любого фосфорорганического вещества примененного в опытах в смеси с полигидроксильными веществами. Увеличение плотности структурирования фосфор содержащих уретановых сополимеров как и добавочное встроение 2—6% ароматических или сахарозных циклов не вызвало понижение горючести полиуретанов.

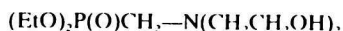
Highly crosslinked cellular urethane copolymers in the form of rigid polyurethane foams are prepared by a fast exothermic reaction of aromatic

* Presented at the 4th IUPAC International Conference "Modified Polymers, Their Preparation and Properties", Bratislava, July 1—4, 1975.

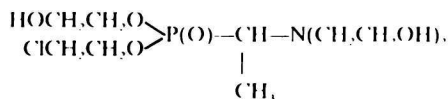
diisocyanates with polyhydroxy compounds in the presence of catalysts, blowing agents, and surfactants [1—3]



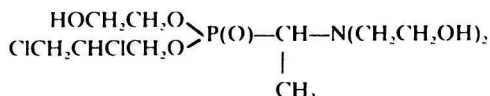
Scheme 1



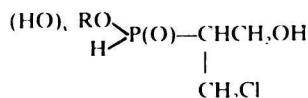
I *Fyrol 6* Stauffer Co., USA
OH value = 460



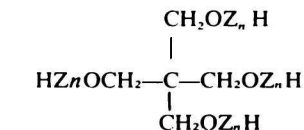
II Synthesized according to [9]
OH value = 500



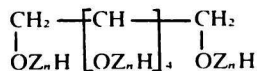
III Synthesized according to [9]
OH value = 460



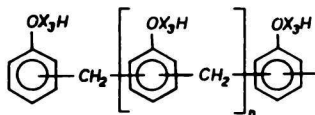
IV (HO), RO(H) — product of addition reaction of epichlorohydrin and glycerol
Polyetherol TGEP [10]
OH value = 550



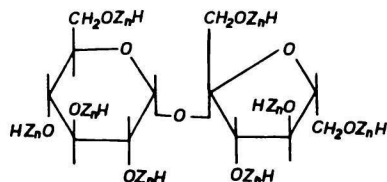
V *Bypolet 45* ICSO, Poland
OH value = 490



VI *Propylan RF 55* Lankro CO., G. Britain
OH value = 495



VII *Isopol K1* ICSO, Poland
OH value = 250, mixed with glycerol to OH value = 495



VIII *Propylan RF 33* Lankro Co., G. Britain
OH value = 495

Generally: $X = (C_2CH_2O)$ $Z = \begin{array}{c} (CH_2CHO) \\ | \\ CH_3 \end{array}$ $n = 1 - 2$

Owing to their highly developed surface the cellular polymers are particularly flammable [4, 5]. A large number of investigations have been made to find new methods which can effectively decrease their flammability [5—8]. One of these methods concerns the use of organo-phosphorus compounds [6, 7].

Scheme 1 gives eight polyhydroxy compounds. Four of them contain phosphorus. The purpose of our investigation was to define the influence of the structure and content of polyhydroxy organo-phosphorus compounds *I—IV*,* containing at least one P—C bond, upon the flammability, thermal resistance, and thermomechanical properties of cellular copolyurethanes. The influence of polyhydroxy compounds *VII* and *VIII* containing two types of structures, aromatic and saccharose, as well as the influence of crosslinking density upon these properties has also been investigated.

Experimental

The compounds *I—IV* in mixtures with aliphatic polyetherols *V* and *VI* were submitted to isocyanate polyaddition reaction with crude diphenylmethane diisocyanate. The obtained cellular polymers have an apparent density of $33 \pm 2 \text{ kg/m}^3$. Organo-phosphorus polyols *I—IV*, having Cl—P ratio from 0 to 6, were investigated with respect to the flammability of cellular urethane copolymers which were obtained from mixtures of these compounds with tetrol *V* and triethanolamine (Table 1).

Table 1

Composition of mixtures of polyhydroxy compounds including different organo-phosphorus polyols for the preparation of rigid urethane foams

Components of polyol mixtures	Parts by weight
Organo-phosphorus polyol (compounds <i>I—IV</i>)	x
Aliphatic tetrol (compound <i>V</i>)	$95 - x$
Triethanolamine	5

Table 2

Composition of mixtures of polyhydroxy compounds including polyols with aromatic or saccharose rings for the preparation of rigid urethane foams

Components of polyol mixtures	Parts by weight
Organo-phosphorus polyol (compound <i>I</i>)	20
Polyol with cyclic groups (compound <i>VII</i> or <i>VIII</i>)	x
Propoxylated sorbitol (compound <i>VI</i>)	$80 - x$

In order to obtain a maximum decrease of the flammability characteristics of cellular polyurethanes, we have examined and compared the influences of aromatic and saccharose rings introduced additionally to polyurethanes containing a constant content of phosphorus and aromatic rings. The urethane copolymers were obtained from the reaction of crude diphenylmethane diisocyanate with mixtures of polyhydroxy compounds given in Table 2.

* The Roman numerals in the following text refer to Scheme 1.

Results and discussion

The crosslinked cellular copolyurethanes, obtained from organo-phosphorus compounds with a large content of chlorine in the molecule, have shown evidently a higher grade of self-extinguishment than cellular polyurethanes obtained from the compound *I* containing no chlorine (Fig. 1). The obtained results were compatible with those reported by *Piechota* [11]. The minimum rate of burning in the ASTM D1692-68 test for the copolymers obtained from the compound *I* was found at a phosphorus content of 1.85%. However, it has been found unexpectedly, that an increase of chlorine content in the organo-phosphorus compound caused a narrowing of the range of phosphorus content in the cellular copolymer having a minimum rate of burning, and it also shifted this range towards lower content of phosphorus (Fig. 1). The effect of phosphorus compounds on the mechanism of extinguishment is not completely explained. Phosphorus, as P_2O_5 , is believed to perform its function in the condensed phase by promoting the formation of a protective char layer, which further inhibits heat transfer, access of oxygen, and the escape of carbon oxides by a physical blockade. Phosphorus (as P_2O_5) acts also as a fluxing and stabilizing agent of the char layer [5]. In our opinion, the excess of phosphorus above a certain specific optimum level in the polymer would probably tend to decrease the coherence of the forming char barrier at fire temperature by an undesirable "overfluxing" acting or by a surface migration (sublimation) of P_2O_5 . This may involve inconsiderable increasing of burning rate of polymer in the ASTM D1692 test and involves no influence of phosphorus over optimum content upon flammability of polymer in other tests. Chlorine may increase the effect of diminishing coherence of char above an optimum level of phosphorus in the polymer.

Introduction of phosphorus to cellular polyurethanes caused a decrease of the starting temperature of their decomposition in comparison with the standard, phosphorus-free polyurethane (Fig. 2). On the other hand, the residue at 400°C from phosphorus-containing copolymers was considerably larger than the residue from phosphorus-free copolymer [12] (Fig. 2). From crosslinked cellular copolyurethanes containing chlorine and phosphorus in the molar ratio 2 : 1, a much larger amount of residue remained at 400°C than from urethane copolymers containing only phosphorus.

Introduction of phosphorus to polymer chains involves usually a deterioration of thermomechanical properties of polymers. It has been found, however, that the heat resistance of cellular copolymers did not change up to the 30% content of an organo-phosphorus compound (Fig. 3). Higher quantities involved a decrease of the heat resistance of cellular copolyurethanes. The copolymers prepared from polyols *II* and *III* which contained more than two OH groups showed better thermomechanical properties than the copolymers based on difunctional monomers.

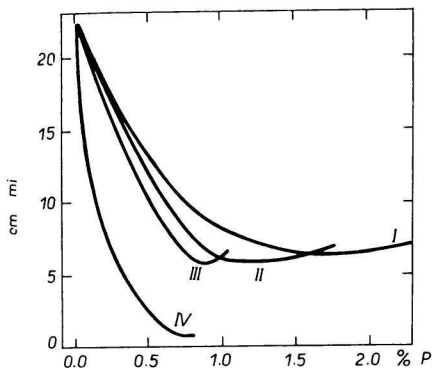


Fig. 1. Burning rate (cm min^{-1} , ASTM D1692) phosphorus content (%) in rigid polyurethanes. I—IV denote the foams obtained from polyol mixtures containing compounds I—IV, according to Table 1.

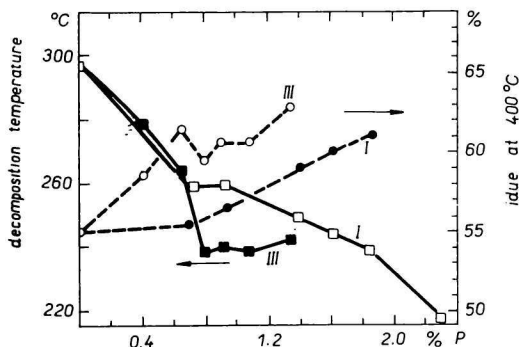


Fig. 2. Thermal decomposition of cellular polyurethanes. I and III denote the rigid foams obtained from polyol mixtures containing compound I or III, according to Table 1.

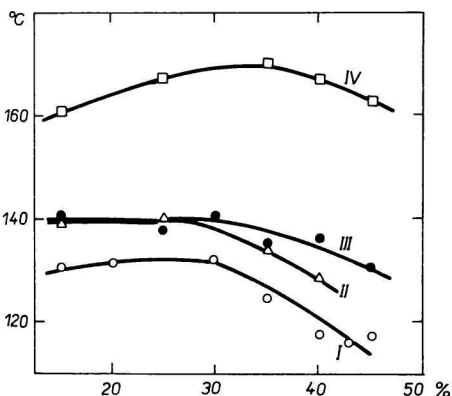


Fig. 3. Relationship between content (%) of compounds I—IV in polyol mixtures (according to Table 1) and thermomechanical properties (softening point, $^{\circ}\text{C}$, DIN 53424-1964) of cellular rigid polyurethanes.

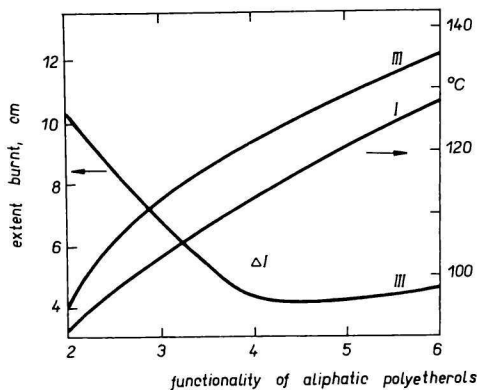


Fig. 4. Functionality of aliphatic polyetherols (V, VI, and others) mixed with compound I or III in the proportion 70 : 30 w/w vs. extent burnt (cm, ASTM D1692) (—) compound III; (Δ) compound I and thermomechanical properties (softening point, $^{\circ}\text{C}$, DIN 53424-1964) of cellular rigid polyurethanes.

Using 30% aminophosphonates I and III in mixtures with different aliphatic polyetherols, their influences on cellular polyurethanes were examined. The increase of functionality of aliphatic polyetherols caused a decrease of flammability of polyurethanes. An increase of crosslinking density of phosphorus-containing urethane copolymers, due to an increased functionality of polyetherols, gave rise to their better thermomechanical properties (Fig. 4).

The cellular copolyurethanes obtained from aromatic polyol *VII* have shown a lesser flammability in the ASTM D1692 test than copolymers obtained from the saccharose polyol *VIII* (Fig. 5). In the Buttler chimney test [13] it was observed that an increase of residue in cellular polyurethanes with additionally inserted aromatic rings is faster than in polyurethanes containing saccharose rings, as the amount of cyclic units in the structure of polyurethanes increased (Fig. 5). On the other hand, the saccharose-containing copolyurethanes have shown an earlier flame extinguishment in the Buttler chimney test (Fig. 5). This can be explained by

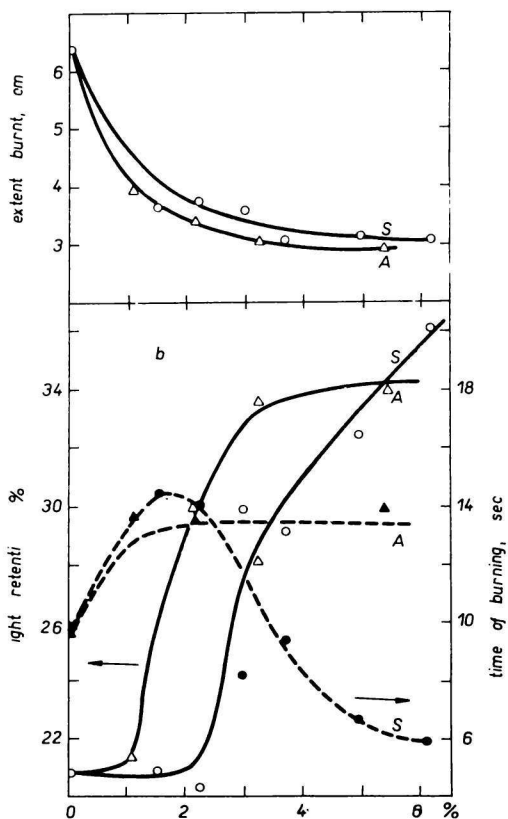


Fig. 5. Relationship between additional content (%) of cyclic structures in cellular polyurethanes and flammability of polyurethanes (constant content of aromatic rings 29%) in the ASTM D1692 (a) and Buttler chimney tests (b).

A and S denote the rigid foams obtained from polyol mixtures containing aromatic polyol *VII* (A) or saccharose polyol *VIII* (S), according to Table 2.

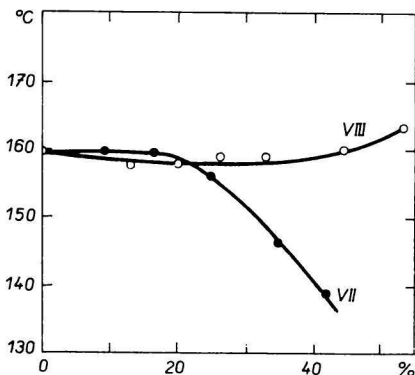


Fig. 6. Relationship between content (%) of compound *VII* and *VIII* in polyol mixtures (according to Table 2) and thermomechanical properties (softening point, °C, DIN 53424-1964) of cellular rigid polyurethanes.

generation of water vapours in the course of pyrolysis of carbohydrate structures [4]. The saccharose rings, due to their rigidity, improved heat resistance of phosphorus-containing polyurethanes (Fig. 6). However, the series of cellular copolyurethanes obtained from aromatic polyetherol *VII* showed deteriorated thermomechanical properties, due to the low functionality of the latter.

Conclusion

It may be stated that the most profitable modification of cellular urethane copolymers aimed at the production of rigid polyurethane foams with a maximally reduced flammability and good thermomechanical properties can be obtained by introducing no more than 0.6% of phosphorus and 3.6% of chlorine or 1.4% of phosphorus without chlorine. Organo-phosphorus compounds are preferred in the form of polyols containing three hydroxyl groups in the molecule. The possibly highest increase of cyclic carbohydrate structures in the polymer or the increased participation of aromatic rings to at least 3% above the normal content of aromatic rings in the polymer with the optimum level of phosphorus causes a considerable decrease of its flammability.

References

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