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Synthesis and properties of urethane foams having a N_3P_3 ring compound

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To prepare the flexible and non-flammable urethane foam, the product formed by the reaction of 1,1-diamino 3,3,5,5-tetraphenoxycyclotriphosphazene, $N_3P_3(NH_2)_2(OC_6H_5)_4$, and TDI-80 consisted of 80% 2,4-tolylenediisocyanate and 20% 2,6-tolylenediisocyanate was carried out with polyol(PPG-BM: (oxypropyrene)triol; M_w = 3000, hydroxyl number 56) and water in the presence of various concentrations of amine (triethylenediamine) and tin (dibutyltin dilaurate) catalysts. The foam without shrinkage was obtained with 0.1 to 0.2 g amine and 0.3 g tin catalysts. It had a limiting oxygen index value of 21 and the tensile strength and elongation of the foam were about 0.075 MPa and 140%, respectively. However, the T_g of the foam estimated from tan δ was −24° C and this was almost the same value as that of the foam without N_3P_3 ring compounds.

1. Introduction

Polymers containing P=N bonds, especially polyphosphazenes, have been studied by many researchers, and many reviews [1] have been published. Linear, cyclolinear and cyclomatrix-type polymers were present in the polyphosphazene groups. Many types of linear polymer have been synthesized and some have been on the market. For example, PNF 100 or PNF 200 elastomer under their commercial names, were initially developed by Fire Stone and Rubber Co., and they have been sold by Ethil Co., in the USA. However, production of the cyclolinear polyphosphazene has been delayed because it is difficult to prepare the polymer with a higher molecular weight [2]. However, if a synthetic route to produce the polymer is devised, the polymer will be stable on heating.

1,1-diamino 3,3,5,5-tetraphenoxycyclotriphosphazene, $N_3P_3(NH_2)_2(OC_6H_5)_4$, is a useful compound as a precursor of the cyclolinear polymer, and has been studied well. The organic and inorganic hybrid material was studied by Kajiwara [3–5].

This report describes the synthesis and properties of hybrid phosphazene–urethane foams prepared using modified tolylenediisocyanate and 1,1-diamino 3,3,5,5-tetraphenoxycyclotriphosphazene.

2. Experimental procedure

2.1. Preparation of $P_3N_3(NH_2)_2(OC_6H_5)_4$ (DAPP)

90 g hexachlorocyclotriphosphazene $(NPCl_2)_3$ were placed in a flask which was equipped with a reflux condenser and a magnetic stirrer. After 400 ml of diethylether was added to dissolve $(NPCl_2)_3$, 270 g of 15 M aqueous ammonia were slowly added by means of a syringe, while the contents of the flask were being stirred. After the addition was complete, the mixture was refluxed for 1 h with continuous stirring. The resulting two-phase system was transferred to a separation funnel, where the ether layer was removed and washed several times with water. The ether solution was then dried over anhydrous calcium chloride, followed by solvent removal with a rotary evaporator. The resulting white solid was heated with 120 ml of *n*-heptane to dissolve the unreacted hexachlorocyclotriphosphazene. The solid remaining after filtration of the cooled suspension was recrystallized from diethyl ether by cooling the saturated solution to −70° C. The product formed was $N_3P_3Cl_4(NH_2)_2$ having a melting point of 163 to 165° C.

A three-necked flask was fitted with a reflex condenser. In this flask were placed 20 ml THF dried over sodium, 0.08 mol phenol and 0.08 mol sodium. After the reaction had been completed, 0.016 mol 1,1-diamino 3,3,5,5-tetraclorocyclotriphosphazene dissolved in 100 ml THF was added to this flask, and the mixture was refluxed with a rotary evaporator. The resulting solid was removed, and washed several times with water. The ether solution was then dried over anhydrous calcium chloride, and the solvent was removed with a rotary evaporator. The crude product was purified by recrystallization from benzene.

The yield based upon $N_3P_3Cl_4(NH_2)_2$ was 60 to 70% and the product had an m.p. of 104 to 104.5° C. The infrared absorption spectrum of the product showed that ν_{NH} and $\nu_{P=N}$ appeared at 3450 and 1200 cm^{-1}, respectively. These results agreed with the analytical data described by McBee [6]. Consequently, it was found that the product formed from this experiment was $N_3P_3(OC_6H_5)_4(NH_2)_2$ (DAPP).

2.2. Reaction of DAPP with TDI-80

The TDI-80 used in this study was composed of 80% 2,4-tolylenediisocyanate and 20% 2,6-tolylenediisocyanate. A typical reaction procedure was as follows: 1.351 g DAPP was reacted with 0.874 g TDI-80 in 100 ml THF solvent at room temperature. The pro-

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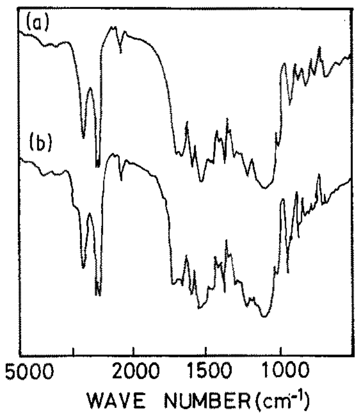


Figure 1 The infrared absorption spectrum of the foams: (a) standard (foam A), (b) modified by DAPP (foam B).

duct obtained after 2 h was labelled I. On the other hand, 2.34 g DAPP was reacted with 6.96 g TDI-80 without solvent at room temperature. This product after 10 h preparation without solvent was labelled II.

The reaction ratio of isocyanate groups was measured by the conventional dibutylamine method.

2.3. Preparation of foams

All foams were prepared by the one-shot technique employing a two-component system. Component A consisted of TDI-80 or TDI-80 and product II, and component B of the polyol(poly(oxypropyrene)triol: $M_w = 3000$, hydroxyl number 56), silicone surfactant (L-520: Nippon Yunika Co., Ltd), H_2O and catalyst (triethylenediamine and dibutyltin dilaurate). The amount of catalyst was adjusted to allow preparation of foams with a density of $0.03 + 0.003\,g\,cm^{-3}$ and an expansion time of 75 to 180 sec. The foams were synthesized at room temperature and were then allowed to age at room temperature for at least 7 d prior to testing.

The infrared absorption spectrum of the hybrid phosphazene/urethane foam is shown in Fig. 1. The frequency of P=N is assigned to about $1170\,cm^{-1}$ [6]. A medium weak band at $2230\,cm^{-1}$ appeared in the spectrum. This was assigned to free $-NCO$ groups and was observed in the standard sample.

2.4. Analysis

The molecular weights of products I and II were determined by gel permeation chromatography using a Toyosoda HLC-901 with G3000H + G2000H. The peaks were calibrated with polystyrene standards. Infrared adsorption spectra were recorded on a Japan Spectroscopic Co., Ltd IR-A1 using KBr discs.

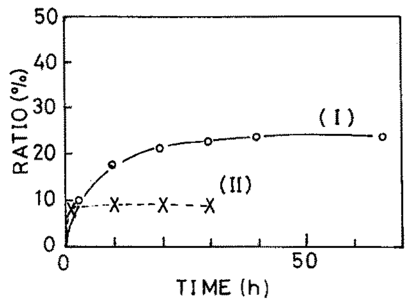


Figure 2 The reaction ratio of -NCO groups; (○) DAPP/TDI-80 (molar ratio) = 1/2 with THF; (x) DAPP/TDI-80 (molar ratio) = 1/10 without solvent.

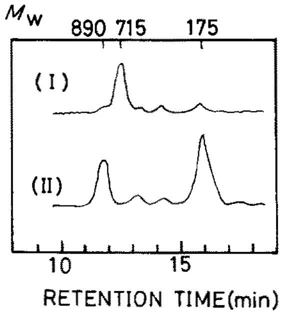


Figure 3 The molecular weight distribution of the products: (I) DAPP/TDI-80 (molar ratio) = 1/2 with THF after 40 h; (II) DAPP/TDI-80 (molar ratio) = 1/10 without solvent after 10 h.

The physical properties of the foam were measured using the method described in ASTM D 1564-71 and the standard procedure for slab cellular materials. Dynamic properties were measured under the following conditions: frequency of vibration 110 Hz thermal rate $1°C\,min^{-1}$ by Rheovibron DDV-III-EA(Toyo Baldwin Co. Ltd).

The flame resistance was determined by ASTM D 1692-67T and the limiting oxygen index (LOI) method. The LOI was determined by a Suga ON-AU testing according to JIS-K-7201. The specimens for LOI and dynamic properties were prepared as follows: 9 to 9.5 g foam was packed into a mould of dimensions 60 mm × 60 mm × 2 mm, and a pressure of $100\,kg\,cm^{-2}$ was applied for 15 min at 140° C.

3. Results and discussion

3.1. The reaction of DAPP with TDI-80

The reaction between DAPP and TDI-80 was carried out with THF as solvent and a molar ratio of DAPP/TDI-80 = 1/2 at room temperature. The percentage reaction is determined by chemical analysis of isocyanate groups in the reaction mixture, and the results are shown in Fig. 2. The reaction does not proceed when only TDI-80 is dissolved in THF. It is seen from Fig. 2 that the reaction per cent is about 25% after 40 h when DAPP is reacted with TDI-80. On the other hand, the reaction rate determined by the analysis for the case without THF solvent is about 10% after 10 h.

The molecular weight distribution of the products I and II prepared with or without THF solvent was determined by gel permeation chromatography, and the results are shown in Fig. 3. Kajiwara [4, 5] reported

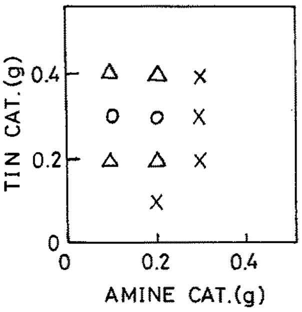


Figure 4 The reaction conditions. (○) Good, (△) shrinkage, (x) collapse.

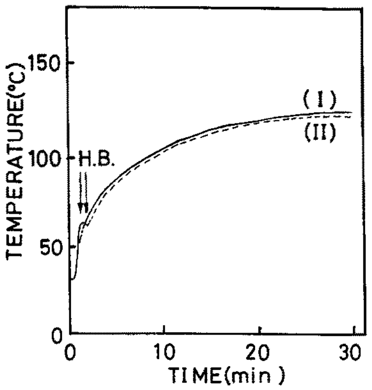
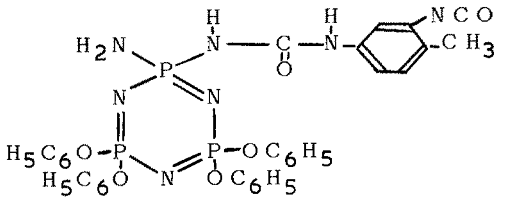


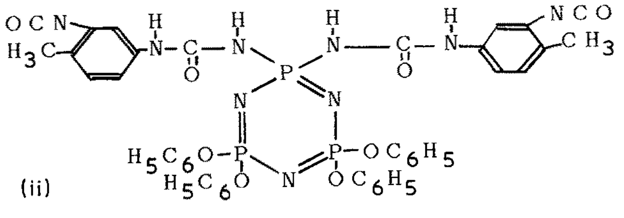
Figure 5 The profile of the internal temperature: (——) standard (foam A); (- - -) modified by DAPP (foam B). H.B. = healthy bubbles.

that the products formed by the reaction between DAPP and 2,4-tolylenediisocyanate were oligomers which had molecular weights of 800 to 2200. The reaction conditions of this study differed from those of Kajiwara in the solvent, the molar ratio of DAPP/TDI-80 and the reaction temperature used. However, the molecular weight of product I is about 715 as shown in Fig. 3 (I). From the molecular weight measurement of product I, it can be presumed that this product has the average structure as shown in Scheme (i). The molecular weight distribution curve of product II prepared after 10 h is given in Fig. 3 (II). The calculated molecular weight of product II is about 890, but unreacted TDI-80 is detected. From this result, it can be presumed that product II having the molecular weight of 890 has a structure such as in Scheme (ii)

(i)



(ii)



3.2. Preparation of the foam

Product II is used for the preparation of the foam, i.e. product II is mixed with TDI-80 and reacted with polyol and water using silicone surfactant, triethylenediamine and dibutyltin dilaurate. One of the representative of compositions is summarized in Table I.

The reaction conditions for foam preparation are summarized in Fig. 4. The foam reaction with the modified TDI-80 is more unstable than with TDI-80. The amount of catalyst required for stable reaction is small. It is presumed from Fig. 2 that the amino group of DAPP had catalysis, so these unstable reactions are caused by the modifed TDI-80.

The relation between the internal temperature of the foam in the course of the polymerization process and the reaction time was studied, and the results are given in Fig. 5.

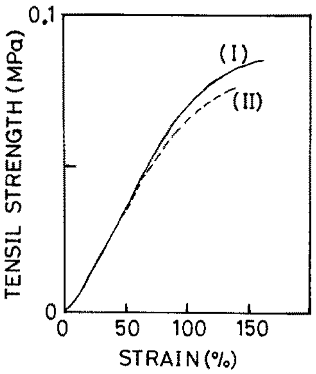


Figure 6 Tensile strength of foams: (——) standard, (foam A); (- - -) modified by DAPP (foam B).

It is found from Fig. 5 that the temperature increases with increasing reaction time, and the increasing rate of the temperature is almost the same for foams A and B. The temperature rise is due to the polymerization reaction between isocyanate groups and hydroxy groups. After 30 min, as shown in Fig. 5, the maximum temperature reaches ~ 120 to 130° C, and the temperature falls at room temperature. During the reaction, the distortion in the region of 1 to 2 min is caused by the healthy bubbles. There is the difference in the amount of catalyst required for stable reaction, but the profiles resembled each other.

3.3. Properties of the foam

Several properties of foams A and B prepared under optimum experimental conditions are summarized in Table II.

Retardation of the combustion of foam B is larger than that of foam A. The LOI of foam B is 21, therefore it is not combustible in air and it has the self-extinguish grade of ASTM D 1692-67T test. As the LOI value of the various poly(aryloxyphosphazenes) ranged from 23 to 34 [7], it seems that foam B has a higher oxygen index, in spite of a small amount of phosphazene.

Generally, a foam's mechanical property depends on its density. Fig. 6 shows the stress–strain curve: the density of foam B is larger than that of foam A, but the tensile strength of foam B is smaller than that of foam A. In order to decrease the effect of open cells,

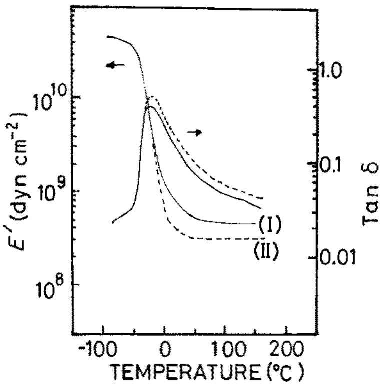


Figure 7 The dynamic properties: (——) standard (foam A); (- - -) modified by DAPP (foam B).

TABLE I Formulation of foams A and B

Formulation	(A)	(B)
Component A		
DAPP	0	10
TDI-80	49.0	52.2
Component B		
Polyol (M_w = 3000: hydroxyl no. 56)	100	100
Water	3.9	3.9
Triethylenediamine	0.1	0.2
Dibutyltin dilaurate	0.3	0.3
Surfactant (L-520)	1.2	1.2
NCO Index	105	105

sheet specimens prepared from the foam are used for measuring the dynamic properties.

E'-temperature and tan δ curves are shown in Fig. 7. E' of the sheet prepared from foam B in the region 0 to 200° C was lower than that of the reference standard, the sheet prepared from foam A. Thus, the modulus of foam B decreases rather more than that of foam A. In contrast with mechanical properties, T_g did not vary, because the damping peak appears at the same temperature, and the transition regions fit each other. T_g of foams A and B estimated from these results are both $-24°$ C.

TABLE II Properties of foams A and B

Properties	A	B
Foam density ($g\,cm^{-3}$)	0.0274	0.0302
Tensile strength (MPa)	0.085	0.075
Elongation (%)	166	140
LOI	17.9	21.0
ASTM D 1692-67T Grade	Burn	Self-extinguish

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