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# Synthesis and properties of polyurethanes blended with poly(bispropoxyphosphazene)

Wen-Yen Chiu [a,*], Pin-Sheng Wang [b], Trong-Ming Don [b1]

[a]*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC*
[b]*Institute of Material Science and Engineering, National Taiwan University, Taipei, Taiwan, ROC*

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**Abstract**

A two-step polymerization was used to synthesize polyurethanes (PU) with different amount of poly(bispropoxyphosphazene) flame retardant, LFR. Diphenylmethane diisocyanate (MDI) was first reacted with poly(tetramethylene oxide), PTMO 1000, to form an isocyanate-terminated prepolymer. The prepolymer was then reacted with a 1,4-butanediol/LFR homogeneous mixture at 70°C for 100 min, followed by 1 h at 100°C. The structures and properties of these modified PU were investigated using a differential scanning calorimeter (DSC), tensile testing machine, dynamic mechanical analysis instrument, Fourier transform infrared spectrophotometer, nuclear magnetic resonance spectroscopy and scanning electronic microscope (SEM). It was found that the addition of LFR would accelerate the urethane reactions and introduce a formation of micro-crosslinks. Consequently, the glass transition temperature (*Tg*) of PU was increased and the rubbery plateau region was extended. From SEM observation, LFR additive phase-separated from the PU matrix with good interfacial bonding. The existence of LFR caused a decrease both in ultimate tensile strength and elongation at break of polyurethanes. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polyurethanes; Poly(bispropoxyphosphazene); Blends; Flame retardant; Diphenylmethane diisocyanate; Poly(tetramethylene oxide)

## 1. Introduction

Polyurethane elastomers are synthetic elastomers with many advantageous properties, which have led to their use in a wide range of applications. They are synthesized from the reactions of polyether-based or polyester-based diols and diisocyanates, followed by the introduction of chain extenders to form the macromolecules. Their basic chemical structure is the urethane group (R-NHCOO-R′). Because the nitrogen atom has a strong tendency to withdraw electrons, the hydrogen atom can form hydrogen bonding with the oxygen atom. As a result, physical crosslinks are produced [1,2], and what so-called hard segments and soft segments are thus introduced to describe the chain structure. The soft segments are mainly from polydiol oligomers. As the chain length of polydiol increases, the glass transition temperature (*Tg*) shifts to lower temperatures, resulting in more phase separation [3,4]. Yet, when the polarity of soft segments increases, a portion of hard segments could dissolve in the soft-segment domain, and, therefore, increase the *Tg* and modulus of PU [5]. The hard segments are from the diisocyanate esters and chain extenders. It is known that extended hydrogen bonding exists in the hard-segment domain due to the high concentration of polar groups. These hard segments disperse in the soft-segment matrix and act as physical crosslinks, which has an effect of reinforcement of the PU material [6,7].

Generally, polymers do not have sufficient flame retardancy and are easily burned. Therefore, the developments of technologies in flame retardancy and flame retardants have been studied for many years with increasing emphasis. Flame retardancy can be improved by adding flame retardants, which can be divided into two groups: additive-type and reactive-type. Among them, phosphorus compounds are increasingly gaining popularity over their halogen counterparts, since they generally give off non-toxic and non-corrosive volatile combustion products. In this study, a poly(bispropoxyphosphazene) flame retardant with high phosphorus and nitrogen content was incorporated into the polyurethanes during the synthesis. Structures and properties of these

* Corresponding author.
[1] Present address: Department of Chemical Engineering, Mingchi Institute of Technology, Taipei, Shein, Taiwan, ROC.

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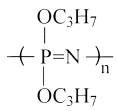
modified polyurethanes were investigated. The thermal degradation behavior and flammability of these modified polyurethanes will be reported in the next paper [8].

## 2. Experimental

### 2.1. Materials

4,4′-Diphenylmethane diisocyanate (MDI) was supplied by BASF Company. MDI was heated in an oven at 65°C and only the upper clear solution was removed for the further synthesis. Poly(tetramethylene oxide), PTMO 1000, from Union Carbide has a molecular weight of 1000. PTMO 1000 and 1, 4-butanediol (1, 4-BD) from Tedia Chemical Company were demoisturized in a vacuum oven with a vacuum pump. Poly(bispropoxyphosphazene), LFR, was kindly supplied by Chung-Shan Institute of Science and Technology. It has a viscosity of 4600 cps at 25°C and chlorine content less than 1%. The chemical structure of this LFR is indicated below.



All the other chemicals were analytical grades and used as received without further purification.

### 2.2. Synthesis

All the polyurethane samples were synthesized by a two-step polymerization.

#### 2.2.1. Synthesis of prepolymer

A certain amount of MDI (see Table 1) was placed into a reactor purged with $N_2$. The reactor was immersed into an isothermal water bath at 45°C. A given amount of PTMO 1000 was added into the reactor and stirred with a speed of 400 rpm for 10 min. The temperature was then gradually increased to 68°C and the reaction was continued for 4 h. Finally, a prepolymer terminated with isocyanate groups was obtained. The end-of-reaction was determined by a titration method using *n*-butyldiamine.

Table 1
The composition of various PU samples (wt%)

| Sample | MDI | PTMO | 1,4-BD | LFR |
|---|---|---|---|---|
| LFR | 0 | 0 | 0 | 100 |
| PU0F | 32.30 | 62.11 | 5.59 | 0 |
| PU3F | 31.36 | 60.30 | 5.43 | 2.91 |
| PU7F | 30.19 | 58.05 | 5.22 | 6.54 |
| PU10F | 29.36 | 56.47 | 5.08 | 9.09 |

#### 2.2.2. Synthesis of LFR-modified polyurethanes

1,4-BD was first mixed with LFR to form a homogeneous mixture. A certain amount of this mixture was then added into the prepolymer in a reactor with strong stirring. It was degassed with a vacuum pump. The ratio of NCO/OH was 1.04. After thorough mixing, the mixture was removed to a mold with dimension 15 x 15 x 0.2 cm. It was heated at 70°C in a hot-press machine for 100 min followed by 2 h at 100°C. Table 1 lists the recipe of PU samples and the phosphorus content is shown in Table 2.

### 2.3. Structure analysis

The chemical structures and surface functional groups of various polyurethanes were investigated by using a Fourier transform infrared (FTIR) spectrophotometer from BIO-RAD FTS-40 and a FTIR with attenuated total reflection (ATR) from JASCO FTIR 300-E, respectively. A nuclear magnetic resonance (NMR) spectroscopy from JEOL EX-400 MHz was used to verify the chemical structure of LFR.

### 2.4. Thermal properties

Du Pont 9900-910 differential scanning calorimeter (DSC) was used to study the optimum reaction condition and the transition temperatures such as glass transition temperature (*Tg*) and melting temperature (*Tm*). The instrument was first calibrated with indium followed by baseline adjustment. Approximately 5–10 mg samples were placed in aluminum pans and were scanned from 20 to 140°C for the study of optimum reaction condition and from −150 to 175°C for the observation of transition temperatures.

### 2.5. Mechanical properties

Tensile properties: ultimate tensile strength, initial modulus and elongation at break, were measured using a Universal Tensile Testing Instrument, RTM-1 T, from Yashima Works Company. The dimension of specimens was 40×6×2 mm and the tensile speed was 100 mm/min.

Table 2
The phosphorous content of LFR and various PU samples

| Sample | Phosphorous content (%) (theoretical value) | Phosphoroous content (%) (experimental value)[a] |
|---|---|---|
| LFR | 21 | 21 |
| PU0F | 0 | < 0.2 |
| PU3F | 0.61 | 0.67 |
| PU7F | 1.37 | 1.47 |
| PU10F | 1.91 | 2.04 |

[a] The phosphorous content of PU samples was determined by colorimetry.

Dynamic mechanical thermal properties were measured using Du Pont 9900-983 dynamic mechanical analyzer, in order to understand the effects of LFR additive on the transition temperatures and structures of polyurethanes. The sample specimens were 50 x 10 x 2 mm and the measured frequency was 1 Hz. The temperature range was from −170° to 175°C and the heating rate was 10°C/min.

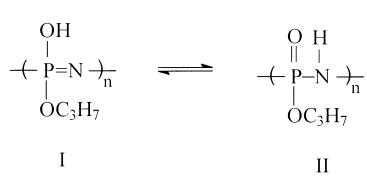
### 2.6. Morphology

A scanning electron microscope, model JEOL TSM-6300, was used to observe the fracture surfaces of modified polyurethanes in order to understand the morphology. In addition, an energy dispersive X-ray analyzer, EDX, was coupled to analyze the composition of dispersed particles in polyurethanes.

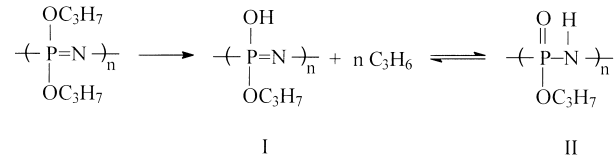
## 3. Results and discussion

### 3.1. Structure of LFR

The structure of LFR was identified by $^{13}$C-NMR, $^{31}$P-NMR, $^{1}$H-NMR and FTIR. The absorption peaks at $\delta = 10$, 23 and 67 ppm in $^{13}$C-NMR were from the carbons at CH3, CH2, and CH2O in the propoxyl groups. The phosphorus atom gave a broad absorption peak from 15 to 20 ppm in $^{31}$P-NMR spectrum as a result of the steric effect due to the existence of both linear and cyclic structures in LFR. The ratio of cyclic to linear structure was estimated as 65–35. In $^{1}$H-NMR spectrum, the proton absorption peaks corresponding to -CH3 , -CH2-, and -CH2O- in propoxyl groups were observed at 0.9, 1.7 and 3.85 ppm. Yet, in addition, two other small peaks were found at 2.18 and 4 ppm, which has been proved to be the hydrogens in the N-H group and O-H group respectively [9–11]. It has been established that this polyphosphazene compound contains small amount of two isomeric compounds:

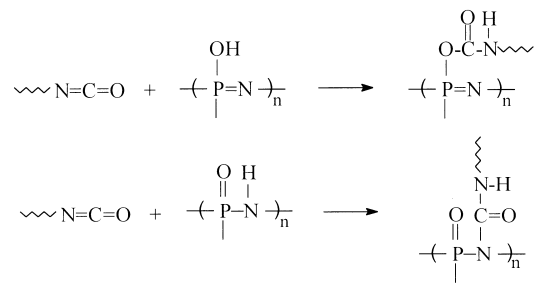



which were increased in amount with thermal treatment. To prove this, a FTIR spectrum of LFR after 3 h at 150°C was shown in Fig. 1. The N-H absorption peak of structure II was observed and increased in intensity after thermal treatment. Denq [11] found that the LFR undergoes a thermal degradation followed by an isomerization at high temperatures. The reactions are shown below:




The discharged gas produced during thermal degradation was proved to be the propylene in the TGA-FTIR analysis [11,12].

From the above analysis, it is highly possible that during the synthesis of LFR-modified polyurethanes, a small amount of isomeric compounds, structures I and II, could be produced from the thermal degradation of LFR, especially in the hot press at 100°C. Since structures I and II contain hydroxyl and secondary amino groups, respectively, which could therefore react with isocyanate groups in prepolymer, thus a micro-crosslink structure possibly could be formed in polyurethanes. A preliminary study shows that a neat PU can dissolve in tetrahydrofuran (THF) solvent, yet not the LFR-modified PU, only swelling. The reactions are indicated below:




### 3.2. Studies on the reaction conditions

A certain amount of prepolymer was added to the 1,4-BD/LFR homogeneous mixture, according to Table 1. After strong stirring, 10 mg of sample was placed in an aluminum pan in DSC and was scanned at a heating rate of 5°C/min to observe the exothermic reaction. It

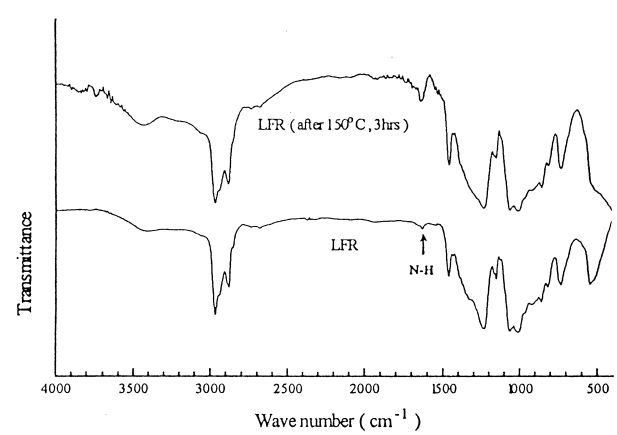



Fig. 1. The FTIR spectra of LFR and LFR after 3 h at 150°C.

was found that the maximum exothermic peak was at 84°C for a neat PU, and the peak value decreased to lower temperatures with the addition of LFR. For PU20F, the maximum peak value decreased to 52°C. These results indicate that the LFR additive could accelerate the synthesis reaction of PU. Basically, LFR has a chemical structure with tertiary amine, which is well known for its catalytic effect in PU synthesis [5]. From DSC results, therefore, 70°C was chosen as the reaction temperature for the synthesis of all PU samples.

When the synthesis of a neat PU was carried out at 70°C for 100 min, the reactions were complete as can be seen in the DSC thermogram using isothermal mode. The curve approached to a plateau already at 50 min. In addition, no exothermic peak was found with further heating at 5°C/min. Yet, only a small amount of sample (10 mg or so) was needed in DSC, the reactions could still be locally incomplete with the quantity of sample needed in the hot press due to the inhomogeneous heating. Therefore, post reaction was required. Generally, the post reaction temperature is in the range of 100–110°C for the synthesis of PU. Therefore, 100°C was chosen and the reaction time was determined by the tensile mechanical properties of PU samples. It was found that the sample with 2 h post-reaction gave the best ultimate tensile strength and adequate elongation at break. In conclusion, the synthesis of various samples was carried out at 70°C for 100 min, followed by 2 h at 100°C. FTIR spectra validated that the isocyanate groups at 2270 $cm^{-1}$ completely disappeared after reaction.

### 3.3. Thermal properties

DSC was used to study the thermal properties of various samples. A glass transition temperature at low temperatures and a melting peak at high temperatures were observed for every PU sample. They were caused by the non-crystalline region of soft segments and strong hydrogen-bonding/crystalline region of the hard segments, respectively. The glass transition temperatures of LFR and a neat PU were at −69 and −42°C, respectively. Yet, with the addition of LFR into PU, Tg values of these modified PU were found to be even higher than the neat PU, Table 3, not in between as generally

Table 3
The glass transition temperature (*Tg*) of LFR and various PU samples in DSC. The heating rate was 10°C/min

| Sample | *Tg*(°C) | |
|---|---|---|
| | First run | Second run |
| LFR | −68.7 | −69.3 |
| PU0F | −41.6 | −20.8 |
| PU3F | −39.3 | −19.6 |
| PU7F | −39.1 | −20.8 |
| PU10F | −38.9 | −21.4 |

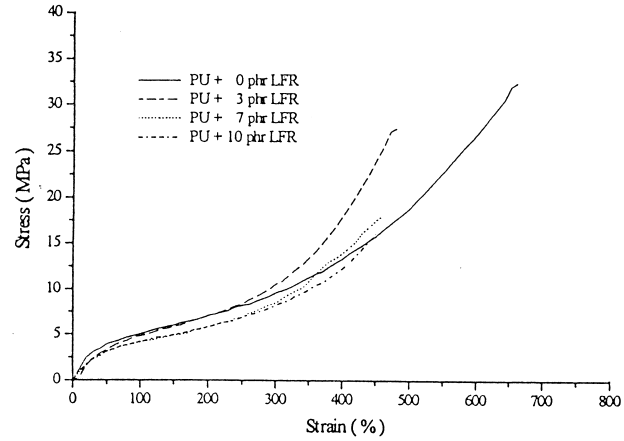



Fig. 2. Stress–strain curves of neat PU and LFR-modified PU samples.

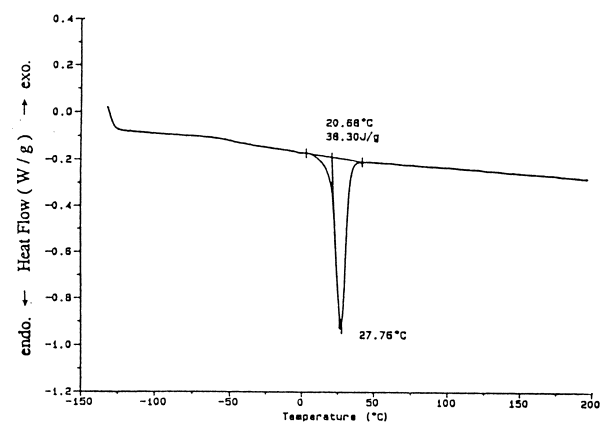



Fig. 3. The DSC thermogram of a neat PU after stretching. The heating rate was 10°C/min.

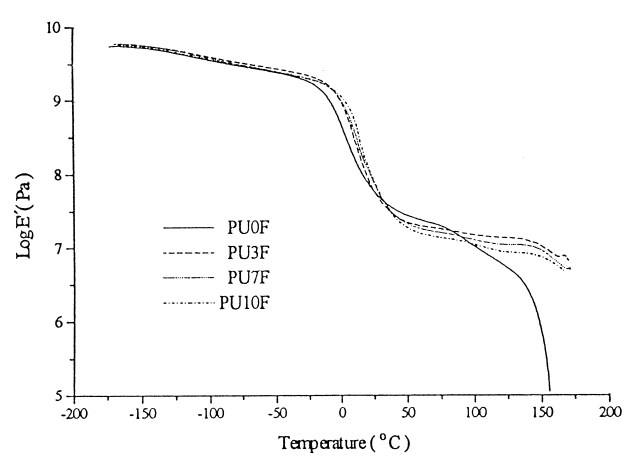



Fig. 4. The dynamic modulus of LFR-modified PU samples compared with a neat PU. The measured frequency was 1 Hz.

observed in the homogeneous blends. This can be explained presumably by the formation of micro-crosslinks as mentioned previously.

By quenching the samples to −150°C after first run in DSC, they were then re-heated to 175°C at 10°C/min. In which, the glass transition temperatures of polyurethanes shifted to higher temperatures compared with the results in the first run, Table 3. This is because the diffusion and mixing of the hard and soft segments, during the heating at high temperatures in the first run, could increase the portion of the hard segments in the soft-segment domain. Consequently, the glass transition temperatures were increased. If the samples were kept at 90°C for 1 h after the second run, hard segments and soft segments began to phase separate again due to the relaxation of molecular chains. Therefore, *Tg* shifted back to low temperatures and the melting peak at high temperatures was restored.

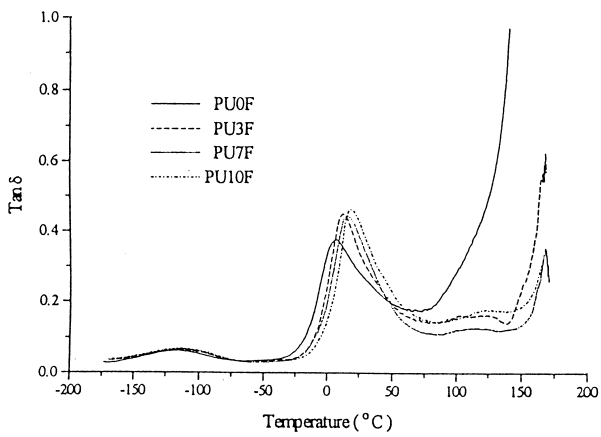



Fig. 5. The loss tanδ curves of LFR-modified PU samples compared with a neat PU. The measured frequency was 1 Hz.

### 3.4. Mechanical and dynamical mechanical properties

The mechanical properties of polyurethanes generally are determined by the intermolecular bonding, domain size of the hard-segment region and the capability of strain-induced crystallization of the soft segment [5]. Fig. 2 shows the stress–strain curves of polyurethanes with different amount of LFR. When extended to high strains, all the PU samples had strain-hardening phenomenon. Hepburn [5] mentioned that the structure regularity of PTMO make them capable of crystallization during stretching. This was indeed observed in the DSC thermogram of a neat PU after stretching, Fig. 3.

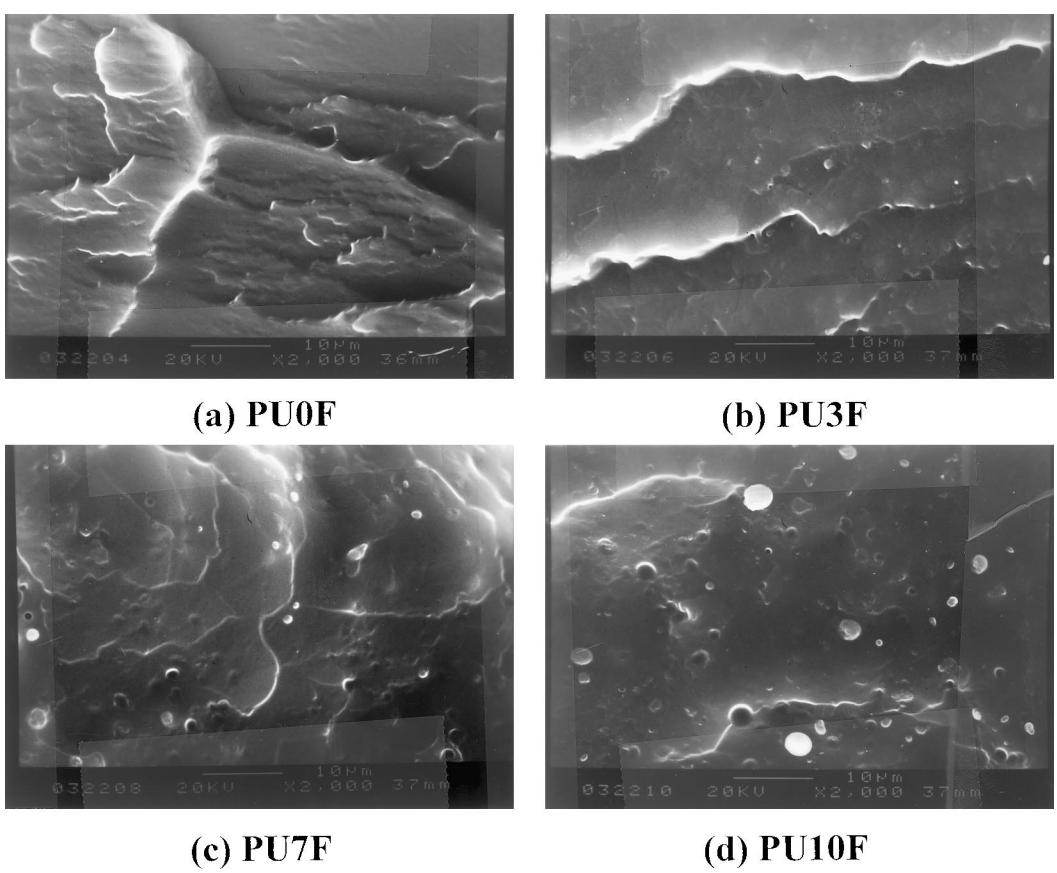



Fig. 6. SEM micrographs of the fracture surface of LFR-modified PU samples compared with a neat PU (×2000).

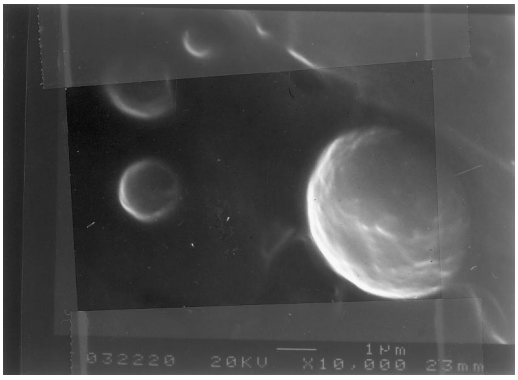



Fig. 7. A SEM micrograph of the fracture surface of a PU10F sample with the magnification of 10000.

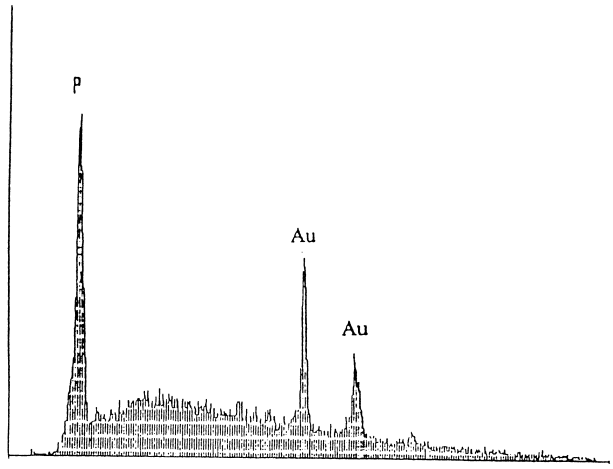



Fig. 8. EDX results of the dispersed particles in a PU10F specimen.

A melting peak at 28°C was found, corresponding to the melting peak at 26°C of the PTMO oligomer. Therefore, that the soft segments of PTMO-based polyure-thanes are capable of strain-induced crystallization was verified. Yet, for the PU containing the LFR additive, the formation of micro-crosslinks decreased the capability of strain-induced crystallization of the soft segments as can be seen in DSC thermograms. The melting peak was obscured for these LFR-modified PU samples after stretching. As a result, the ultimate tensile strength and elongation at break were decreased with the addition of LFR in PU.

Figs. 4 and 5 are the dynamic modulus and loss tanδ curves of various PU samples, respectively. A β-transition in the range of −160 to −120°C was observed for all the PU samples. This β transition was due to the crankshaft motion of methylene groups in PTMO chain segments. The addition of LFR did not have any effect on the β transition temperature; yet it increased the *Tg* of PU, in agreement with the results in DSC studies. In addition, the formation of micro-crosslinks in LFR-modified PU also can explain the increase in rubbery plateau region compared with the neat PU, Fig. 4. The increase in tanδ peak value and its area indicates that probably the LFR-modified PU had higher fracture toughness than the neat PU.

### 3.5. Morphology observation

With the increase in the amount of LFR additive, dispersed particles began to appear in the matrix and increased in number, as can be seen on the fracture surface of various PU samples, Figs. 6 and 7 shows that there was no void or debonding between the particles and matrix, indicating that they had good interfacial bonding. By using Energy Dispersive X-ray Analyzer, EDX, the main component of these particles was phosphorus, Fig. 8. In other words, these particles were principally composed of LFR. The average particle size for the sample PU10F was about 2 μm. In conclusion, during the synthesis of LFR-modified PU, a small portion of LFR having OH and/or NH groups could react with isocyanate groups in prepolymer, forming micro-crosslink structure. As the reactions proceeded to some extent, the increase in molecular weight caused a decrease in entropy of mixing. Therefore, the LFR additive precipitated out as a second dispersed phase and the chemical bonding between LFR and PU provided a good interfacial bonding.

## 4. Conclusions

1. The poly(bispropoxyphosphazene), LFR, has a structure of tertiary amine which can accelerate the synthesis of polyurethanes.
2. During the PU sample preparation, a small amount of LFR could degrade to two isomeric compounds having hydroxyl groups and secondary amino groups, respectively. These isomers could further react with isocyanate groups to form copolymers, and even a micro-crosslink structure.
3. The glass transition temperature and the rubbery plateau region were increased with the addition of LFR, which can be explained by the formation of micro-crosslinks. However, the β transition due to the crankshaft motion of methylene groups in PU was not affected.
4. Because of the structure regularity of PTMO, this polyether-based PU was capable of strain-induced crystallization, which gave excellent mechanical properties. However, the LFR additive retarded the crystallization of PU during stretching.

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