

Studies on Curing Reaction Kinetics and Properties of the CPE as a Modifier of Polyester-Urethane Elastomer

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SYNOPSIS

Chlorinated polyethylene (CPE)-modified polyester prepolymers with NCO end groups were synthesized. The chain-extension reactions of the prepolymers with 3,3'-dichloro-4,4'-diaminodiphenylmethane were studied by Fourier transform infrared spectrometry and found to change from second-order reaction at lower temperature to first-order reaction at higher temperature for these reaction systems. The properties of CPE-modified polyurethane (PU) elastomers was also studied by dynamic mechanical property analysis. The experimental results showed that the CPE content increase would lead to a decrease of the mechanical properties of PU elastomers and result in a prolongation of the cream time of curing reaction systems, but would make the manufacturing process easier than before. It is suggested that the CPE may be selected as a delayed-action activator of curing reaction.

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INTRODUCTION

Polyurethane (PU) is a type of important polymeric material, widely used in performance materials such as adhesives, sealants, cast elastomers, coatings, etc. Their properties depend greatly on the reactivity of hard and soft segments. The curing reaction kinetics of PU have been extensively studied.¹⁻⁶ The results showed that the reaction of isocyanate with small molecular alcohol follows a second-order mechanism, but there is sometimes a small deviation at high temperature. Up to now, the reaction kinetics of amine as a curing agent have been seldom studied, because the isocyanate reaction with amine is very fast and complicated. We have studied the curing reaction kinetics in the preliminary period of reactions between 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) and prepolymers which have different soft segments [e.g., poly(ethylene-co-prepylene adipate) (PEPA) or poly(tetramethylene oxide) PTMO] terminated with NCO groups by Fourier transform infrared (FTIR) tracing methods.⁷

Recently Koscielecka and our lab reported that chlorinated polyethylene (CPE) might act as a modifier to improve the thermal stability of PU⁸ and to prolong the pour time for cast polyester-urethanes, respectively.⁹ It is necessary to study the curing reaction kinetics in the PU forming process when CPE acts as modifier of polyester-urethane; the investigations were made by FTIR tracing technique. The FTIR results showed that the chain-extending reaction order changed from a second-order to a first-order when temperature was raised after CPE was added to PU systems. Therefore, the reactivity of PU systems with CPE as a modifier was investigated in this paper. The purpose is to study the effects of CPE additive on the reactions and dynamic properties of PU elastomers.

EXPERIMENTAL

Materials

The PEPA samples with a number average molecular weight of $M_n = 2,000$ and terminated with hydroxyl groups were made in the Yan Tai (Yan Tai, P.R.C.) synthetic leather factory. The toluene di-

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isocyanate (2,4-TDI) was produced by the Shanghai Chemical Agent Factory (Shanghai, P.R.C.) and re-purified by distilling before use in preparation of prepolymers.

The MOCA used as a chain extender was produced by the factory of Qian Jin Chemistry Industry in Su Zhiu, P.R.C. It was recrystallized before use.

CPE with a number average molecular weight of $M_n = 49,000$ and containing 41% by weight of chlorine was produced by the Wu Hou Factory Chemical Industry (Wu Hou, P.R.C.).

Prepolymers terminated with NCO groups and with different CPE weight contents were prepared as follows: the mixture of PEPA and CPE was degassed and dried under high vacuum (16 Pa) at 105°C for 3 h, then 2,4-TDI was charged into the reaction flask at a molar ratio NCO/OH = 2/1 after the temperature of the reaction system was cooled to 70°C or so, and finally the reaction was conducted at 70°C for 3 h. The products were kept in a desiccator. The cast PU elastomers were prepared as follows: the prepolymer and MOCA were dissolved in dry solvent CH_2Cl_2 , respectively. The two solutions were then mixed according to the molar ratio NCO/NH₂ = 1/0.9, the mixture was shaken thoroughly, and PU elastomer films were obtained by casting the mixed solution into a Teflon mold. The solvent CH_2Cl_2 was allowed to evaporate at room temperature for 2 days, and the resulting films were kept under reduced pressure at 30°C for 1 wk in order to remove residual solvent. Then the film samples were postcured for 8 h at 110°C. The characteristics of elastomer samples are listed in Table I.

MEASUREMENTS

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical property measurements were made on Toyo Baldwin DDV-IV-Viscoelastic ap-

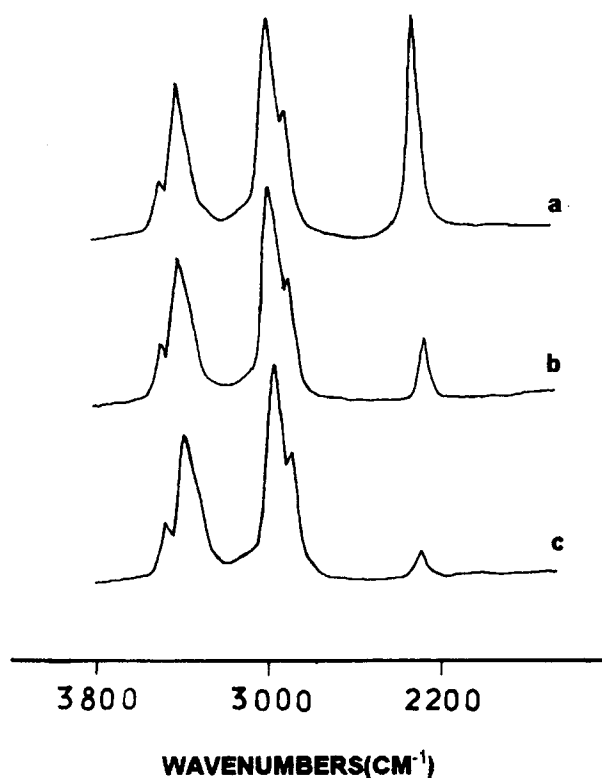


Figure 1 The change of NCO absorption band with time in the chain extension of CPE-modified PEPA prepolymer with MOCA at 373.2 K. (a) 104 s; (b) 967 s; (c) 1532 s.

paratus in a nitrogen atmosphere; specimen dimensions: $3.5 \times 6 \times 2 \text{ mm}^{-3}$. The temperature ranged from -150°C to 250°C with a frequency of 35 Hz and a heating rate of $2^\circ\text{C}/\text{min}$.

Infrared Measurement

The chain-extension reaction of NCO end prepolymer containing 3% by weight of CPE with MOCA was monitored by a Nicolet 170SX Fourier Transform Infrared Spectrometer. The stretching vibra-

Table I The Dynamic Properties of CPE-Modified Polyurethane Elastomers

Samples	Molar Ratio TDI/PEPA/MOCA	CPE (wt %)	Dynamic Mechanical Analysis*					
			T_β (°C)	TAN δ_β	T_α (°C)	TAN δ_α	$G_1 \times 10^{-10}$ (N/m ²)	$G_2 \times 10^{-8}$ (N/m ²)
PU-A	2/1/0.9	0	-67.1	0.038	-9.2	0.524	3.96	4.12
PU-B	2/1/0.9	3	-69.8	0.044	-6.0	0.581	3.80	3.14
PU-C	2/1/0.9	5	-71.5	0.039	-3.2	0.508	3.61	2.88
PU-D	2/1/0.9	10	-75.3	0.037	6.8	0.566	3.33	1.11

* G_1 and G_2 stand for shear modulus of PU samples at T_α and 100°C temperature, respectively.

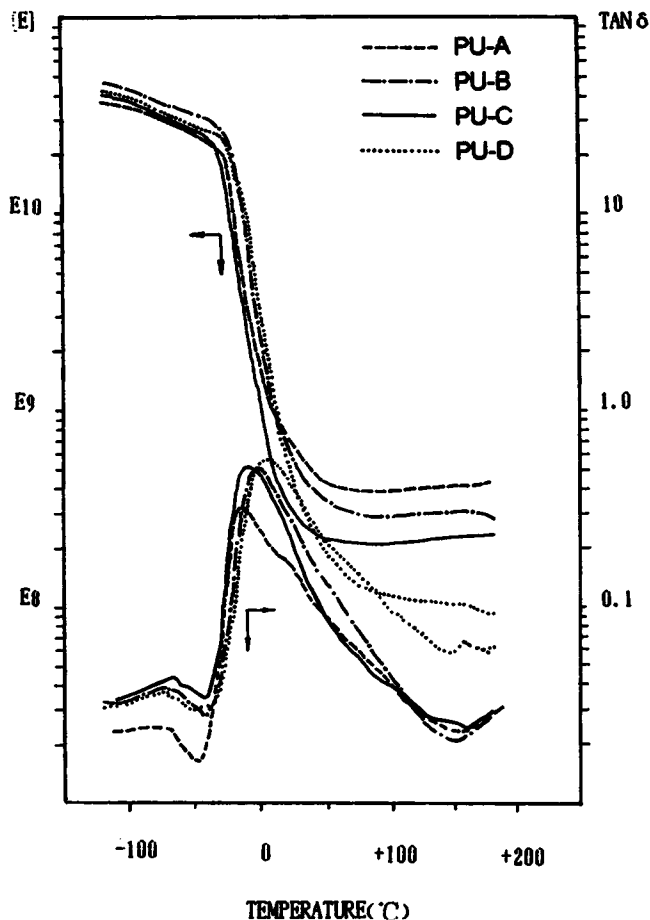


Figure 2 The Dynamical mechanical spectrum of CPE-modified PU elastomers at different CPE content.

tion band of the —NCO group in prepolymer at 2274 cm^{-1} is sensitive and is used to trace the chain-extension reaction, as shown in Figure 1. At the same time, the C—H stretching vibration bands at 2951 cm^{-1} and 2869 cm^{-1} for extending reaction mixture do not change during reaction and were chosen as internal reference standards. Spectra of the kinetic runs were taken with a software-controlled data collection routine. All spectra were run at the resolution of 2 cm^{-1} and were signal averaged for 32 scans. The temperature of the sample oven was controlled by a thermoregulator.

The samples for study of the chain-extension reaction by infrared measurements were prepared as follows: the prepolymers containing 3% by weight of CPE and MOCA were dissolved in the dry solvent CH_2Cl_2 at an equimolar ratio NCO/ NH_2 . The mixture solution was first dropped on a NaCl plate, then transferred into a desiccator with a pump, and the solvent CH_2Cl_2 was removed in a vacuum at a room

temperature of 20°C . The second NaCl plate covered the dried samples, and after fixing it was again put into the oven at a chosen reaction temperature to measure the change of the band at 2274 cm^{-1} with time.

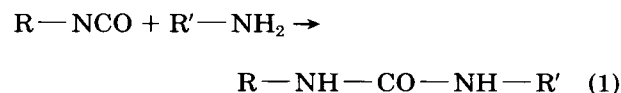
RESULTS AND DISCUSSION

Dynamic Mechanical Analysis

The dynamic properties of CPE-modified PU elastomers were presented. The dynamic mechanical spectrum of those PU samples appears in Figure 2. All DMA results are summarized in Table I. With adding CPE to the system, the single T_g of PU system is elevated. This indicated that CPE and PU were miscible such as PVC with PU,¹⁰ because of specific interactions in chlorinated polymers and polymers containing carbonyl groups. The DMA spectra also showed that the platform of viscoelasticity drops with adding CPE to PU systems. But the range of platform dropping is not remarkable, because PU elastomer contains $< 5\%$ by weight of CPE. Certainly, the rate of extending reaction of PU system was decreased as CPE was added to the PU system. At the same time, the density of cross-linking point was dropped, then the cream and pot time were prolonged in the process of extending reaction. This proved that the effect of the addition of a small amount CPE on the mechanical properties of PU is not notable, such as in the PU-B sample. It might be said that a small amount of CPE as a modifier for PU casting processing will be easier and more convenient.

FTIR Spectroscopy

It is well known that the reaction of isocyanate with diamine can be described by the following formula:



At the same time, secondary reactions may be led by the formation of biuret and allophanate:

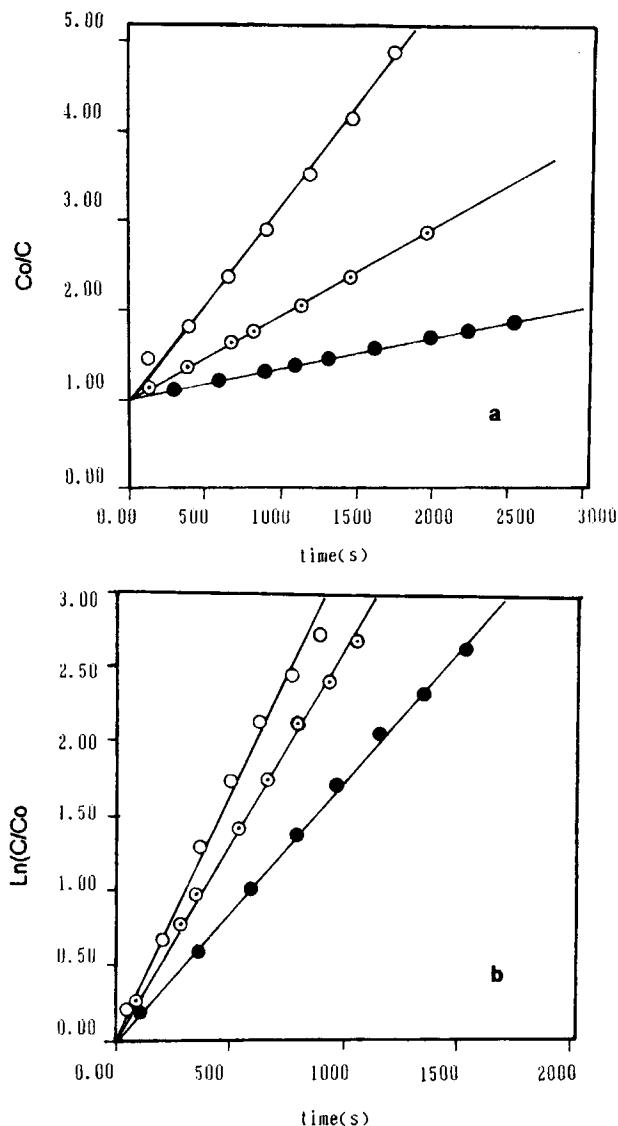
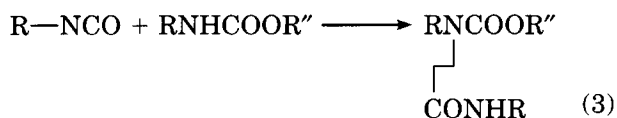
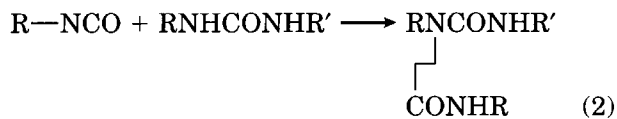


Figure 3 (a) The second-order reaction fitting curve for CPE-modified PU curing system. (●) 343.2 K; (○) 353.2 K; (○) 363.2 K. (b) The first-order reaction fitting curve for CPE-modified PU curing system. (●) 373.2 K; (○) 398.2 K; (○) 413.2 K.



Generally, these secondary reactions occur at higher temperatures. The possibility of forming allophanate is smaller, in particular. The formation of biuret and

allophanate means that branching and crosslinking occur in the system, which are important considerations for cast elastomers. In order to simplify this investigation, an equal molar ratio NCO/NH_2 in the cast PU system was used. Under the equal molar ratio NCO/NH_2 , i.e., at 100% of the theoretical MOCA level, the degree of branching and crosslinking is at a minimum. (In industry, to obtain an acceptable level of general properties the theoretical

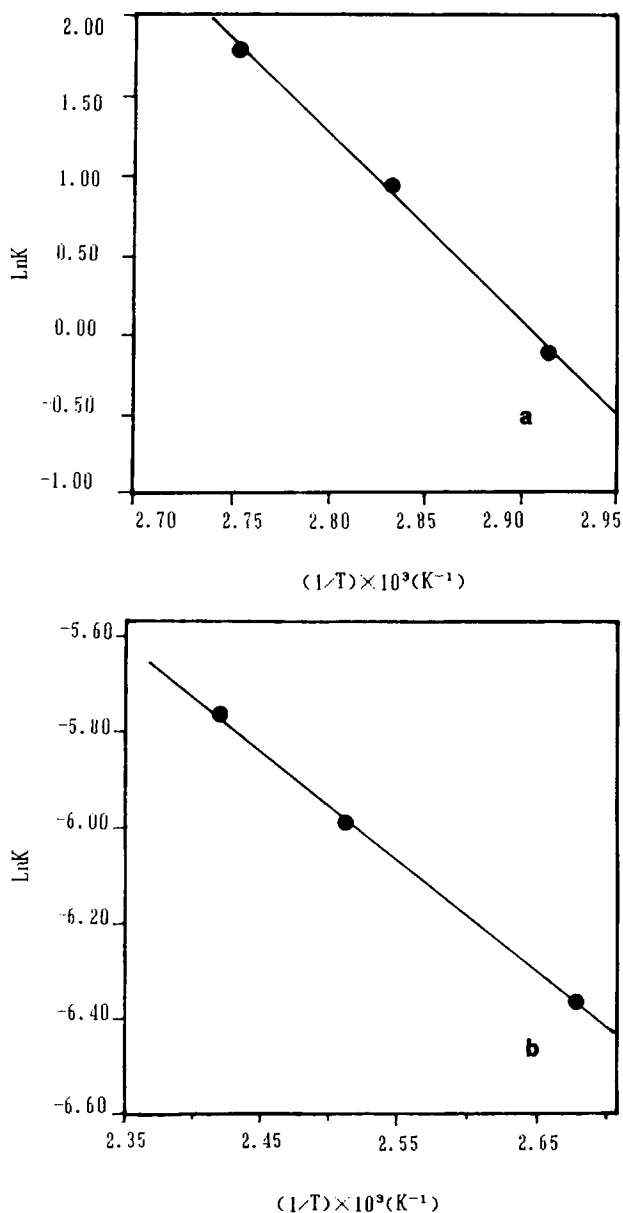


Figure 4 (a) The plot of $\ln k_2$ versus $(1/T)$ at lower temperature for CPE-modified PU curing system. (b) The plot of $\ln k_1$ versus $(1/T)$ at higher temperature for CPE-modified PU curing system.

Table II The Kinetic Data of CPE-Modified PU System

Temp (k)	Fitting Reaction Order	Reaction Rate Constant	Activation Energy
343.2	2	0.45 (g/mol s)	99.04 (KJ/mol)
353.2	2	1.27 (g/mol s)	99.04 (KJ/mol)
363.2	2	3.01 (g/mol s)	99.04 (KJ/mol)
373.2	1	1.72×10^{-3} (s ⁻¹)	19.2 (KJ/mol)
398.2	1	2.5×10^{-3} (s ⁻¹)	19.2 (KJ/mol)
413.2	1	3.11×10^{-3} (s ⁻¹)	19.2 (KJ/mol)

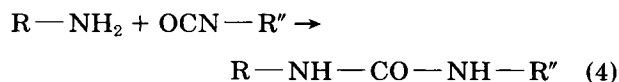
concentration of 90–95% of MOCA is recommended). It can be concluded that in the system of prepolymers and MOCA with equal molar ratio NCO/NH₂ at a suitable temperature, the chain-extension reaction should predominate. In such a case, the reaction rate formula is simple:

$$d[\text{Urea}]/dt = k[\text{NCO}][\text{NH}_2]$$

As for the system of MOCA and NCO-terminated polyester (PEPA) prepolymer modified by CPE, the NCO group stretching vibration band at 2274 cm⁻¹ is an isolated and sharp band, which is ideal for observation of kinetics.

The chain-extension reactions of the systems of CPE-PEPA prepolymer-MOCA were observed. At six different temperatures the changes of the NCO concentration with reaction time were measured. C_0 is the NCO concentration before beginning reaction, and is 6.78×10^{-4} mol/g. The concentrations C were determined by using the corrected band area at 2274 cm⁻¹ and original concentration C_0 . According to the change of the NCO concentration C with time of chain-extension reaction, the kinetic result was fitted by the first- or second-order reaction. In other words, if the curve $\ln(C/C_0)$ plotted against time is a straight line, the mechanism of this reaction follows a first order. If the curve (C_0/C) plotted against time is a straight line, the mechanism of this reaction follows a second order. The experimental results show that the reaction order is transformed from a second to a first order when tracing temperature from low to high, as shown in Figure 3. According to the gradient of the straight line, the second- or first-order reaction rate constant of corresponding temperature should be obtained. The curve of $\ln k$ versus $1/T$ is shown in Figure 4 and the results are listed in Table II. From the experimental results, it can be seen that the curing reaction activation energy rises notably at lower temperature; and with increasing curing reaction temperature, the order of this reaction change from a second-order to a first-

order. These results were elucidated as follows: CPE contains a large number of C—Cl polar bonds, and those bonds with the NH₂— group of MOCA have some force for inducing polarizing action, which makes the reacting rate of the NH₂— groups of MOCA with the NCO— groups of prepolymer decrease in the nucleophilic addition reaction, and the extension reaction gelation time is prolonged. Then the activation energy of this reaction becomes larger and the curing reaction follows a second-order reaction. But with the temperature raised, the active hydrogen concentration that can react with the NCO— groups of prepolymer is increasing, which may be because that the active hydrogen does not disappear when the NH₂— group of MOCA reacts with the NCO— group of prepolymer. This active hydrogen was transferred from the NH₂— group to the uret group in the curing reaction. It can be described by the following formula:



With the temperature enhanced, the polarizing complex compounds of the NH₂— group and CPE molecule were disintegrated, and all kinds of amine (primary amine, secondary amine, amide, uret, etc.) were becoming activated. The total concentration of activated hydrogen is getting higher and higher. Relatively, the concentration of active hydrogen is becoming a constant. Therefore, the reaction rate of [NCO] with [NH₂] could be determined by the concentration of NCO— groups, then the curing became a first-order reaction. At the same time, the activation energy of extension reaction was decreased. The experimental results also suggested that the rate of PU formation was decreased by adding CPE to the PU curing system. But the CPE does not lead to an incomplete PU reaction in later periods of reaction provided the temperature was increased. The same result in which the reacting order

changed from second- to first-order was reported in literature.^{11,12} It may be useful that a small amount of CPE be used for controlling the rate of curing reaction of PU systems in the primary stage of reaction.

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