Polymer Bulletin 39, 339–346 (1997)

Polymer Bulletin

Kinetics of formation of polyurethane/ polymethylmethacrylate grafted semi-interpenetrating polymer networks based on the functional prepolymers

A. Anžlovar, I. Anžur, T. Malavašič

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

Received: 2 May 1997/Revised version: 11 July 1997/Accepted: 16 July 1997

Summary

The kinetics of formation of the polyurethane network by crosslinking the polyurethane prepolymer in polyurethane/polymethacrylate grafted semi-interpenetrating networks (semi-IPN) was monitored by Fourier transform infrared spectroscopy, and the kinetic parameters were thus determined. It was found that carboxylic groups in the hard segments of the PU component substantially decrease the reaction rate and increase the activation energy. Tertiary amine groups in the PM component catalyse the crosslinking reaction. The PM component acts as a diluent in the mixture of PU and PM reducing the reaction rate and increasing the activation energy of the crosslinking reaction. At temperatures below the T_g of the PM component, the reaction of formation of IPN becomes diffusion controlled.

Introduction

Interpenetrating polymer networks (IPNs) are mixtures of crosslinked polymers without covalent bonds between them. Therefore, they can be considered as polymer catenanes[1,2]. IPNs, synthesised in situ (by conventional sequential or simultaneous procedures), are not suitable for coating applications due to the presence of highly volatile monomers. For environmental reasons, the synthesis of IPN for this application is started from the low molecular weight prepolymers. The compatibility of the prepolymers can be improved by the incorporation of functional groups[3-5]. In our work, IPNs were prepared from hydroxy terminated polyurethane (PU) prepolymers with carboxylic functional groups in the polymer backbone and from polymethacrylic (PM) copolymers with tertiary amine functional groups and some hydroxyl groups in the polymer backbone. PU prepolymers and PM copolymers were mixed and crosslinked with isocyanatohexamethylene diisocyanate (DDA).

The kinetics of the crosslinking is essential for the synthesis of interpenetrating polymer networks. The dependence of the crosslinking on the temperature, on the chemical composition of the prepolymers, on the formulation of the mixture, on the humidity of the air and on other reaction conditions influences the properties of the materials to be obtained [6].

Due to the specific and defined signal of the NCO group, IR spectroscopy is suitable for the study of the crosslinking kinetics when isocyanates are one of the reacting species. The important advantages of IR spectroscopy are that: it allows the study of the crosslinking reaction in a film on a NaCl plate simulating conditions at coatings application; the crosslinking reaction can be followed from the beginning to the complete conversion by using a temperature cell; the temperature can be precisely controlled and programmed[7-11]. Due to the insolubility of the crosslinked films, many other methods usually applied in the kinetic studies cannot be efficiently used for this purpose[9]. The requirement for the IR spectroscopy to be used for quantitative measurements is that the Beer-Lambert law be valid for the absorption bands[8,9].

Studies were made on the influence of the composition of prepolymers changing the concentration of both functional groups and the mass ratio between them, and of the air humidity on the reaction kinetics.

Experimental

Synthesis of prepolymers:

Hydroxy terminated PU prepolymers with carboxylic functional groups in the chain were synthesised according to the procedure described in the literature[12] from isophoronediisocyanate (IPDI), polytetramethylene oxide (PTMO), M_n = 2000 g/mol, 1,4-butanediol (BD) and 2,2'-bis(hydroxymethyl) propionic acid (DMPA). The molar ratio between hydroxy and isocyanate compounds was 1.05/1. The molar ratio of (BD+DMPA)/PTMO was 4/1. The amount of DMPA varied so that the concentration of carboxylic groups was between 0 and 45 mmol/g of polymer. Methacrylic (PM) copolymers with tertiary amine functional groups were synthesised from methyl methacrylate (MMA), N,N-dimethylaminoethyl methacrylate (DMAEM) and hydroxyethyl methacrylate (HEM) by radical chain polymerisation in solution. The mass share of HEM in the PM copolymer was 0.5%, while the amount of DMAEM varied so that the concentration of tertiary amine functional groups in the polymethacrylic component was between 0 to 0.45 mmol/g of polymer. The role of carboxylic groups in the PU chains and tertiary amine functional groups in the PM chains was to induce the interactions between them and thus to enhance their miscibility.

Preparation of IPNs:

Polyurethane and polymethacrylic components were mixed in the equimolar (Table 2 and 3) or non-equimolar (Table 5) ratio of the functional groups and diluted by ethylmethyl ketone to a 10% concentration. The concentration of functional groups in PU and PM mixtures was the concentration of carboxylic and tertiary amine group pairs, meaning that in the case of their equimolar ratio, this value was equal to the concentration of carboxylic groups in the PU prepolymer or tertiary amine groups in PM copolymer. The solution was homogenised by mixing and the crosslinking agent was added in a 100% excess to the theoretical value. The mixture was homogenised again: a small portion was cast on a NaCl plate and dried for 15 min at room temperature. Then, the plate was placed into a temperature cell and isothermal measurements were performed by a Perkin-Elmer 1725X FTIR spectrometer. As a crosslinking agent, 1,3,5 isocyanatohexamethylene diisocyanate (Desmodur-DA (DDA), Bayer, technical grade) was used to react with hydoxyl groups of PU and PM prepolymers. Beside the reaction of isocyanate with hydroxyl groups, the reaction with air humidity or the biuret reaction can take place in the system studied. The detailed scheme of the preparation of IPN is shown in Figure 1.

FT-IR Measurements

The decrease of the NCO signal at 2270 cm^{-1} was monitored as a function of time relative to the absorption band of the CH bond (internal standard) at 3000 cm^{-1} isothermally at temperatures 90, 95 100 and 105 °C. The relative areas A were used to calculate the extent of the reaction α, using the equation[6,8] (1):

$$\alpha = 1 - \frac{A_t}{A_{t=0}} \tag{1}$$

where A_t is the relative area at a certain time and $A_{t=0}$ is the initial relative area. For description of the kinetic behaviour, the equation (2) was used[6];

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

k being the rate constant, supposed to be temperature dependent according to the Arrhenius equation. The overall order of the reaction was calculated by fitting the parameter n in the equation (3) with the experimental values[6]:

$$t = \frac{1-(1-\alpha)^{1-n}}{1-(0.5)^{1-n}} . t_{0.5} \tag{3}$$

where $t_{0.5}$ is the time elapsed from the start of the experiment to the time when α = 0.5 and n is the overall order of the reaction.

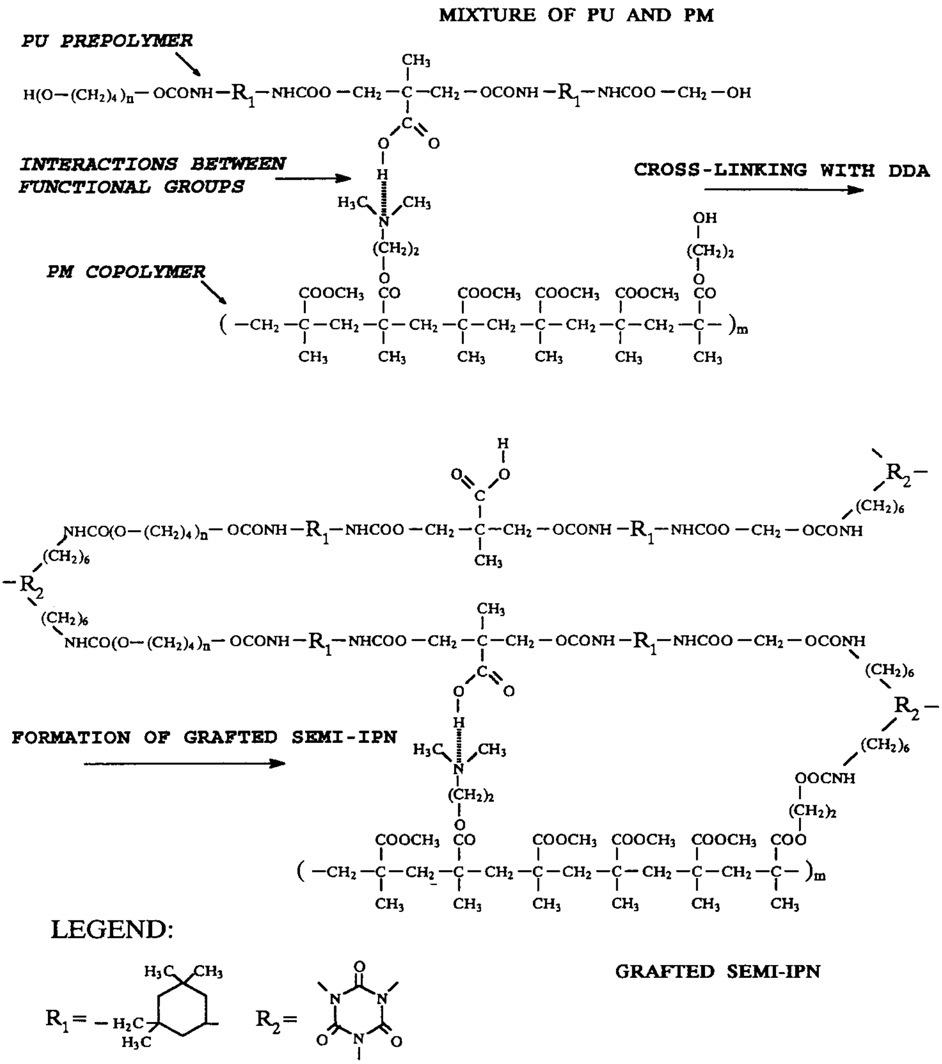

Figure 1: The scheme of preparation of grafted semi-IPN from PU prepolymer and PM copolymer

The reaction rate constants were calculated from the slope in the plot g(α) vs. t, where g(α) is defined as[6]:

$$g(\alpha) = \int_0^{\alpha} \frac{d(\alpha)}{(1-\alpha)} = \frac{1-(1-\alpha)^{1-n}}{1-n} = kt \tag{4}$$

The Arrhenius diagram was drawn, and from the slope the activation energy (E_a) was calculated. Linear regression was performed using Quattro-Pro 5.0, while fitting was made by the MicroCal-Origin program.

Results and discussion

The plot of the absorbance against the concentration (Figure 2) shows that the Beer-Lambert law is valid up to an isocyanate concentration of 8.3 10^{-4} mol/g.

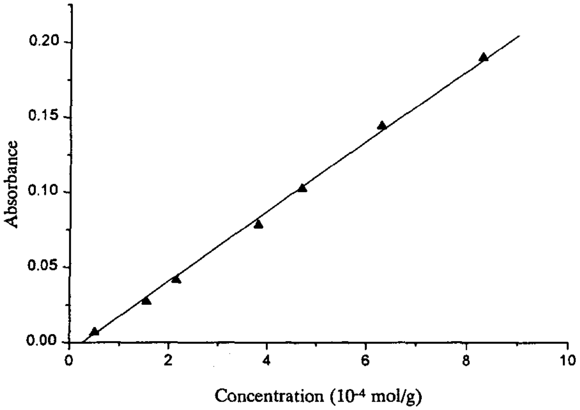

Figure 2: NCO absorbance as a function of the concentration

The influence of the concentration of carboxyl groups in PU and of tertiary amine groups in the PM component on the kinetics of crosslinking was determined by monitoring the crosslinking reaction of pure components. The kinetic parameters of PU prepolymers with different concentration of carboxyl groups are given in Table 1. The relative reaction rate constant and the reaction rate decreased by increasing the concentration of carboxyl groups, while the reaction order n was not influenced.

The catalytic activity of tertiary amine functional groups was studied by monitoring the crosslinking reaction of DDA with hydroxyl groups of PM components having different concentrations of amine functional groups (Figure 3). In the PM sample without tertiary amine groups, the reaction proceeded most slowly, thus confirming that they acted as a catalyst in the crosslinking reaction.

In Figure 4, the conversion profiles of pure PU component and of its mixture with PM component (0.45 mmol of functional groups/g of polymer, T = 90 °C) are shown. The PM component slightly reduced the reaction rate constant (from 1.8 x 10^{-3} s^{-1} for pure PU to 1.2 x 10^{-3} s^{-1} for the mixture). However, this influence is smaller than the influence of increased concentration of carboxylic groups in the pure PU component (Table 1), and was ascribed to the dilution of the PU component with PM component[11].

Table 1: The influence of the concentration of carboxyl groups in the PU prepolymer on the kinetics of the crosslinking with DDA (Temperature = 90 °C)

Concentration of functional groups (mmol/g)	n	k (s^{-1} x 10^3)
0.00	2.4 ± 0.2	3.4 ± 0.13
0.25	2.6 ± 0.2	2.3 ± 0.09
0.45	2.6 ± 0.1	1.8 ± 0.03

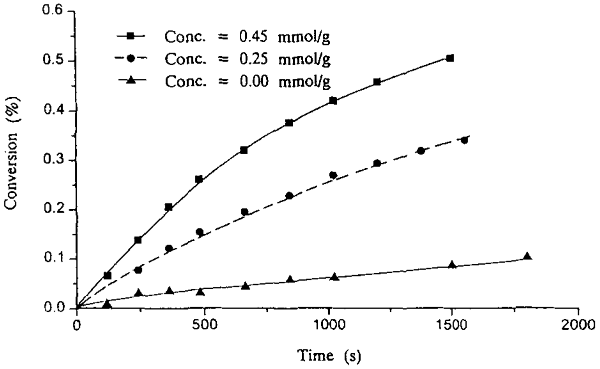

Figure 3: Conversion profile for PM copolymer with different concentrations of tertiary amine groups (T = 105 °C)

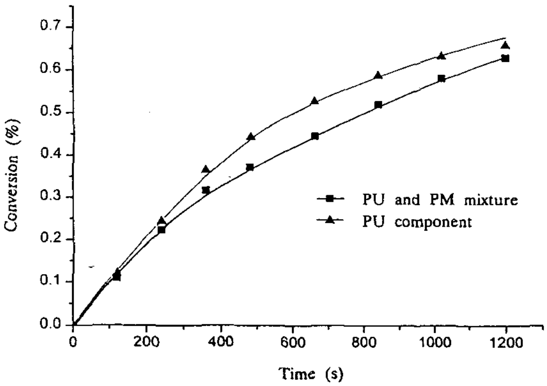

Figure 4: Conversion profile of pure PU prepolymer and the profile of its mixture with the PM component (PU/PM = 0.5/0.5, T = 90 °C)

The apparent reaction orders (n) for the crosslinking of the PU and PM mixtures in dependence on the concentration of functional groups are given in Table 2. For the samples with a concentration of functional groups lower than 0.15 mmol/g, the reaction order appreciably changed with temperature. High values of n at temperatures within or below the glass transition temperature of the PM component led to the assumption that reaction was diffusion controlled[15].

For the samples with concentrations of functional groups amounting to 0.25 mmol/g and higher, n were between 1.4 and 1.8 and were practically independent of temperature (Table 2), indicating that in this region the crosslinking reaction was kinetically controlled. Reaction orders between 1.5 and 2 have also been found by other authors for simultaneous interpenetrating polymerisation of PU with polystyrene[8] and PU with PMMA[11].

Table 2: Overall reaction order of PU and PM mixtures as a function of the concentration of carboxyl and amine functional groups and of the reaction temperature

Conc. of functional groups (mmol/g)	n T=90°C	n T=95°C	n T=100°C	n T=105°C	T_g of PM (°C)
0.00	4.8 ± 0.1	3.4 ± 0.1	2.6 ± 0.2	-	96 ± 2
0.15	3.3 ± 0.2	3.2 ± 0.2	2.6 ± 0.2	2.6 ± 0.2	90 ± 2
0.25	1.9 ± 0.2	1.7 ± 0.1	1.7 ± 0.1	1.5 ± 0.1	78 ± 2
0.45	1.4 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	1.6 ± 0.1	81 ± 2

The values of n under 2 were assumed to be the consequence of the air humidity taking part in the crosslinking reaction. Namely, the Sato[13,16] kinetic equation becomes of the pseudofirst order due to the large excess of water. In the subsequent experiments, the reaction was followed between two NaCl plates in order to avoid the presence of humidity. The obtained reaction orders are given in Table 3. Comparison of these results with the results in Table 2, revealed an appreciable increase in n thus confirming that the presence of humidity lowered the order of the reaction. The n between 2.7 and 3.7 indicated that the crosslinking reaction was partially diffusion controlled.

Table 3: Overall reaction order of PU and PM mixtures as a function of the concentration of carboxyl and amine functional groups at different crosslinking temperatures

Conc. of functional groups (mmol/g)	n T=90°C	n T=95°C	n T=100°C	n T=105°C	T_g of PM (°C)
0.00	3.3 ± 0.1	3.7 ± 0.2	3.6 ± 0.3	2.7 ± 0.3	96 ± 2
0.25	2.9 ± 0.3	3.0 ± 0.3	3.3 ± 0.3	2.9 ± 0.2	78 ± 2
0.45	3.2 ± 0.1	3.3 ± 0.1	3.0 ± 0.2	3.5 ± 0.1	81 ± 2

In Table 4, the relative reaction rate constants at 100 °C for the crosslinking reaction of the mixtures having the concentration of the functional groups from 0 to 0.45 mmol/g are given. Reaction rate constants slightly increased by increasing the concentration of the functional groups. This can be explained by the catalytic effect of tertiary amine groups in the PM component.

The reaction rate of the crosslinking was measured at 90, 95, 100 and 105 °C, and the constants were calculated for the PU component without (PU_1) and with a maximal amount of functional groups (PU_2), and for a mixture of PU_2 in the isoelectric ratio with PM. The activation energies were calculated from the Arrhenius plots (Figure 5). Comparing the activation energies of PU_2 and PU_1 and the activation energy of the mixture of PU_2 with PM (Figure 5) it can be concluded that the PM component increases the activation energy in the system, but the influence is smaller than the influence of the concentration of carboxylic groups of PU prepolymers.

Table 4: Relative reaction rate constant of crosslinking in the mixture of PU and PM component as a function of the concentration of functional groups (T = 100 °C, PU/PM = 0.5/0.5)

Conc. of functional groups (mmol/g)	k $(s^{-1} \times 10^{3})$
0.00	1.7 ± 0.05
0.15	1.7 ± 0.06
0.25	2.3 ± 0.04
0.45	2.0 ± 0.04

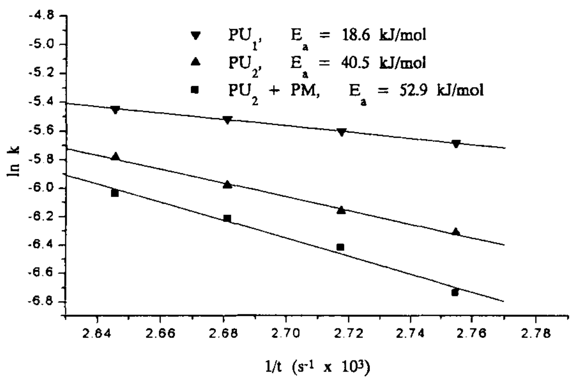

Figure 5: Arrhenius plots of the crosslinking reaction of two pure PU components having 0.00 (PU_1) and 0.45 mmol (PU_2) of carboxyl groups/ g of polymer and of the mixture of PU_2 with PM component with 0.45 mmol of carboxyl and amine groups/ g of polymer

The obtained activation energies were for approximately 50% lower than values reported for the noncatalysed systems in the literature[14], while the values reported for the catalysed simultaneous interpenetrating polymerisation are comparable[8] to, or lower[11] than our results. However, our system can be considered as catalysed due to the presence of dibutil tin dilaurate, which originates from the synthesis of the PU prepolymer, and due to the presence of tertiary amine groups of the PM component.

The influence of the ratio between the PU and PM components, with the concentration of functional groups of 0.35 mmol/g of polymer, on the order of the reaction and on the reaction rate constant at 100 °C, was also investigated (Table 5). By increasing the content of the PM, the reaction order goes through a minimum at a PM/PU ratio of 0.5/0.5 and then increases. This was ascribed to the diffusion-controlled reaction when the PM component was in excess. The reaction rate constant decreased by increasing the ratio PM/PU due to the dilution-retardation effect of the PM component.

Table 5: Overall reaction order and reaction rate constant of PU and PM mixtures as a function of the ratio of polymer components (concentration of carboxyl and amine groups = 0.35 mmol/g of polymer, T = 100 °C)

Ratio PU/PM	n	k (s^{-1} x 10^3)
1.0/0	2.6 ± 0.1	4.7 ± 0.08
0.75/0.25	2.6 ± 0.2	4.6 ± 0.25
0.6/0.4	2.0 ± 0.2	2.7 ± 0.06
0.5/0.5	1.5 ± 0.1	2.0 ± 0.04
0.4/0.6	2.4 ± 0.1	1.9 ± 0.05
0.25/0.75	3.4 ± 0.2	0.9 ± 0.03

Conclusions

Fourier transform infrared spectroscopy was used for studying the crosslinking kinetics of PU and PM prepolymers forming semi-IPNs. By monitoring the crosslinking of a pure PU component, it was found that carboxylic groups in the PU prepolymer reduce the reaction rate and substantially increase the activation energy, while the order of the reaction remains unchanged. By monitoring the crosslinking reaction of the pure PM component, the catalytic effect of tertiary amine functional groups on the crosslinking reaction was confirmed.

The PM component in the system acts as a dilution agent reducing the reaction rate and increasing the activation energy. Similar effects have been observed by other authors for the formation of IPNs starting from monomers[8,11]. When T_g of the PM component is within the same temperature region as the measurements were performed, it appreciably influences the crosslinking reaction of the PU component.

The influence of air humidity on the crosslinking reaction was confirmed by monitoring the reaction between two NaCl plates: In the absence of air humidity, the apparent reaction orders came up to the third order, while in its presence a reaction order was 1.5.

Acknowledgement: This work is a part of the project J2-5157 financed by the Ministry of Science and Technology of the Republic of Slovenia. The financial support is gratefully acknowledged.

References

1. H.X. Xiao, K.C. Frisch, H.L. Frisch, (1983) J.Polym.Sci.Polym.Chem. Ed., **21**: 2547
2. K.C. Frisch, D. Klempner, H.X. Xiao, E. Cassidy, H.L. Frisch, (1985) Polym.Eng. Sci., **25**,(12): 758
3. A. Patsis, H.X. Xiao, K.C. Frich, S. Al-Khatib, (1986) J.Coat.Technol., **58**(743): 41
4. H.X. Xiao, K.C. Frisch, H.L. Frisch, (1984) J.Polym.Sci.Polym.Chem.Ed., **22**: 1095
5. S. Lu, E.M. Pearce, T.K. Kwei, (1995) Polymer, **36**: 2435
6. M. Claybourn, M. Reading, (1992) J. Appl. Polym. Sci., **44**: 565
7. T. Provder, (1989) J. Coatings Tech., **61**: 32
8. Shu-chang X., Zhi-ping Z., Sheng-kang Y., (1989) Polymer, **30**: 1269
9. S.R. Jin, G.C. Meyer, (1986) Polymer, **27**: 592
10. S.R. Jin, J.M. Widmaier, G.C. Meyer, (1988) Polymer, **29**: 346
11. S.R. Jin, J.M. Widmaier, G.C. Meyer, (1988) Polym. Comm., **29**: 26
12. R.E. Tirpak, P.H. Markusch, (1986) J. Coat. Technol., **58**: 49
13. A.V. Cunliffe, A. Davis, M. Farey, J. Wright, (1985) Polymer, **26**: 301
14. Malavasic T., Anzur I., Osredkar U., The Study of the Polyurethane reactions by Differential Scanning Calorimetry in: Lemstra P.J, Kleintjens L.A.(eds.), Integration of Fundamental Polymer Science and Technology - 4, Elsevier Science Publishers Ltd., London (1990), pp. 75
15. K. Dusek, (1986) Adv. Polym. Sci., **78**: 1
16. M. Sato, (1960) J. Am. Chem. Soc., **82**: 3893