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Cross-linking kinetics and swelling behaviour of aliphatic polyurethane

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Abstract

The curing processes of three types of aliphatic polyurethanes (PUs) were monitored through measuring changes in the IR absorption of the isocyanate group. Two exponential fittings were used to present the decrease of the absorption band of the isocyanate group as a function of the curing time. The curing process contained chemically and diffusionally controlled periods. According to a cross-linking kinetics analysis, one of the PUs followed a first-order, and two others a second-order reaction. The swelling behaviour of the aliphatic PUs was described with a gel fraction and the degree of the cross-linking after the samples cured.

Keywords: Cross-linking kinetics; Polyurethane; Swelling behaviour

1. Introduction

Polyurethanes (PUs) are addition polymers formed by a reaction of di- or poly-isocyanates with polyols, water, and amines containing an active hydrogen atom. The molecular structures vary from rigid cross-linked polymers to linear, highly extensible elastomers. The use of materials derived from PU has grown considerably. Thousands of practical applications such as foams, plastics, rubber, and adhesives have been found, thanks to their properties and outstanding molecular design. From the application point of view, PUs can be designed to have any properties to satisfy different material requirements.

The curing of thermosets, especially the curing of PUs, involves the formation of a three-dimensional network through reactions among polyfunctional groups. The curing process starts from a formation and linear growth of a chain. Soon the chain starts to branch and then to cross-link. As the curing proceeds, the molecular weight increases rapidly, the molecular size expands and several chains are linked together into a network of infinite molecular weight.

A gelation is a typical characteristic of thermoset polymers and a phenomenon that takes place during thermosetting polymer cure reactions [1,2]. It corresponds to the incipient formation of a network with an infinite weight-average molecular weight. Gelation occurs at a well-defined stage in the course of the cure reaction and depends on the stoichiometry, functionality, and reactivity of reactants, and temperature. This phenomenon typically occurs for conversions between 55 and 80% (fractional conversion is 0.55–0.80). Prior to the gelation, the sample can be dissolved in appropriate solvents. After the gel point, however, the network will not dissolve but swell in good solvents. Soluble small and branched molecules are present. Thus the curing sample contains sol as well as gel fractions. Recently, several research reports have been published to describe the polymerization kinetics of the thermoset polymers [3–7].

Polyurethanes based on methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), are widely used because of their mechanical properties. In aliphatic PUs which are based on hexamethylene diisocyanate the main chain is aliphatic. Its low energy consumption in low temperature polymerization processes, easily adjustable process conditions, and product properties, have led to specific applications of this PU.

In order to study the cross-linking kinetics we focused our attention upon the curing process of three different aliphatic PUs by monitoring the isocyanate group by the Fourier transform infrared (FTIR) spectroscopy. Two exponential fittings were successfully applied to present the change of the absorption of the isocyanate group as a function of the curing time. The curing process contained chemically and diffusionally controlled periods. The swelling behaviour of the aliphatic PU is described by the gel fraction and the degree of the cross-linking.

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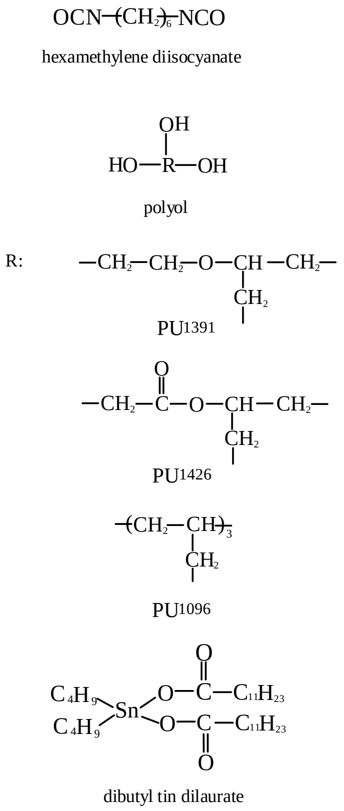

Fig. 1. Chemical structures of the components of the PUs studied in this work.

2. Experimental

2.1. Materials

Three PUs, PU1096, PU1391 and PU1426 provided by Gairesa Ltd, Spain, have been employed throughout the work. The chemical structures of the PUs are shown in Fig. 1, the relative compositions are listed in Table 1. The curing temperature was ambient (about 23°C) throughout the work.

2.2. FTIR spectroscopy

Polyol, pre-dissolved with dibutyl tin dilaurate, and isocyanate were weighed according to the relative compositions listed in Table 1, and the mixture was stirred manually in 3 min. A thin film on a PTFE-IR Card was coated with 2–3 mg of this mixture. FTIR spectra were measured with a Perkin–Elmer FTIR 1725X with 4 cm^{-1} resolution.

Table 1
Relative compositions of the PUs

Ratio	Polyol (wt%)	Hexamethylene diisocyanate (wt%)	Dibutyl tin dilaurate (accelerator) (wt%)
PU1096	58.7	41.3	0.117
PU1391	28	72	0.05
PU1426	41.7	58.3	0.02

2.3. Gel fraction determination

The gel time was measured using a solubility method, where the time when insoluble polymer first appears in a dimethyl formamide (DMF) solvent is measured at room temperature, they are presented in Table 2. Small pieces of polymers were cut from the curing sample at different curing times. They were weighed and extracted in DMF at room temperature for more than 12 h. The solvent was changed every 4 h. Finally, when the swelling gel reached an equilibrium at higher concentrations of solution in the gel phase, the solvent was vaporized. The percentage of the insoluble portion of the initial sample gave the gel fraction (*G*) [8].

2.4. Swelling measurements

Two approaches, the swelling and mechanical measurements, are widely used to determine the degree of the cross-linking experimentally [9]. Here the swelling measurement was used. When a cross-linked polymer is immersed in an appropriate solvent, the polymer imbibes the solvent and undergoes swelling to an extent determined by the nature of the polymer and the solvent. In the equilibrium, the swelling is given by Refs [10,11]

$$M_c = 2d_r V_1 / V_p^{5/3}(1 - 2\chi) \tag{1}$$

Here M_c (g/mol) is the weight-average molecular weight of polymer chains between cross-links; d_r (g/ml) the density of the polymer; V_1 (ml/mol) the molar volume of the solvent; V_p the volume fraction of the polymer in the swollen mass; the reciprocal of V_p is the swelling ratio q, and χ is the polymer–solvent interaction parameter. The volume fraction (Q) of the polymer in the swollen mass and the swelling ratio can be obtained by the following equations [12]:

$$V_p = \frac{1}{1 + Q} \tag{2}$$

$$q = 1 + Q \tag{3}$$

$$Q = \frac{w_s}{w_g} \times \frac{d_r}{d_s} \tag{4}$$

Here w_s (g) is the weight of the solvent in gel, w_g (g) the weight of the gel, d_s (g/ml) is the density of the solvent. Small cured PU pieces of $15 \times 5 \times 3\ \text{mm}^3$ were immersed into the DMF solvent at room temperature for a week until swollen equilibrium was obtained. Measurements were repeated for at least three parallel samples in each case and the results were averaged.

3. Results and discussion

3.1. FTIR spectroscopy

The isocyanate group is often used to monitor the curing

Table 2

Correlation between the absorption of the isocyanate group and the curing time of PUs from FTIR at room temperature (A_0 is the area of absorption at the initial time, A_t the area of absorption at any time during the curing process, A_∞ the final area of absorption at infinite time, t_c is the gel time from experiment, p_c is the critical curing degree at gel point from experiment)

PU	PU1096	PU1426	PU1391
$(A_t - A_\infty)/(A_0 - A_\infty)$	$0.047 + 0.52e^{-0.032t} + 0.47e^{-0.005t}$	$0.86e^{-0.0015t} + 0.14e^{-0.040t}$	$0.049 + 0.51e^{-0.00187t} + 0.347e^{-0.00095t}$
Critical point (min)[a]	90	700	900
t_c (min)	70	800	1000
p_c	0.61	0.56	0.59

[a] The critical point fitted for the first and second part exponential, respectively; it is close to the gel point from experiment.

process of PUs. The isocyanate absorption band occurs at approximately 2300–2200 cm^{-1} in the mid infrared spectrum as shown in Fig. 2. For scaling the decrease of the isocyanate absorbance, the C–H stretch absorption (2960 cm^{-1}) was chosen as the internal standard [6]. Baseline corrections were fitted to all absorption peak areas. Assuming that there are no side reactions, the decrease of the area (A_t) at the band can be used to monitor the conversion during the reaction.

From Fig. 2 one can see that during the curing process, the isocyanate absorption decreases due to its reaction with hydroxyl groups. The isocyanate absorption does not disappear completely if isocyanate is present in excess. The isocyanate absorptions at different times during the curing process are shown in Fig. 3.

If the one exponential fitting is applied to the data, deviations will appear after the gel point. Before the gel point, the reaction rate is controlled by the rate of the chemical reaction because the chains are flexible due to the lower molecular weight. After the gel point, the mobility of the reactive groups is hindered and restricted and the curing is controlled by the diffusion rather than by the chemical factors. This change is due to the onset of the gelation, which is the transition from a viscous liquid to an elastic gel and to the vitrification process, which is the transition from either a viscous liquid or elastic gel to a vitrous solid. In this case, it is better to use two exponential fittings (shown in Fig. 3). The obtained results are shown in Table 2. The first part represents the chemically controlled period and the second part the diffusion controlled period. The critical point between these two parts is close to the gel point (t_c, min) obtained by the solubility method (shown in Table 2).

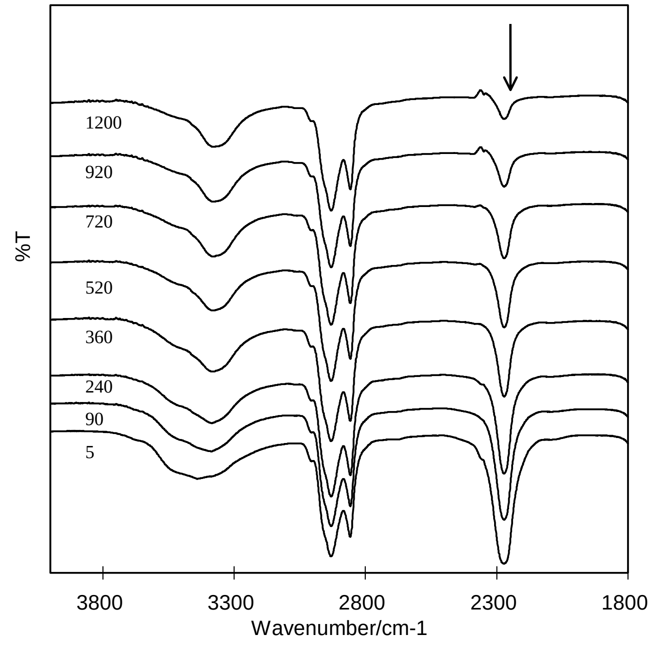

Fig. 2. FTIR spectra of PU1096 at different curing times.

In order to obtain the degree of curing it is assumed that there are no side reactions. Hence the isocyanate conversion can be used as the degree of curing as follows:

$$\text{Isocyanate conversion } (p) = 1 - \frac{A_t - A_\infty}{A_0 - A_\infty} \tag{5}$$

Here, A_0 is the normalized area of the absorption at the initial time, A_t the normalized area of the absorption at a certain time during the curing process, and A_∞ is the final normalized area of the absorption at infinite time. The results are shown in Fig. 4.

During the curing reactions of PUs, the critical conversion for the onset of the diffusion controlled reactions is taken as the point at which a three-dimensional cross-linking network is formed [13]. This seems reasonable since at

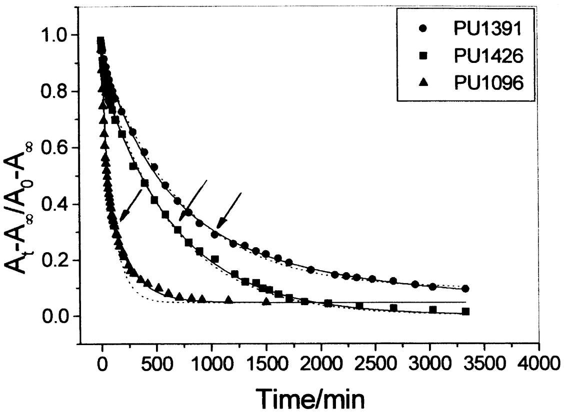

Fig. 3. Changes of isocyanate at different curing times during the curing process.

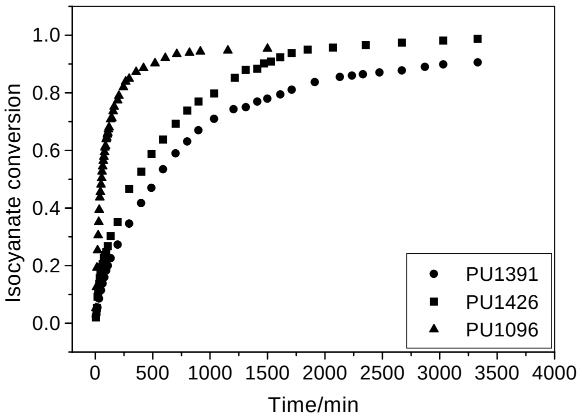

Fig. 4. Isocyanate conversion *versus* curing time of PUs.

this point the molecular weight of the reacting system increases dramatically. Because the behaviour of the systems is different before and after the gel points it can be characterized by two exponential equations. The critical degree of the curing (p_c) at the gel point can be obtained by applying Eq. (5) and the gel point determined (as shown in Table 2). All the values obtained are very close to the value of 58% predicted by Flory [3]. For this reason, it is assumed that for the aliphatic PUs studied here, the gelation corresponds to an isoconversion process, ($p_{gel} = 0.59$), and two exponential fittings can be successfully used to present the curing process.

3.2. Cross-linking kinetics

Chemical reactions that take place during the curing reaction of a thermoset determine the polymer morphology, which is a key factor in determining the properties of the cured thermoset. Consequently, the understanding of the mechanism and kinetics of the curing is very important in the evaluation of structure–morphology–property relationships of a material. The degree of cure p can be expressed as

$$p(t) = \int_0^t \mathrm{d}p \tag{6}$$

Based on empirical rate laws, a variety of kinetic models [14] can be adopted to describe the curing process of thermosetting systems. The rate of the curing degree can be expressed as a function of the curing degree and temperature [15].

A basic kinetic equation is

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k(T)f(p), \tag{7}$$

and when presented in isothermal conditions

$$\frac{\mathrm{d}p}{\mathrm{d}t} = A\exp\left[\frac{-E}{\mathrm{R}T}\right]f(p). \tag{8}$$

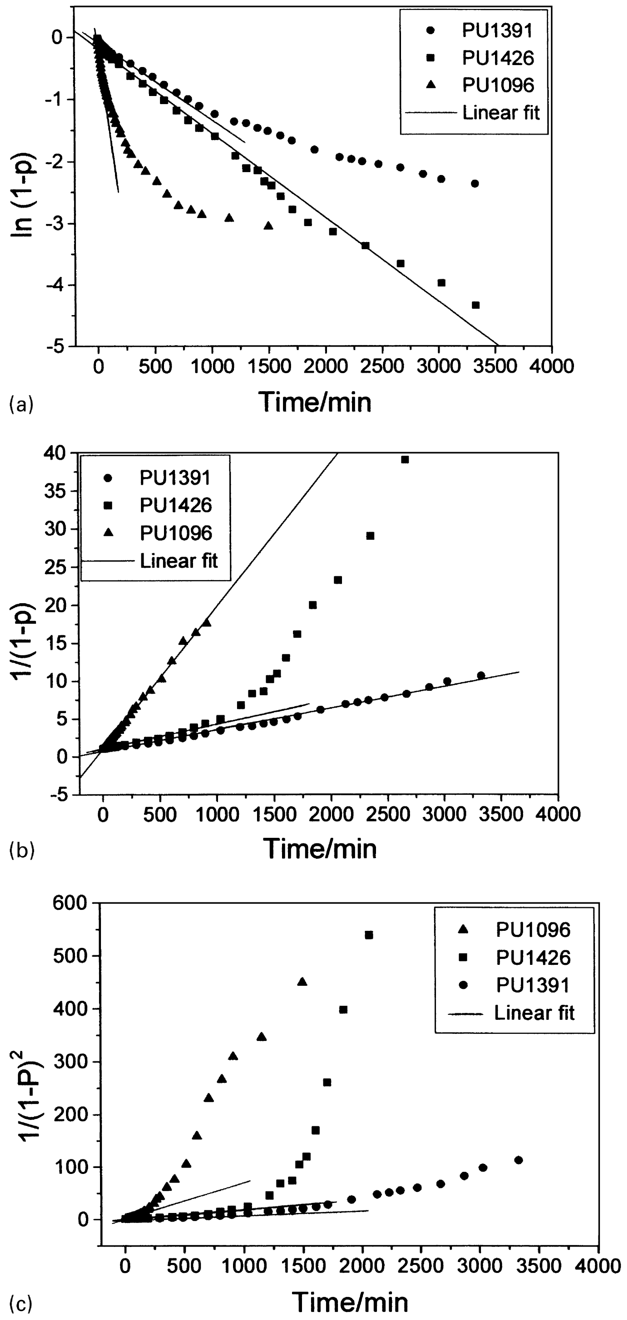

Fig. 5. Relationship between p and curing time of PU.

In a nonisothermal condition ($\beta = \mathrm{d}T/\mathrm{d}t$), and

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{A}{\beta}\exp\left[\frac{-E}{\mathrm{R}T}\right]f(p). \tag{9}$$

Two empirical schemes, nth-order and autoaccelerated models, are widely used for modelling the cure kinetics for thermosetting materials [16,17]. The nth-order kinetics can be expressed as

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k_0(1-p)^n, \tag{10}$$

Table 3
Rate constants and fitting results for the curing process of PU (p, range of curing degree fitted to the reaction order; k, rate constants (min); Er, the standard error of rate constants; SD, standard deviation of the fit)

PU/parameters		PU1096	PU1391	PU1426
First-order	p	0.12–0.71	0.05–0.65	*0.06–0.90*
	k	0.0062	0.0010	*0.0014*
	Er	2.8×10^{-4}	9.97×10^{-5}	*1.42×10^{-5}*
	SD	0.206	0.196	*0.099*
Second-order	p	*0–0.98*	*0–0.87*	0–0.78
	k	*0.0188*	*0.0028*	0.0037
	Er	*1.45×10^{-5}*	*4.5×10^{-6}*	6.93×10^{-5}
	SD	*0.119*	*0.060*	0.194
Third-order	p	0–0.65	0–0.70	0–0.75
	k	0.088	0.0122	0.016
	Er	0.0028	$6.26\times^{-4}$	$9.14\times^{-4}$
	SD	0.677	1.48	1.24

and the autoaccelerated model as

$$\frac{dp}{dt} = (k_1 + k_2p^m)(1-p)^n, \tag{11}$$

Here k_0, k_1, and k_2 are constants related to the rate constants, which depend on temperature. Parameters m and n are related to the reaction order. The method is based on the search of the parameters m and n in order to obtain a linear relationship between experimental and theoretical data. Here we used the nth-order approach for modelling the curing kinetics of PUs.

$$\text{If } n = 1, \quad \ln(1-p) = -k_0t + C \tag{12}$$

$$\text{If } n = 2, \quad \frac{1}{1-p} = k_0t + C \tag{13}$$

$$\text{If } n = 3, \quad \frac{1}{(1-p)^2} = k_0t + C \tag{14}$$

The curves where these three equations are applied for the three PUs studied are shown in Fig. 5. The fitting results are summarized in Table 3. Comparing the results, it is evident that PU1426 supports the first-order reaction, but PU1391 and PU1096 support the second-order reaction.

From above, this method attempts to adjust the equation to handle such reactions applied here but not suitable for the whole reaction process. Although it seems to be applicable, the nth-order approach has some limits as the reaction becomes more complex. In a polymerization process, the liquid resin slowly becomes solid as the reaction proceeds and obviously the reaction mechanisms are changing. Kinetic equations can describe the larger part of the reaction at the beginning but not towards the end because the reaction is controlled by the diffusion.

3.3. Gel fraction

From the soluble method we can obtain the gel fraction of thermoset polymers, Fig. 6 shows the relationship between the gel fraction (G) and the curing time for the three PU systems. These curves provide a clear picture of the curing process. No gel is formed at the beginning, but after an induction period, which depends largely on the types and the ratios of isocyanate and polyol, gel is formed and the gel fraction increases very quickly as the cure proceeds. At the gel point, where insoluble polymer starts to appear, the rate of the gel fraction increases, then slows down, and gradually levels off. In a highly cross-linked network, still some unreacted functional groups exist at the end of the curing process, some chains with low molecular weight are entrapped in the network and rendered inactive [18]. A high level of the gel fraction can be achieved at the early stages during the cure of PU1096, as the result shown in Fig. 6, where the gel fraction of 97% is reached.

Various models for sol–gel transition have been proposed, among them the most known are the percolation theory [19] and the aggregation approach [20]. The percolation theory is applied for modelling various phenomena in disordered media, including the characterization of porous materials, ground water flow in aquifers,

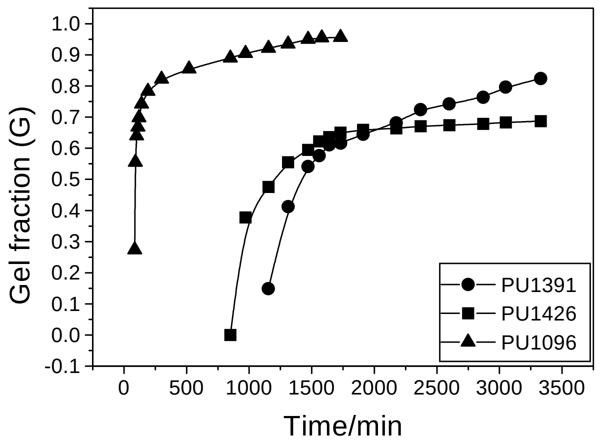

Fig. 6. Dependence of gel fraction on the curing time of PU at room temperature.

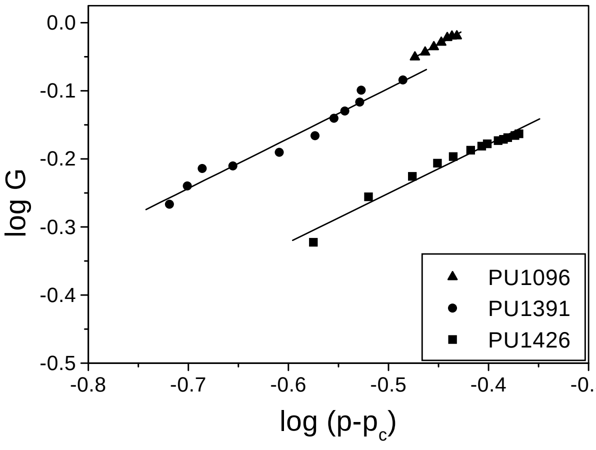

Fig. 7. log G *versus* log($p - p_c$) of PUs, with the slopes of critical exponents β.

Table 4
Swelling ratio, degree of cross-linking of cured PU and critical exponent from percolation theory

PU	PU1096	PU1426	PU1391
Swelling ratio (q)	2.25 ± 0.01	5.62 ± 0.03	4.78 ± 0.02
Degree of cross-linking (M_c) (g/mol)	2500 ± 100	11500 ± 2000	8900 ± 1000
p_c (critical point)	0.61	0.56	0.59
β (critical exponent)	0.80	0.72	0.73

gel networks, semiconductors, and biological membranes. Based on a cubic percolation theory, the Monte Carlo simulation was applied to the gelation of phenolic resins and gave an exact gel point, which was in excellent agreement with the observed value of critical fractional conversion (p_c) [21]. Concentration dependence of the sol–gel transition point and the network formation of polymer gels was also studied with the percolation theory [22]. Near the sol–gel phase transition, the percolation model can predict critical exponents for the gel fraction, weight-average degree of polymerization, radius of gyration, etc. The sol–gel transition occurs asymptotically near the sol–gel transition point, and the gel fraction (G) satisfies the following relation [23]:

$$G \propto (p - p_c)^{\beta} \qquad (15)$$

$$\text{or} \quad \ln G \propto \beta \ln(p - p_c) \qquad (16)$$

containing a constant β, called the critical exponent. The plots of $\log G$ versus $\log(p - p_c)$ are presented in Fig. 7. The values of β are determined from the slopes and are listed in Table 4 together with the corresponding p_c values. Furthermore, the average β value was found to be around 0.75, which was not affected by the ratio of the components. This value can be used to predict the gel fraction if only curing degrees are available. It can also be used to compare the results obtained from computer simulations using the percolation theory for the sol–gel transitions.

3.4. Degree of cross-linking

The swelling ratio (q) and the degree of the cross-linking (M_c) of the cured PUs are shown in Table 4. The swelling ratio q is proportional to M_c and can be used as a parameter for the degree of the cross-linking [24]. The degree of the cross-linking of the PUs increases in the following order:

$$\text{PU1096} < \text{PU1391} < \text{PU1426}$$

The result agrees with the results of the gel fraction. An increment of the curing degree increases the polymer's strength and the modulus, but decreases its flexibility.

4. Conclusion

This paper presents results of investigations where FTIR spectroscopy has been employed for monitoring the curing of three different PUs. Gel fractions were measured to obtain information on the swelling behaviour of the aliphatic PUs. Two exponential fittings were successfully used to present kinetics of the curing. The curing process contained two periods, chemically controlled and diffusionally controlled. The curing process of PU1426 supports the first-order reaction, and of PU1391 and PU1096 conform to the second-order reaction. Based on the percolation theory, the three PU systems have the critical exponents β close to 0.75.

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