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Studies on the effect of curing conditions on the curing rate and mechanical properties of moisture-cured poly(urethane-urea) elastomers containing oligocarbonate segments

Summary – In this paper the results of studies on the effect of the curing conditions on the mechanical properties, appearance and curing rate of poly(urethane-urea) elastomer (PURE) obtained by moisture-curing of the corresponding urethane prepolymer (URE) synthesized from isophorone diisocyanate (IPDI) and oligocarbonate diol (OCD) are presented. OCD was synthesized from dimethyl carbonate and 1,6-hexanediol. A designed experiment was conducted where two parameters [curing temperature ($T_c - X_1$) and relative air humidity ($RH - X_2$)] were changed at the same time according to the standard 2^2 model. The results were analyzed by Statistica computer programme and were presented in the form of X_1 - X_2 graphs. The graphs were produced for a set of Y parameters characterizing the properties of PURE (mechanical properties, curing rate and sample appearance). The $Y = f(X_1, X_2)$ equations were also obtained. The results showed the distinct dependence of the curing rate and PURE properties on curing parameters and allowed to select a range of optimum curing conditions.

Keywords: polyurethane elastomers, poly(urethane-urea), oligocarbonate diol, 1,6-hexanediol, dimethyl carbonate, isophorone diisocyanate, mechanical properties, moisture curing.

BADANIA WPŁYWU WARUNKÓW UTWARDZANIA NA SZYBKOŚĆ UTWARDZANIA I WŁAŚCIWOŚCI MECHANICZNE ELASTOMERÓW POLI(URETANO-MOCZNIKOWYCH) UTWARDZANYCH WILGOCIĄ

Streszczenie – W artykule przedstawiono wyniki badań nad wpływem warunków utwardzania wilgocią na właściwości mechaniczne, wygląd oraz szybkość utwardzania elastomeru poli(uretano-mocznikowego) (PURE) otrzymanego w wyniku utwardzania wilgocią odpowiedniego prepolimeru uretanowego (URE) syntezowanego z izoforonodiizocyanianu (IPDI) i oligowęglanodiolu (OCD). OCD otrzymano z węglanu dimetylu i 1,6-heksanodiolu. Przeprowadzono zaplanowane zgodnie ze standardowym modelem 2^2 doświadczenie czynnikowe, w którym zmieniano dwa parametry [temperaturę utwardzania ($T_c - X_1$) i wilgotność względną powietrza ($RH - X_2$)]. Wyniki analizowano za pomocą programu komputerowego Statistica i przedstawiono je w postaci wykresów szeregu parametrów Y charakteryzujących właściwości PURE (właściwości mechaniczne, szybkość utwardzania, wygląd próbki) w zależności od parametrów X_1 - X_2 . Otrzymano również równania opisujące funkcje $Y = f(X_1, X_2)$. Wyniki pokazały, że istnieje wyraźna zależność szybkości utwardzania i właściwości PURE od parametrów utwardzania. W szczególności zauważono, że nie tylko wytrzymałość na rozciąganie, ale także wydłużenie przy zerwaniu wzrasta ze wzrostem T_c i RH . Analiza wyników doświadczenia czynnikowego umożliwiła wybór optymalnego zakresu parametrów $T_c = 70-75$ °C i $RH = 60$ %, których zastosowanie pozwala uzyskać przezroczyste, pozbawione pęcherzy elastomery o znakomitych właściwościach mechanicznych.
Słowa kluczowe: elastomery poliuretanowe, poli(uretano-mocznik), oligowęglanodiol, 1,6-heksanodiol, węglan dimetylu, diizocyanian izoforonu, właściwości mechaniczne, utwardzanie wilgocią.

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Polyurethanes containing oligocarbonate segments synthesized from oligocarbonate diols and diisocyanates [also called poly(carbonate-urethane)s] combine good hydrolytic stability of poly(ether urethane)s and good resistance to oxidation of poly(ester urethane)s and there-

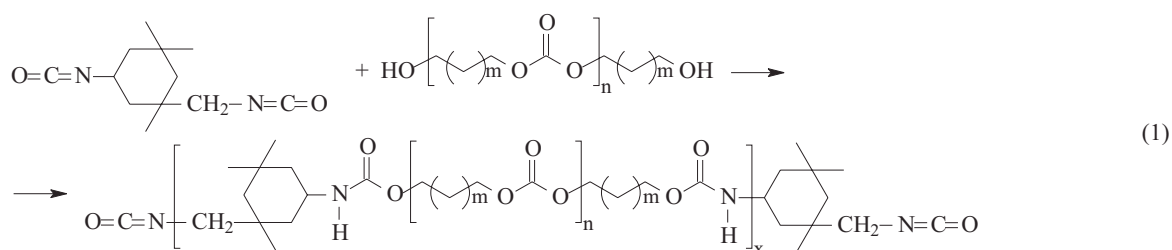
fore are widely used in highly responsible medical applications [1–3] and also in certain other highly demanding sectors like specialty coatings for exterior use or sealants [4–6]. The same is true for polyureas containing oligo-carbonate segments synthesized from oligocarbonate diols and diamines [also called poly(carbonate-urea)s] [7, 8] and for poly(urethane-urea)s containing oligo-carbonate segments obtained from NCO-terminated urethane-carbonate prepolymers synthesized from oligo-carbonate diols and diisocyanates [also called poly(carbonate-urethane-urea)s]. In July 2009 a poly(carbonate-urethane-urea) elastomer scaffold material produced by Biomerix was given “Biomaterial of the Month” name by The Society for Biomaterials [9]. An excellent hydrolytic stability of poly(carbonate-urethane-urea)s was proved in our recent studies [10]. As poly(carbo-

Synthesis of OCD, URE and PURE

For the purpose of this study OCD, URE and PURE were synthesized according to the procedure described in detail in our earlier paper [10]. OCD was synthesized from dimethylcarbonate and 1,6-hexanediol by using a two-step condensation reaction [14].

Bis(methylenecarbonate)hexamethylene that was formed in the first step of that reaction was further reacted with 1,6-hexanediol in the presence of a catalyst (potassium carbonate) to yield OCD of molecular weight $M_w = 2200$ as determined by ^1H NMR.

URE of NCO content of 5.86 % was synthesized from OCD and isophorone diisocyanate (IPDI) by using NCO/OH ratio = 3/1. The reaction proceeds according to following equation:



$m = 4, n = 16, x = 2-3$

nate-urethane-urea)s are obtained by moisture-curing, understanding the effect of curing conditions on their properties is essential for the selection of curing parameters that would allow for the optimum performance of the resulting cured material. In spite of that, no data have been found in the literature on such effect, but there are reports available on the investigations of moisture curing conditions on the properties of other poly(urethane-urea) materials [11, 12]. Earlier, a detailed study on the effect of moisture curing conditions on the properties of poly(urethane-urea) sealants used in the construction industry was made in a statistically designed experiment [13].

In this paper the results of the study on the effect of curing conditions on the curing rate and mechanical properties of poly(urethane-urea) elastomers (PURE) obtained by moisture-curing of the corresponding urethane prepolymer containing oligocarbonate segments (URE) synthesized from isophorone diisocyanate (IPDI) and oligocarbonate diol (OCD) are presented. This study was conducted as a statistically designed experiment.

EXPERIMENTAL

Materials

Anhydrous dimethyl carbonate (DMC) and 1,6-hexanediol (purity of 97 %) were supplied by Aldrich. Isophorone diisocyanate (trade name VESTANAT IPDI) was obtained from EVONIK Industries.

PURE was obtained *via* moisture-curing of URE at a curing temperature $T_c = 70$ °C and relative air humidity $RH = 10$ % for two days, followed by the temperature and humidity regime specific for the particular experiment according to the curing parameters fixed in the experiment design. The moisture curing process of URE that leads to PURE is shown in Scheme A.

Methods of testing

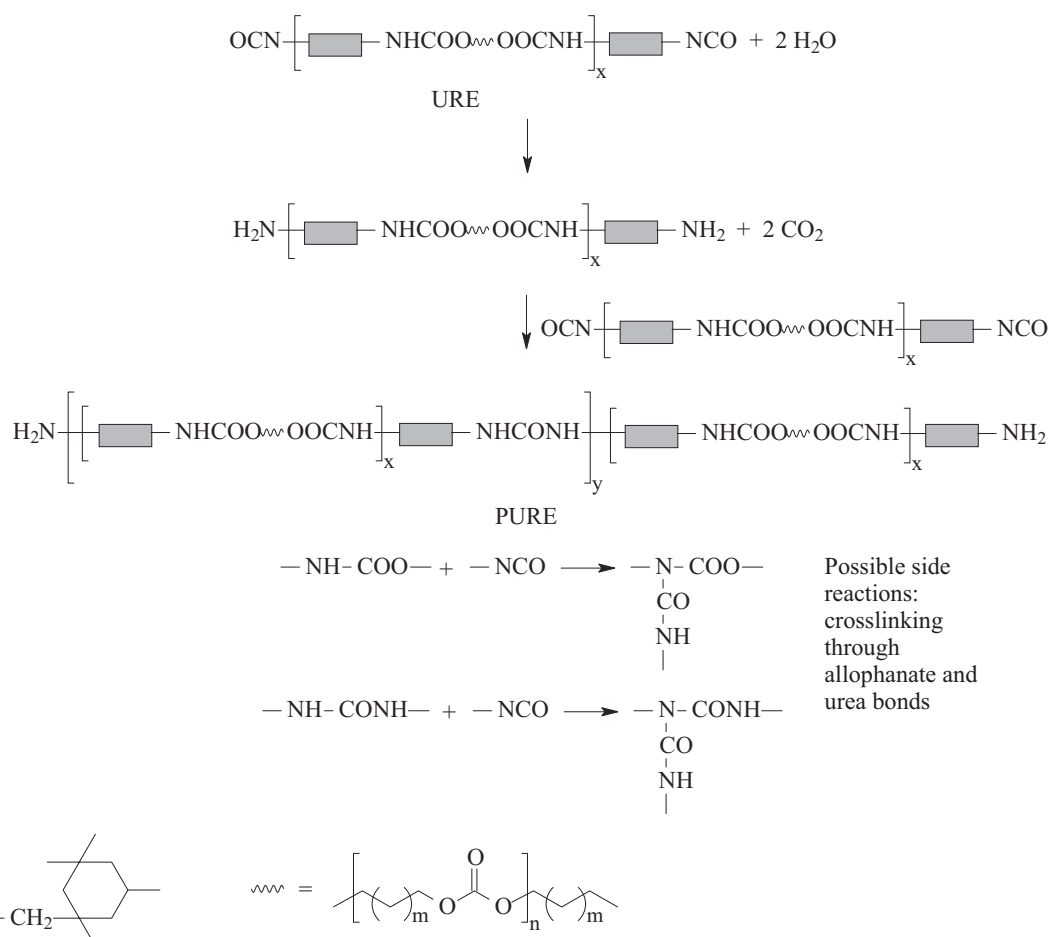
NCO content in the URE was determined by titration with amine according to standard EN ISO 14896. The mechanical properties of the PURE samples were measured on Instron 4505 apparatus at a speed of 50 mm/min using dumb-bell shaped tensile test specimens, as described in EN ISO 527 standard. The dimensions of the operative part of the specimen were $30 \times 6 \times 1$ mm.

Relative integral absorbancy (RIA) of NCO groups was calculated as:

$$RIA = \frac{[\text{C-H/NCO}]_o}{[\text{C-H/NCO}]_t} \cdot 100 \% \quad (2)$$

where: $[\text{C-H/NCO}]_o$ – ratio of integral absorbancy of the sum of C-H stretching ($3145-2780 \text{ cm}^{-1}$) bands to integral absorbancy of NCO stretching band ($2323-2200 \text{ cm}^{-1}$) measured by FT-IR before curing, $[\text{C-H/NCO}]_t$ – ratio of integral absorbancy of the sum of C-H bands to integral absorbancy of NCO band measured by FT-IR after 7 days of curing.

Curing rate was calculated as the ratio of the sum of C-H stretching ($3145-2780 \text{ cm}^{-1}$) bands/NCO stretching band ($2323-2200 \text{ cm}^{-1}$) integral absorbancy measured by



Scheme A. The moisture-curing process of urethane prepolymer containing oligocarbonate segments (URE) leading to poly(urethane-urea) elastomer containing oligocarbonate segments (PURE) and side reactions of allophanate bond or urea bond formation that lead to crosslinking of PURE

FT-IR after 7 days of curing at conditions set for a given experimental point to the sum of C-H bands/NCO band integral absorbancy measured by FT-IR before curing.

Experiment design

Before the designed experiment was started the preliminary test of moisture-curing of URE prepolymer at relatively mild conditions ($RH = 35\%$ and $T_c = 55^\circ\text{C}$) was conducted in order to see what level of a lower limit of RH and T_c could guarantee that the moisture curing would be completed in 7 days (fixed curing time for all experimental points in the designed experiment). It was found that $RH = 35\%$ was not sufficient for achieving the curing in 7 days, so $RH = 45\%$ was selected as the minimum RH level for the designed experiment.

The designed experiment was planned to be conducted in a 2^2 mode, with two independent variables *i.e.* $T_c - X_1$ and $RH - X_2$. Based on the instructions from Statistica computer programme (that was used for the experiment design and the analysis of the results) five experimental points were selected. Four points were situated in the corners of the experiment space and one in the centre of the experiment space as it was presented in

Figure 1. In Table 1 the virtual designations of experimental points and corresponding real curing conditions are presented. For five different curing conditions given by (X_1, X_2) variables the following dependent variables (Y), *i.e.* measured parameters, were selected:

- Y_1 – tensile strength (stress at maximum load),
- Y_2 – stress at break,

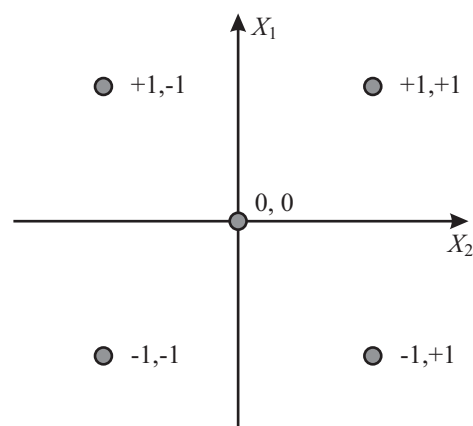


Fig. 1. Plan of a designed experiment conducted in a 2^2 mode with virtual designations of experimental points

Y_3 – stress at 100 % elongation,
 Y_4 – elongation at break,
 Y_5 – Shore A hardness,
 Y_6 – curing rate,
 Y_7 – film transparency, visual assessment in 1 to 5 scale (1 correspond to the highest transparency),
 Y_8 – degree of sample bubbling, visual assessment in 1 to 5 scale (1 correspond to the lowest degree of bubbling).

Table 1. Virtual designations of curing conditions (X_1 and X_2) and corresponding real curing conditions (T_c and RH) for five cured samples

Number of cure sample	Virtual independent variables		Real curing conditions	
	X_1	X_2	T_c , °C	RH , %
1	-1	-1	55	45
2	0	0	65	60
3	-1	+1	55	75
4	+1	-1	75	45
5	+1	+1	75	75

RESULTS AND DISCUSSION

All results obtained in the designed experiment, *i.e.* the values of measured parameters Y obtained for particular curing conditions are presented in Table 2.

Table 2. Results of dependent variables (Y) corresponding to the properties of five samples cured in conditions specified by independent variables X_1 and X_2

Dependent variable	Unit	Y values obtained for particular (X_1 , X_2) values				
		(-1, -1)	(0, 0)	(-1, +1)	(+1, -1)	(+1, +1)
Y_1	MPa	7.7 (12.7) ^{a)}	29.1	24.0	25.7	29.6
			24.2			
			28.2			
			26.8			
Y_2	MPa	7.6 (12.7) ^{a)}	29.1	24.0	23.0	29.6
			24.2			
			28.2			
			26.8			
Y_3	MPa	3.7 (6.1) ^{a)}	3.8	4.2	4.4	4.1
			3.9			
			3.8			
			4.0			
Y_4	%	478 (503) ^{a)}	651	638	658	668
			664			
			712			
			655			

Y_5	°ShA	76.6	64.5	65.8	69.8	63.6
			64.5			
			64.5			
			64.5			
Y_6	–	7	31	20	27	25
Y_7	–	5	1	1	1	1.5
Y_8	–	1	2	2.5	1	3

^{a)} The results in brackets are obtained for additional tests made after two weeks because the film prepared after 7 days of curing was not fully cured.

Effect of curing conditions on mechanical properties of PURE

The analysis of mechanical properties results was conducted with the assistance of the Statistica computer program and the results of that analysis are shown on graphs (Figures 2–6). In each of those figures the dependence of Y on X_1 and X_2 is presented graphically as a function $Y = f(X_1, X_2)$.

The first important observation from the results shown in Table 2 and Figs. 2–6 is that the mechanical properties of PURE containing oligocarbonate segments obtained by moisture-curing of the corresponding urethane prepolymers terminated with NCO groups are generally excellent. After 7 days of moisture-curing in appropriate conditions PURE of tensile strength (Y_1) of *ca.* 30 MPa, elongation at break (Y_4) of *ca.* 600 % and Shore A hardness (Y_5) of *ca.* 65 °ShA could be obtained. It is also essential that despite very high tensile strength, the stress at 100 % elongation (Y_3) was still quite low, what meant that the sample elasticity was very good.

It is clear from Fig. 2 and 3 that tensile strength and stress at break (Y_2) distinctly increase with the increase in both curing parameters, *i.e.* T_c (X_1) and RH (X_2) that were independent variables changed in the designed experiment. Those results show that in order to achieve reasonable tensile strength of 20 MPa in 7 days of moisture-curing, raising T_c to 60 °C and RH to 55 % would be necessary. It also seems that tensile strength is more dependent on T_c than on RH , while the opposite effect is observed for stress at break.

Similar observations can be made based on the analysis of Fig. 5 where elongation at break (Y_4) is plotted against the same two curing parameters. The higher T_c and RH – the higher is elongation at break, and here the effect of T_c seems to be significantly stronger than the effect of RH and generally stronger than in the case of tensile strength.

The increase in tensile strength with the increase in T_c and RH can be explained by a higher degree of crosslinking that was reported to occur in moisture-cured poly(urethane-urea)s [15]. It should be noted, that in this process two types of crosslinking are possible: derived from covalent bonds formation (allophanate and biuret linkages) and hydrogen bonds formation between ure-

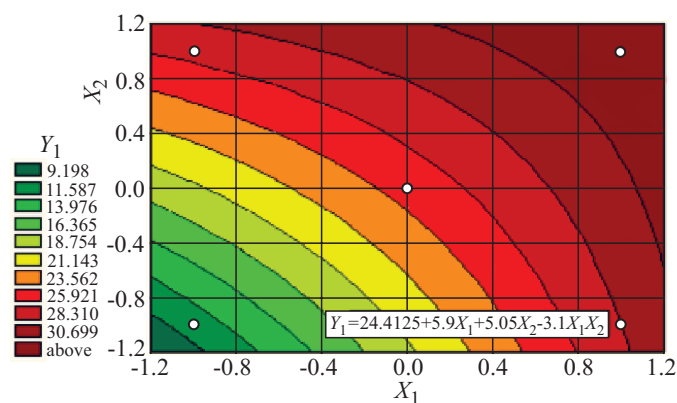


Fig. 2. Effect of moisture-curing conditions on tensile strength (Y_1) of PURE presented graphically as $Y_1 = f(X_1, X_2)$ function

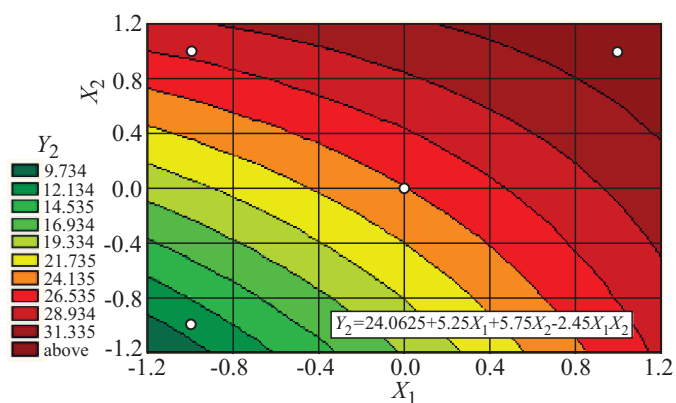


Fig. 3. Effect of moisture-curing conditions on stress at break (Y_2) of PURE presented graphically as $Y_2 = f(X_1, X_2)$ function

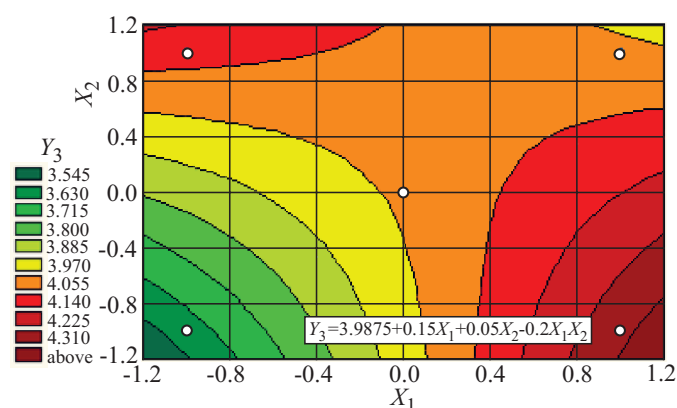


Fig. 4. Effect of moisture-curing conditions on stress at 100% elongation (Y_3) of PURE presented graphically as $Y_3 = f(X_1, X_2)$ function

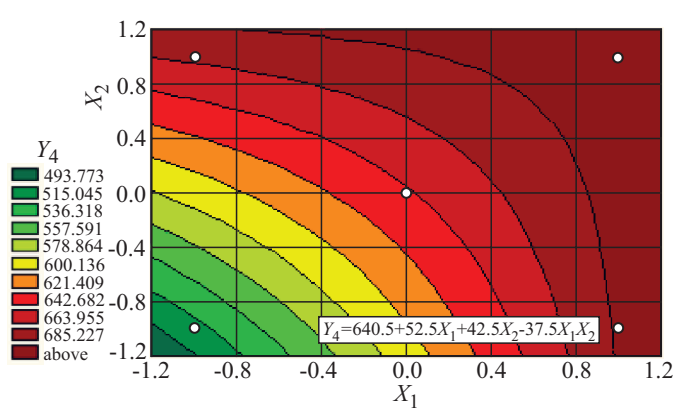


Fig. 5. Effect of moisture-curing conditions on elongation at break (Y_4) of PURE presented graphically as $Y_4 = f(X_1, X_2)$ function

thane and urea groups [16, 17]. At higher temperature, the higher molecules mobility can lead to their better organization and more hydrogen bonds can be formed, so the mechanical strength of the polymer increases. At higher temperature more allophanate and urea linkages can also be formed what may also result in higher mechanical strength. However, it is difficult to explain the simultaneous increase in elongation at break with an increase in the same curing parameters. As it is known that conditions of the formation of poly(urethane-urea) during the moisture-curing process may affect the domain microstructure of the cured polymer [18] and that, subsequently, the microstructure affects the mechanical properties, one explanation could be that the said observed effect is due to the different domain structure of the same polymer obtained at higher T_c with higher RH and at lower T_c with lower RH. However, detailed studies of the microstructure by SAXS would be needed to confirm that suggestion. A more obvious explanation could be that at higher T_c and RH the reaction between NCO and H_2O proceeds to a more advanced stage, so the number of longer polymer chains is increased what results in higher elongation at break (see Scheme A). That suggestion

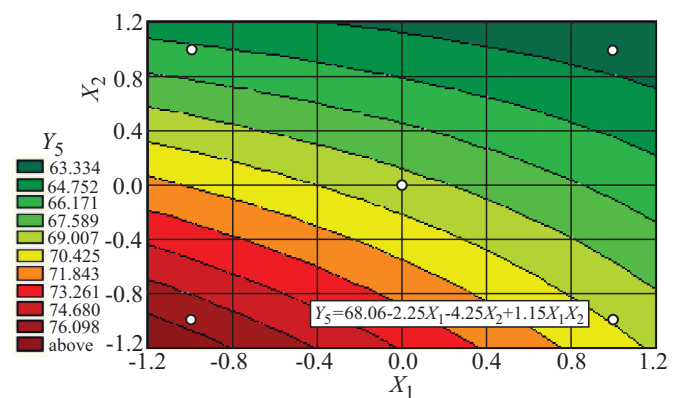


Fig. 6. Effect of moisture-curing conditions on Shore A hardness (Y_5) of PURE presented graphically as $Y_5 = f(X_1, X_2)$ function

could be confirmed by the determination of the molecular weight, but attempts to make such determinations failed due to lack of solubility of PURE in standard solvents used for GPC.

Regarding the effect of the curing conditions on other mechanical properties it is clear from Fig. 4 that the stress

at 100 % elongation (Y_3) does not depend distinctly on the curing parameters. However, as it could be expected, the increase in tensile strength and elongation at break with an increase in T_c and RH correlates well with a decrease in Shore A hardness (Y_5) (see Fig. 6).

Effect of curing conditions on the curing rate of PURE

The results of the analysis of the curing rate using program Statistica are presented in Figure 7. Curing rate (Y_6) depends more on T_c than on RH but it increases with an increase in those two curing parameters only up to a certain level (ca. $T_c = 67^\circ\text{C}$ and $RH = 70\%$). Above that level

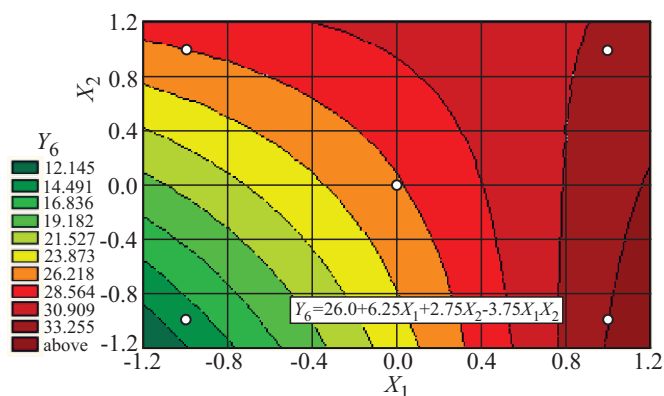


Fig. 7. Effect of moisture-curing conditions on curing rate (Y_6) of PURE presented graphically as $Y_6 = f(X_1, X_2)$ function

the curing rate remains practically unchanged. This phenomenon can also be observed in Figure 8 that shows how the relative integral absorbancy (RIA) of NCO groups was diminishing with the progress of the moisture curing process depending on the curing conditions. In the first phase of curing the decrease in NCO groups content was fast and in the next phase it slowed down significantly. A similar behavior was reported in [11], where

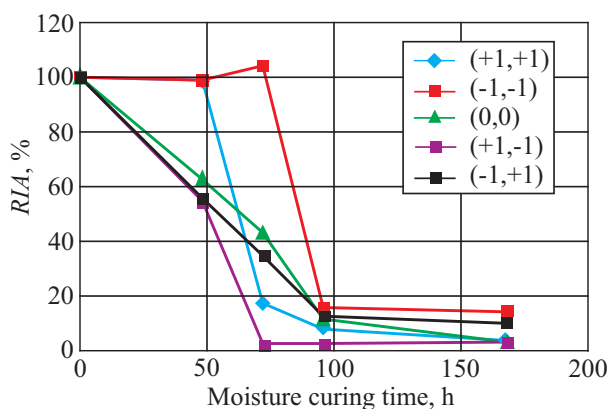


Fig. 8. Effect of curing conditions on the character of the decrease in relative integral absorbancy (RIA) of NCO groups with curing time

the moisture curing kinetics of various urethane prepolymer were described.

Effect of curing conditions on visual appearance of PURE

The results of the analysis of film transparency and degree of bubbling are presented in Figures 9 and 10. As it can be seen from Fig. 9, the transparency of moisture-cured PURE containing oligocarbonate segments (Y_7) depends equally on both T_c and RH and becomes satisfactory when T_c value is above 65°C and RH is above 60%. A further increase in T_c and RH leads to still better sample transparency. However, as it is evident from Fig. 10, the degree of bubbling seems to depend practically only on RH . The higher RH , the higher the degree of bubbling.

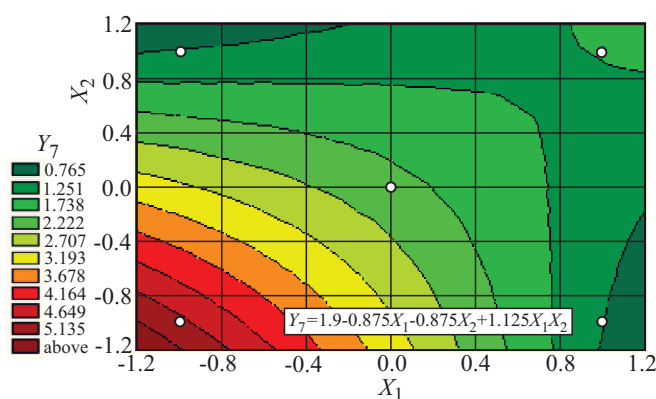


Fig. 9. Effect of moisture-curing conditions on film transparency (Y_7) of PURE presented graphically as $Y_7 = f(X_1, X_2)$ function

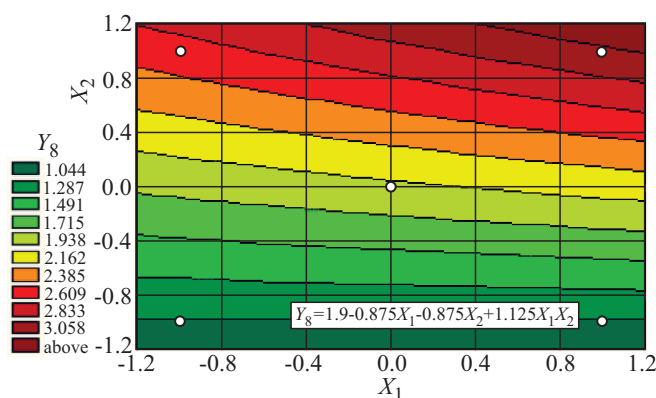


Fig. 10. Effect of moisture-curing conditions on the degree of bubbling (Y_8) of PURE presented graphically as $Y_8 = f(X_1, X_2)$ function

The results presented above could be used to find out the optimum range of T_c and RH values which would allow for obtaining moisture-cured PURE of satisfactory

properties. From the practical point of view, the limiting factors should be good transparency (*i.e.* $Y_7 < 2$ what corresponds to $T_c > 60$ °C, $RH > 70$ %), and in the same time a minimum degree of bubbling ($Y_8 < 2$ what corresponds to $RH < 65$ %) for any T_c value in the investigated range. Based on that analysis it can be concluded that optimum RH level should be 60–65 %.

CONCLUSIONS

The combined effect of moisture-curing conditions (T_c and RH) on the curing rate, appearance and mechanical properties of cured PURE containing oligocarbonate segments was studied in the designed experiment. It was found that not only tensile strength but also elongation at break increased with the increase in T_c and RH . That phenomenon was explained by a higher chance of formation of allophanate and urea linkages (covalent crosslinking) and better organization of macromolecules assisting in hydrogen bonds formation (physical crosslinking), and simultaneous higher chance of formation of longer polymer chains at higher temperatures. The analysis of all results of that experiment by the Statistica computer program led to the selection of optimum values of $T_c = 70$ – 75 °C and $RH = 60$ % at which transparent, bubble-free elastomers of excellent mechanical properties — tensile strength (*ca.* 30 MPa), elongation at break (*ca.* 600 %) and Shore A hardness (*ca.* 65 °ShA) can be obtained.

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