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## REACTIONS IN SOLID STATE WITHIN POLYURETHANES. KINETICS AND POSTCURE REACTION MECHANISM IN CASTING POLYURETHANE ELASTOMERS

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Key Words: Postcuring, Mechanical Properties, Polyurethane Elastomers, and Solid State Reaction

### ABSTRACT

The solid state postcure reaction mechanism of polyurethane elastomers (PU) synthesized using a relatively small excess (up to 10%) of isocyanate was studied. The postcure process succeeds especially with the assistance of atmospheric humidity and, its process velocity depends on PU sample thickness. The polymer network is consolidated mainly by the formation of a new urea group. The formation of allophanate, uretidinedione, and isocyanurate groups and possible reticulations by the intermediary amine groups formed, play only a secondary role in the studied conditions. Kinetic equations regarding the postcure evolution were followed by means of the changes in mechanical properties. The evolution of the process was correlated to different kinetic measurements regarding the elementary processes involved like the consumption of NCO groups, absorption of water from the atmospheric humidity, and desorption of CO<sub>2</sub>

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resulted during the formation of urea group. The CO<sub>2</sub> desorption appears to be the slowest dynamic process.

## INTRODUCTION

The postcure processes developed in solid state [1-4] play an important role in the polymer synthesis. Although an old subject, the postcuring mechanism of polyurethanes remained so far incompletely elucidated.

In the casting of polyurethane elastomers (PU), which are traditionally synthesized using a small excess of up to 10% isocyanic groups (NCO) against the total amount of hydroxyl groups (OH) present in the system ("index number" [5]  $I = 110$ ), the mechanical properties intensifies with time.

Even though the atmosphere humidity has a vast access for thin films and porous materials, the preponderance of urea group formation was unambiguously proven [5-9]. The nature of the process, which performs in the depth of solid cast elastomers where water penetration is much more difficult, still remains open.

For the NCO excess group consumption many more reactions were suggested. Also evidenced was the spontaneous isocyanate group dimerization at room temperature [10-11]. In the hot cure reaction, the principal process, admitted by A. Awater, is the appearance of the allophanate and/or biuret linkages [12]. K. A. Piggot [13] also presumed that the presence of some base or metal as a trace catalyst in the raw starting polyol can favor the biuret, allophanate of the trimerisation process. If considering the relatively long time of the postcure reaction, it is difficult to predict which of these reactions mainly continue to perform.

Once the usual hot cure reaction has finished, it was demonstrated that when kept in time at room temperature, a cast polyurethane continues to change its properties [14].

This change appears as a function of environmental exposure, extended use, or chemical reactions intrinsic to the material itself [5, 14-16].

This phenomenon was observed by us on different types of PU [14] with variable  $I$  values, and also using different reaction components.

The mechanistic study performed in the present work as a result of the corroboration between different possible influential factors, refers only to one of the most representative PU cases studied by us, i.e., hydroxy terminated polyethylene adipate  $\bar{M} = 2000$  ( $PEA_{2000}$ ), 4,4'-dibenzyl diisocyanate (DBDI), diethyl-



ene glycol (DEG) (PEA<sub>2000</sub> - DBDI - DEG) in a molar ratio 1:3.03:1.754 having an I value of 110. From the various diisocyanates studied by us, we have chosen here DBDI, due to the fact that this isocyanate leads to the most stable PU toward environmental factors [17]. In this way, we intended to avoid the interference between the favorable postcure processes and the eventual incipient parallel degradative phenomena as much as possible.

Recently, an excellent study presented by D. W. Duff and G. E. Maciel [18], proved that solid-state <sup>15</sup>N and <sup>13</sup>C CP/MAS NMR could be an extremely useful tool in pursuing the postcure reaction chemistry of residual isocyanate in isocyanurate resins. As reported by the authors, the predominant postcure process should be due to the reaction of isocyanate group with the atmospheric humidity to form an amine which further condense with an additional isocyanate from the immediate vicinity to form an urea linkage.

So far, this method was not extended to the post cure processes of polyurethanes. However, if its use is intended, there are difficulties to be expected. The overlapping of the NMR nitrogen resonance signals as isocyanate with amine and urea with biuret mentioned by the authors [18], will be complicated here even more by overlapping with other additional nitrogen signals characteristic to polyurethane system, like urethane and possible allophanate nitrogens [18, 19-21].

Our own work was motivated by the hope that more detailed information on the postcure process of polyurethane elastomers could be obtained by combining the quantitative measurements like the enhancement in the mechanical properties in time with various dynamic processes which take place concomitantly, similarly as performed by A. Toffey and W. S. Classer in the case of cellulose crosslinking by urethane groups when the dynamic mechanical thermal analysis (DMTA) was used.

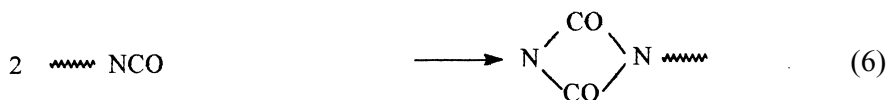
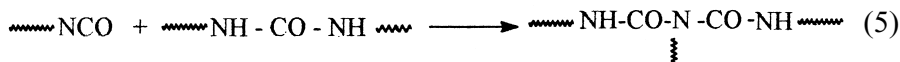
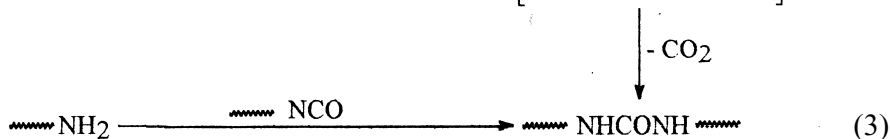
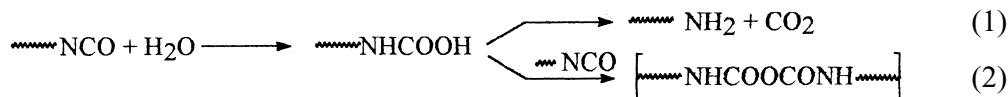
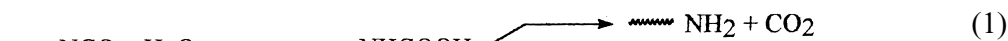
In an earlier report, we evidenced that major postcure effects are observed during the first month after synthesis only in the case of the polyurethanes still containing free residual isocyanate groups [14].

Beside the initial excess concentration of -NCO groups, it was found that the rate of maturation also depends on both the soft and hard segment polyurethane structure [14].

It is reasonable to suggest that the main process involved in the polyurethanes maturation observed on the PU having a slight -NCO excess ( $I \leq 110$ ) is one of a chemical nature. The presence of air humidity certainly plays a decisive role, but also, it cannot exclude other side reactions. These side reactions are well known, yet the results of the competition of these reactions in solid state



during the long time postcuring and the correlation effects between the mechanical properties enhancement and also, such structure modification are not clear. Theoretically, several principal ways can be rationalized for the excess isocyanate consumption.



The intermediary appearance of the  $-\text{NH}_2$  group in PU as a result of water reaction (Equation 1) was already confirmed quite a while ago [23]. Taking into account the necessity of the reactive end groups collision, the low concentration of these end groups and their quasi limited mobility, special care should be dedicated to other possible  $-\text{NH}_2$  group consumption. Under the circumstances, the much slower reactions with other groups like urethane and ester groups, which are present in PU in high concentrations, should also be considered. As already mentioned, the aliphatic polyesters can be degraded by the amine groups yielding amide derivatives [24].

On the other hand, the interaction between the amine and urethane groups can also lead to the urea group formation [5].

Obviously, these reactions normally perform at higher temperatures, yet it is necessary to determine if during the long period of the post cure phenomenon, such processes may or may not perform to some extent, as in the case of the slow hydrolytic degradation process in time.

As observed, the considerable decrease in the rate of maturation process at room temperature in the absence of humidity [14] suggests that in our case the



allophanate, biuret, uretidinedione and isocyanurate group formation Equations (4, 5, and 6 should play only a minor role in the polyurethanes consolidation.

The aim of the present work is to obtain new clarifications regarding the preponderant reactions responsible for the PU consolidation process and to study the evolution of the polyurethane mechanical performance during the post cure process in correlation with the dynamics of different diffusion processes like water absorption and CO<sub>2</sub> desorption.

## EXPERIMENTAL

### Synthesis of PUs

#### *Materials*

Hydroxyterminated polyethylene adipate  $M = 2000 \pm 50$  (PEA<sub>2000</sub>) commercial product (CIFC Savinesti, Romania), 4,4'-dibenzoyldiisocyanate (DBDI) as an experimental product from the pilot plant (CIFC Savinesti, Romania) was recrystallized twice from anhydrous cyclohexane m.p. 89-89.5°C. Anhydrous diethylene glycol (DEG) adipate p.a. was furnished by Fluka.

#### *Polyaddition Procedure and Postcure Conditions*

The polyaddition was performed in two steps via the prepolymer route. 1000 g (0.5mol) PEA<sub>2000</sub> was dehydrated under mixing at 115°C and vacuum (< 1mm Hg) for 2 hours. Then, 400 g (1.5151mol) of DBDI crystals were added under intense mixing to the anhydrous macrodiol and the vacuum was restored. After 30 minutes of mixing under vacuum at 100°C, the temperature was reduced at 90°C, and the vacuum was removed, then 93.1 g (0.877 mol) anhydrous DEG were added at once under very rapid stirring. The mixing was continued for a maximum of 40 seconds. The seconds "pot life" of this nature is about 5 minutes; during this time the liquid mixture was cast onto closed teflonated moldings pre-heated at 90°C so as to avoid the interference of air humidity during the cure process. In the case of open molding the presence of air usually leads to some perturbing uncontrolled and unhomogeneous enhancement of the mechanical properties. PUs sheets of 1,2,3,4,5, and 6 mm thick and about 20μ PUs thin films were thus obtained. For the cure process after casting, the closed moldings were maintained at 110°C for 24 hours. After an additional 24 hours at room temperature, PU sheets were demolded. No release agent was used in order to avoid the disturbance of diffusion processes between air atmosphere and polymer during the postcure process.



This procedure results in a polyurethane with an I value of 110, which corresponds, in our case, to an excess of 0.0185 eq. NCO groups/100 g PUs. The density of this PUs was 1.22 g/ml.

The changes in mechanical properties were monitored starting immediately after demolding. In order to follow the postcure process, the sample was maintained in a tightly closed thermostat under controlled atmospheric conditions i.e.,  $t = 25^{\circ}\text{C}$  and  $50 \pm 2\%$  RH. The RH was maintained as a result of the equilibrium between the air and a water solution of 44.1%  $\text{H}_2\text{SO}_4$ , which is placed in a thermostat large open cuvette and monitored by a Precision Hygrometer (VEB MAB SCHKEUDITZ, Berlin).

### 300% Tensile Stress Determination

300% tensile stress determination was made in accordance with standard procedures from the stress-strain curve data of simple tension. The specimens for the testing were cut from the films using the dimensions given in ASTM D1708, i.e., a dumbbell-shaped specimen with a gauge length of 20 mm, a width of 58 mm, and a variable thickness of up to 6 mm. The stress-strain data on these specimens presented here were taken by using an Universal Instron Testing Machine at room temperature ( $T = 25^{\circ}\text{C}$ ).

### IR Determination

IR spectra were measured at different time intervals on about  $20\mu$  PU films by using a Carl Jena Specord M 80 apparatus.

### Water Absorption and Desorption

PUs sheets of different thickness, previously completely postcure matured, were anhydrided at  $60^{\circ}\text{C}$  under vacuum of 0.1 mm Hg in the presence of anhydrous  $\text{CaCl}_2$  up to constant weights. On these films, the humidity absorption rate was measured by the increase of their weight under the same atmosphere conditions as that used in the maturation postcure process (e.g.  $25^{\circ}\text{C}$  and 50% RH).

To determine water desorption, PU sheets of different thickness previously matured, have been immersed for 7 days in water, then the surface humidity is wiped off and maintained at the same controlled atmosphere of 50% RH and  $t = 25^{\circ}\text{C}$ ; decrease of weight due to gradual drying was followed.



### CO<sub>2</sub> Desorption

In different experiments, PU sheets having various thickness were introduced in stainless steel pressure tubes and submitted in every case for two days to different CO<sub>2</sub> pressures (between 0.5 and 6 MPa). During this time, the PU samples absorbed variable quantities of CO<sub>2</sub> depending on the CO<sub>2</sub> pressure to which they were subjected. The samples were withdrawn from the pressure tubes and the CO<sub>2</sub> desorption was followed by the weight decrease in time at atmosphere pressure, 25°C and 50% RH.

### Preparation of PU Films Containing MDA

10 g of linear PU prepared from PEA<sub>2000</sub>, DBDI, and DEG in a molar ratio 1:3:2 I=100 (i.e., without excess diisocyanate), adopting the same procedure as described before were dissolved at 60°C in 50 ml N-methyl-2-pyrrolidone (NMP). Then, 0.198 g ( $1 \times 10^{-3}$  mol) 4,4'-diaminodiphenylmethane (MDA) was dissolved in the solution. Thin films of PUs with MDA of about 0.5 mm thickness were obtained by evaporation from solution at 60°C. The traces of NMP were eliminated by immersion of these films in water for 24 hours and then dried at 60°C. The comparison of the changes in mechanical properties with time was made toward similar films obtained without the addition of MDA.

## RESULTS AND DISCUSSION

From the data mentioned in the Introduction, the first hypothesis regarding the modality of excess -NCO group consumption during the PU postcure process appears to be related to the reactions leading to the formation of a urea group (Equation 1-3).

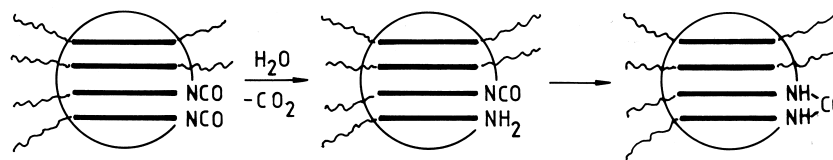
The development of reaction (1) in solid state leading to the appearance of amine group does not seem to present problems due to the possibility of small water molecule able to diffuse relatively easy into the solid polymer.

Regarding the further steps in the ureic groups formation according to Equations 2 and 3, although the reaction between -NCO and -NH<sub>2</sub> groups would be by all means the fastest one, the fact remains that in the solid state the probability of different macromolecule end groups colliding is low.

In the alternative possibility, consideration should also be given to the fact that within the polyurethanes matrix there occurs phase separations which segregate the hard segments in narrow areas. Taking into account that the free







**Figure 1.** Schematic representation of hard segment and chain end groups segregation.

isocyanate groups are always bonded to hard segments, these groups could be included in the hard block associates bringing the free isocyanate groups in a reciprocal proximity which would enhance the probability of the reaction (2) taking place.

Taking into account the complexity of these problems, we proposed first to find a kinetic equation which could represent the change of mechanical properties of PU with the time of maturation and to correlate it to the dynamics of other parallel processes related to these changes i.e., the decrease of free isocyanate group content, absorption of water from atmosphere and release of CO<sub>2</sub> resulted from reaction.

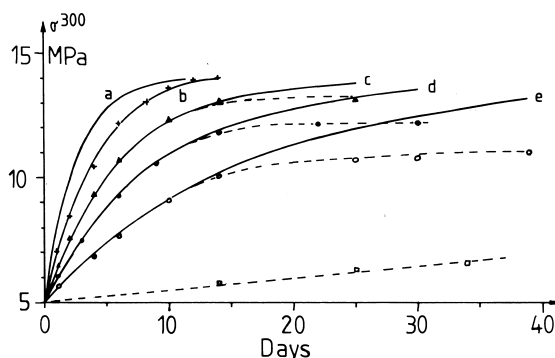
### Kinetics of Maturation Phenomenon

300% Tensile stress ( $\sigma^{300}$ ), as part of stress-strain data of uniaxial static simple tension testing, has proved to be a valuable criterion to follow the mechanical properties evolution within maturation phenomenon of 1,2,3,4,5, and 6 mm thick PU sheets: the 300% stretching range was chosen because in this region of the  $\sigma$ - $\epsilon$  curves the  $\sigma$ -time variation is high enough to ensure good monitoring and is, in our case, sufficiently far from the polymer rupture region. Figure 2 illustratively presents the results for the 1,2,4, and 6 mm thick PU sheets.

We avoided using the ultimate tensile strength value because, in this case, the reproducibility of the obtained data was lower. In order to express  $\sigma^{300}$  time-evolution, the maximum possible value reached by  $\sigma^{300}$  was used as a reference. In our case, this value was  $\sigma_{\infty}^{300} = 14.1$  MPa and was established as corresponding to a 1 mm thick PU, 60 days after synthesis. By using this reference, the simulated maturation phenomenon was found, expressed by  $\sigma_{t \text{ calc}}^{300}$  with the aid of the exponential equation:

$$\sigma_{t \text{ calc}}^{300} = \sigma_o^{300} + (\sigma_{\infty}^{300} - \sigma_o^{300}) (1 - e^{-k_m t}) \quad (7)$$





**Figure 2.** Evolution of 300% tensile stress ( $\sigma^{300}$ ) during postcure at 25° C and 50% relative humidity (RH) for different polyurethane sheet thickness  $\delta$ . Experimental (----): (+) - 1mm; ( $\Delta$ ) - 2mm; ( $\bullet$ ) - 4mm and ( $\circ$ ) - 6mm. Calculated (—): (a) - virtual  $\delta_{lim} \rightarrow 0$ ; (b)- 1mm; (c) - 2mm; (d) - 4mm; (e) - 6mm. ( $\blacktriangleright$ ) - Experimental  $\sigma^{300}$  for 2mm sheet in anhydrous atmosphere.

where the  $\sigma_0^{300} = \sigma^{300}$  value found experimentally immediately after synthesis (in our case 5.15 MPa);  $t$  = maturation time (days);  $k_m$  = maturation process rate constant, leads to a fairly good agreement with the real  $\sigma^{300}$  time - evolution.

The  $k_m$  values corresponding to different thick PU sheets have been experimentally determined as the respective straight line slopes derived from Equation 8:

$$\ln(\sigma_{\infty}^{300} - \sigma_{t \text{ exp}}^{300}) = -k_m t \quad (8)$$

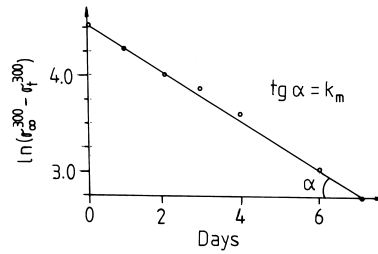
where  $\sigma_{t \text{ exp}}^{300} = \sigma^{300}$  values found experimentally at the time  $t$  (days). Figure 3 shows an exemplification for the 1 mm thick PU sheet case.

The corresponding  $k_m$  values to the six different sheet thickness are shown in Figure 4.

As can be observed from Figure 2, Equation 7 has represented the maturation evolution so successfully that better PU films are thinner and the rate of process is higher.

Since PU films are thicker, the maturation proceeds slower and it is most likely that the weight of the slower reaction leading to allophanate bridges Equation 4 should increase. The final  $\sigma^{300}$  values which could be reached, are all much lower since the PU films thickness is higher. The existence of such a secondary process is supported by the fact that even in anhydrous atmosphere there exists however, a low increase of  $\sigma^{300}$  with time (see Figure 2).



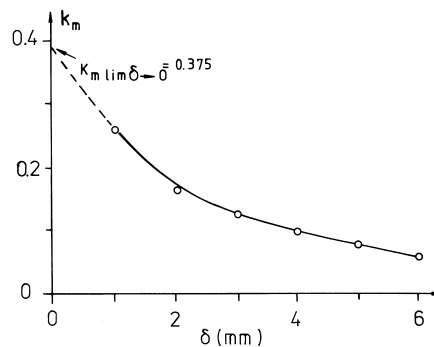


**Figure 3.** Graphic maturation rate constant  $k_m$  determination using  $\sigma^{300}$  variation.

With regards to computer simulation of maturation process, if in Equation 7 the unique value  $\sigma_{\infty}^{300} = 14.1$  MPa is replaced in every case by the particular  $\sigma^{300}$  maximum values reached with time for every sheet thickness, it is possible therefore, to obtain a much better agreement between the calculated  $\sigma_{t\text{ calc}}^{300}$  values and the experimentally found  $\sigma_{t\text{ exp}}^{300}$  values.

We also observed that by calculating the product  $\delta k_m$ , it was found that for PU films thicker than  $\delta = 2$  mm, a relatively constant value of about  $0.371 \pm 0.03$  is obtained. This relation can be useful to estimate  $k_m$  values for other thickness and therefore, to approximate the length of the maturation process in other cases.

Starting from the data in Figure 4, we have extrapolated the  $k_m$  values to the zero thickness ( $\delta \rightarrow 0$ ), characteristic to surface reaction, where neither water diffusion nor  $\text{CO}_2$  desorption rates are involved; the value of  $k_{m \text{ lim } \delta \rightarrow 0}$  was found to be 0.375. The virtual  $\sigma^{300}$  increase simulation, calculated with Equation 7) for an idealized ultra thin PU film by using  $k_m = 0.375$ , is revealed in Figure 2 by the solid line (a).



**Figure 4.** Rate constant  $k_m$  versus thickness  $\delta$  dependence.

### Kinetics of NCO Excess Consumption Process

The infrared method for the estimation of the decrease in NCO groups in the PU postcure processes has been used by many authors [25-27].

In the case of our polyurethanes, we have determined the decrease in NCO group absorbance of IR spectrum at  $2290\text{ cm}^{-1}$  on  $20\mu$  thin PU films cast from the reaction melt between two teflon sheets. The kinetic measurements starts immediately after demolding. The films were maintained under the same maturation conditions maturation used for the thicker sheets. These values have been converted into a NCO group equivalent concentrations per unit volume of polymer taking into account the measured absorbance and the polymer thickness. In every case, corrections for variation of thickness of PU films with time were made. The NCO group molar extinction coefficient was established on standard solutions of DBDI in benzene.

The kinetics of this process was tested by using an exponential equation similar to Equation 7, e.g. Equation 9:

$$[\text{NCO}]_t = [\text{NCO}]_0 e^{-k_{\text{NCO}} t} \quad (9)$$

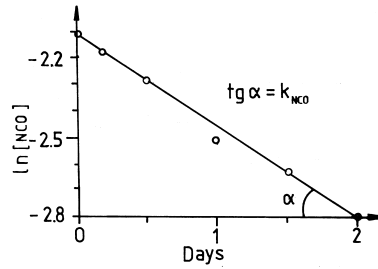
where:  $[\text{NCO}]_t$  = NCO group concentration at the time  $t$  (eq/l);  $[\text{NCO}]_0$  = the initial NCO groups excess concentration in polymer calculated from the ratio between reactants i.e., for ( $I = 110$ )  $0.227\text{ eq./l}$  polymer (before starting the postcure process);  $k_{\text{NCO}}$  = NCO consumption rate constant;  $t$  = time of exposure to atmosphere humidity (days).

Following the  $\ln[\text{NCO}]$  variation as a function of time, an almost linear dependence could be observed for the initial stages characteristic to the surface process when the excess NCO consumption does not exceed more than 10% from its initial value. This conclusion allows calculating the  $k_{\text{NCO}}$  value as shown in Figure 5.

As the reaction advances inside the depth of PU film with time, the process becomes dependent also on the water diffusion rate in polymer.

$K_{\text{NCO}}$  value corresponding to a first stage of up to 10% NCO groups conversion, was found to be 0.35. In order to compare this value to that of the  $k_{m \lim \delta \rightarrow 0}$  value, both of them being characteristic to the surface processes, we compared the time evolution degree of both processes expressed in % in relation to their respective final values. The virtual percentage of maturation was expressed by Equation 10:





**Figure 5.** Graphic determination of NCO groups disappearance rate constant  $k_{NCO}$ .

$$\text{Maturation \%} = [(\sigma_{t \text{ calc}}^{300} - \sigma_0) / (\sigma_{\infty} - \sigma_0)] 100 \quad (10)$$

By combining Equations 10 and 7, Equation 11 is obtained.

$$\text{Maturation \%} = (1 - e^{-k_m t}) 100 \quad (11)$$

when for the PU thickness  $\delta_{\text{lim}} \rightarrow 0$  it obtains  $k_{m \text{ lim } \delta \rightarrow 0} = 0.375$ .

The percentage evolution of virtual surface NCO groups consumption  $NCO_{\text{cons \%}}$  (representing the percent consumption from the initial  $[NCO]_0$  content) was calculated by using a similar equation:

$$NCO_{\text{cons \%}} = \{([NCO]_0 - [NCO]_{\text{calc}}) / [NCO]_0\} 100 \quad (12)$$

where  $[NCO]_0$  represents the initial NCO group excess concentration i.e., (for  $I = 110$ ), 0.227 eq/l. By combining Equations 12 and 9, is obtained Equation 13, similar to Equation 11:

$$NCO_{\text{cons \%}} = (1 - e^{-k_{NCO} t}) 100 \quad (13)$$

For the incipient NCO consumption process, we found  $k_{NCO} = 0.35$  corresponding to the initial up to 10% NCO groups conversion (Figure 4). We calculated the 300% tensile stress enhance (Maturation %) and the NCO group consumption for the for the virtual PU thickness  $\delta_{\text{lim}} \rightarrow 0$ . The results are presented in the following Table 1.

Both the data series obtained are practically equal showing that under these limit extrapolation conditions, both surface processes, representing the sur-

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TABLE 1. The Calculated Evolution in Time of 300% Tensile Stress Increase (Maturation %) and NCO Group Consumption ( $NCO_{cons\%}$ ) for a Virtual PU Thickness  $\delta_{lim} \rightarrow 0$

Time., [Days]	Maturation, [%]	$NCO_{cons}$ , [%]	Difference, $\Delta(a - b)$
0.5	<b>17.10</b>	<b>16.05</b>	<b>1.05</b>
1.	<b>31.28</b>	<b>29.53</b>	<b>1.75</b>
2.	<b>52.77</b>	<b>50.34</b>	<b>2.43</b>
4	<b>77.70</b>	<b>75.34</b>	<b>2.36</b>
8	<b>95.04</b>	<b>93.92</b>	<b>1.12</b>
12	<b>98.90</b>	<b>98.50</b>	<b>0.40</b>
16	<b>99.77</b>	<b>99.63</b>	<b>0.14</b>
32	<b>100.0</b>	<b>99.90</b>	<b>0.01</b>

face NCO group consumption and respectively the virtual surface  $\sigma^{300}$  increase, proceed identically and are practically completed after 12 days (98.5%). When extending these findings to the processes which perform in the depth of the polymeric material, it should be taken into account also the influence of some possible changes in the polymer morphology. The DSC measurement shows some peak changes when passing from a 20  $\mu$  thin PU film to a 1 mm thick PU sheet. However, the further PU thickness increase over the value of 1, up to 6 mm, does not produce more significant changes in the DSC peaks.

### Water Absorption Kinetics in Polymer

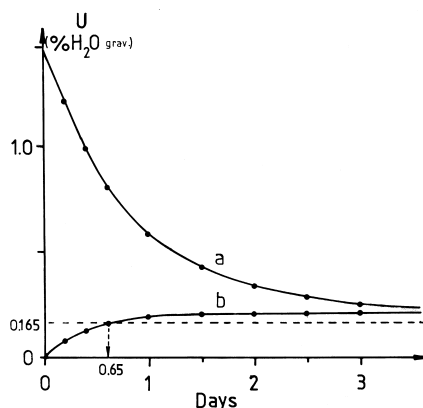
It has already been reported that polyurethanes absorb a moderate quantity of water which increases with the hard segment concentration [28].

In our study we have followed the increase in weight of already matured 2 mm thick PUs sheets previously anhydrided and then submitted to a controlled atmosphere with 50% RH at 25°C i.e., preserving the same conditions as for maturation.

Gravimetric increase i.e., variation of U with time for 2 mm thick PUs films is plotted as shown in Figure 6, curve (b):

As can be observed, water is absorbed very quickly. A saturation limit of U about 0.2% gravimetric is achieved in less than 2 days. This maximum degree of water saturation in PU sheets, corresponding to the atmospheric conditions of





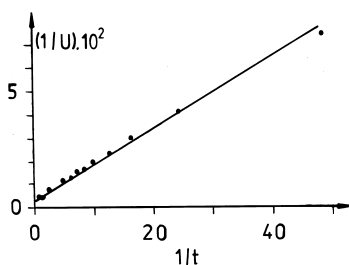
**Figure 6.** Water desorption (a) and absorption (b) in  $\delta = 2$  mm polyurethane sheet at 25°C and 50% RH; (- - - -) the stoicheometric quantity of water necessary to react with 10% NCO excess groups.

50% RH and 25°C, was also confirmed by following the kinetics of desorption on similar PUs sheets which were previously hydrated by immersion in water and then kept under the same atmospheric conditions (Figure 6, curve a). With respect to water absorption process kinetics, a linear dependence between  $1/U$  and  $1/t$  values were obtained (Figure 7):

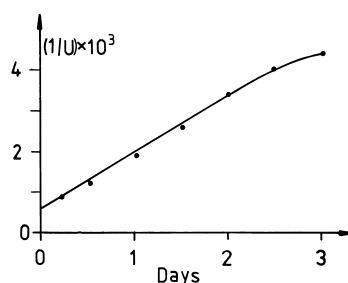
Therefore, the hydration process could be represented by Equation 14:

$$U = t / (at + b) \tag{14}$$

where  $U = \text{g water} / 100 \text{ g polymer}$ ;  $a, b = \text{constants}$ .



**Figure 7.**  $1/U$  versus  $1/t$  dependence during water absorption ( $U = \text{g water}/100\text{g PU}$   $t = \text{time days}$ ) for  $\delta = 2\text{mm}$  at 25°C and 50% RH atmosphere.



**Figure 8.**  $1/U$  versus time dependence during water desorption ( $U = \text{g water}/100 \text{ g PU}$ ) for  $\delta = 2\text{mm}$  in  $25^\circ\text{C}$  and  $50\% \text{RH}$  atmosphere.

The constants values constants which resulted from the above graph are  $a = 3.89 \cdot 10^{-3}$  and  $b = 1.56 \cdot 10^{-3}$ .

In the case of the water desorption process, the function which describes the decrease of  $U$  with time ( $t$ ) is different. In this case a linear dependence can be also obtained when plotting  $1/U$  against  $t$ , see Figure 8.

As a consequence, the following equation can be written (15):

$$U = c / (t + d) \tag{15}$$

where  $c, d =$  constants that can be determined from the plot:  $c = 0.795$  and  $d = 0,4818$ .

From the above mentioned data, it is concluded that for up to 2 mm thin PU sheets, the theoretical quantity of water theoretical necessary to consume the initial 10% NCO excess (i.e., 0.165 g water/100 g PU) is quickly absorbed in about 1 day, unlike the findings concerning the dynamics of maturation process for these sheets which requires at least 15 days. This fact leads us to conclude that the water diffusion rate inside the polymer does not control the rate of maturation process and thus, it is necessary to also realize that other factors such as the desorption of  $\text{CO}_2$  resulted from reactions (1) or (2).

### **CO<sub>2</sub> Desorption Kinetics**

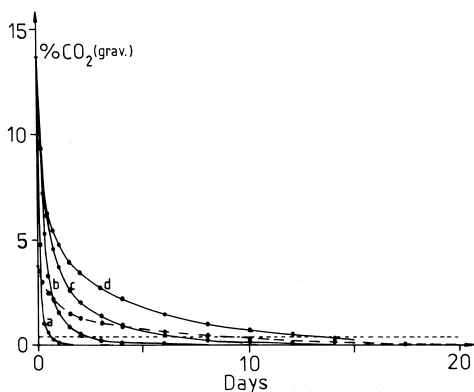
The capacity of polyurethanes to absorb appreciable quantities of  $\text{CO}_2$  was recently mentioned [29, 30]. Previous experiments conducted by us have lead to the conclusion that when our PUs samples are kept for 48 hours under liquid  $\text{CO}_2$  pressure at room temperature, they may absorb high quantities of  $\text{CO}_2$

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**Figure 9.** CO<sub>2</sub> desorption rate for different PU sheet thickness and different initial CO<sub>2</sub> content: (—): 13.7% grav. initial CO<sub>2</sub> content: (a) = 1 mm; (b) = 2 mm; (c) = 4 mm; (d) = 6 mm. (---) : 3.8% grav. initial CO<sub>2</sub> content in 2 mm polyurethane sheet thickness; (----) : Calculated total stoichiometric CO<sub>2</sub><sup>S</sup> content evolved from 10% NCO groups excess reaction with water = 0.406 g CO<sub>2</sub>/100g PU.

(up to 14% grav.). Unusual phenomena are observed in the case of the reversed phenomenon. The desorption curves are quite different depending on PUs sample thickness and apparently unexpected, on the initial absorbed quantity of CO<sub>2</sub> (Figure 9).

We studied the behavior of two 2 mm thickness PUs sheets with two different initial CO<sub>2</sub> concentrations  $C_1 = 13.7\%$  grav and  $C_2 = 3.8\%$  grav., respectively (Figure 9). After a period of time, the concentration of CO<sub>2</sub> in the first case became equal to the initial concentration of the second case  $C_2$ . Surprisingly, the further CO<sub>2</sub> desorption rate for the first sample was not equal to the desorption rate observed in the second case, even though at that time, the CO<sub>2</sub> content is equal in both cases. It was observed that the lower the initial concentration of CO<sub>2</sub>, the slower the rate of CO<sub>2</sub> desorption (Figure 9).

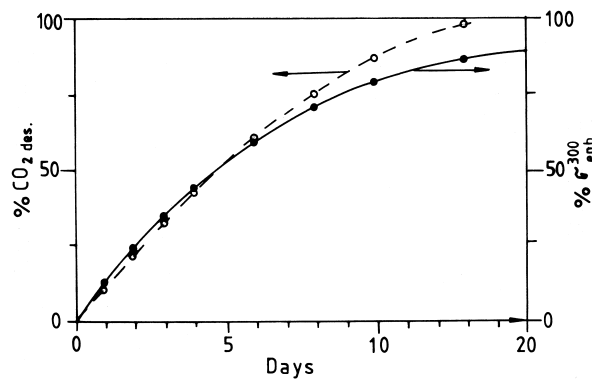
This behavior can probably be explained as a result of a process of supramolecular structure loosening as a consequence of a polymer plastification effect determined by CO<sub>2</sub>, which allows the quicker removal of CO<sub>2</sub>. The obvious consequence is that the kinetics equations established for every particular case (PUs sheet thickness or CO<sub>2</sub> concentration) depend on the initial CO<sub>2</sub> concentration. Taking into account our situation when the calculated quantity of CO<sub>2</sub> resulted from reaction (1) is very poor, ( $9.23 \times 10^{-3}$  moles of CO<sub>2</sub>/100 g PUs, i.e., 0.406 g CO<sub>2</sub>/100 g PUs), we were obliged to focus our attention especially upon

the cases of the desorptions regarding samples with a low initial concentration of CO<sub>2</sub>, i.e., up to 0.5 g CO<sub>2</sub>/100 g PUs.

As we proceeded, before we tried to find a correlation between the rate of CO<sub>2</sub> desorption process and the  $\sigma^{300}$  - time evolution achieved under the same conditions. The experiment was also performed with 2 mm thin PUs sheets. To enable these different dynamic processes to be compared, both of them were expressed in percentages of evolution towards the final state as we proceeded in the case of  $\sigma^{300}$  and [NCO] group time evolution comparison. As a consequence, for each situation we should have in view the initial and final values of  $\sigma^{300}$  and CO<sub>2</sub> content (see Figure 10).

In connection with this, some remarks could be made in accordance with Equations 1 or 2, CO<sub>2</sub> appears in PUs as time proceeds and consequently, its desorption depends both on the rate of the reactions and on the CO<sub>2</sub> diffusion rate.

As observed from the CO<sub>2</sub> desorption kinetics, the CO<sub>2</sub> diffusion from the polymer is very slow. The quantity of 0.406 g CO<sub>2</sub>/100 g PUs, equivalent to the entire quantity of CO<sub>2</sub> resulted from the reaction, needs under our working conditions, at least two weeks to diffuse totally from the 2 mm PUs sheets. In fact, the reaction with water proceeds as time passes and CO<sub>2</sub> is formed gradually so that the CO<sub>2</sub> desorption process becomes even slower and under the circumstances, its rate becomes comparable with the real rate of the maturation



**Figure 10.** Comparison between percent desorption of CO<sub>2</sub> (% CO<sub>2</sub> des) and parallel percent  $\sigma^{300}$  enhance (%  $\sigma^{300}$  enh) in time during the postcure process:  $\%CO_2\text{ des} = [(\%CO_2^S - \%CO_2^t)/\%CO_2^S]100$ , where  $\%CO_2^S$  = the total stoichiometric quantity of CO<sub>2</sub> resulted from reaction i.e.,: 0.406 g CO<sub>2</sub>/100 g PU.  $\%CO_2^t$  = the residual CO<sub>2</sub> content in PU at the time t (g CO<sub>2</sub>/100 g PU)  $\sigma^{300}_{\text{enh}} = [(\sigma_t^{300} - \sigma_o^{300})/(\sigma_\infty^{300} - \sigma_o^{300})]100$ , where  $\sigma_o^{300} = 5.15\text{MPa}$ ,  $\sigma_\infty^{300} = 14.1\text{MPa}$  and  $\sigma_t^{300} = \sigma^{300}$  at time t (days).



process. This dependence would seem at a first sight difficult to understand due to the fact that the overall reaction of the NCO groups leading to urea groups at room temperature is not an reversible process.

Even in some earlier works [5, 31], it was also assumed that the  $\text{CO}_2$  gas evolution is apparently complicated by the stability of a possible intermediary anhydride complex between isocyanate and the carbonic acid (Equation 2) and this hypothesis could also be emphasized for the solid state conditions of PU.

The discrepancy between the rate of isocyanate group disappearance and the rate of  $\text{CO}_2$  evolution was already mentioned even in the case when the reactions were performed in dioxane [31]. On the other hand, interactions between the evolved  $\text{CO}_2$  and  $\text{H}_2\text{O}$  could be possible, leading to carbonic acid and other hydrogen bonded mix associates.

The reactivity of water, bounded in such associates towards the NCO groups is expected to decrease so that the maturation process should be prolonged. As a consequence, the diminution in the rate of water-NCO group reaction allows us to promote, to some extent, the slow competitive reaction of the NCO groups with urethane, leading to allophanate linkages (Equation 4).

### **Possible Excess - NCO Groups Consumption Reactions Performed Under Water Assistance**

As presented in the Introduction, the postcure process is very intense as the index number  $I$  is higher and is strongly influenced by the presence of the atmospheric humidity.

The principal postcure process should be as in other similar cases [18], the appearance of the urea groups according to Equations 1-3, together with the slow reaction leading to the appearance of the allophanate group Equation 4.

Taking into account the molecule low mobility in the solid polymer matrix with amine end groups formed as intermediate groups, we should also consider the other possible reaction of amine groups such as that with the urethane or ester groups from the PU chain. The enhancement in the values of mechanical properties would be produced in this case by the substitution of some urethane or ester groups by transreactions leading to the more polar urea or amide groups, respectively.

Even though such reactions usually need usually high temperatures, it should be verified whether they would however, take place to some extent or not during the long period of the postcure process. The relative higher concentration of urethane and ester groups from the macromolecular chain in the solid polymer could encourage such a reaction.



In order to verify the possibility of the contribution of these reactions to the change in mechanical properties, some quantities of 4,4'-diamino—diphenyl methane were incorporated into the polymeric material, so as to obtain an equivalent quantity of -NH<sub>2</sub> groups equal to 0.02 g/100 g of a linear PUs (equal to the excess initial concentration of -NCO groups corresponding to 1 = 110).

The changes in mechanical properties during 60 days were followed similarly as in the case of the presented maturation study. The observed changes in mechanical properties were insignificant both in the case of the films containing MDA, as well as in the reference films, leading to the conclusion that the mentioned aminoaldehyde reactions rarely occur at room temperature.

### The Influence of Thickness on the Final Mechanical Properties of PU

The final mechanical properties determined on different totally post-cured sheets after more than two months revealed the interesting fact that even if these samples were made and stored simultaneously under the same conditions, the final mechanical properties are not totally equal (Table 2).

As observed, the values of  $\sigma^{300}$  tensile stress and tensile strength are somewhat higher in thinner films probably because in this case the more polar urea group formation is favored to the prejudice of allophanate groups appearance. With respect to 100% tensile stress we find that this value is similar for all the cases due to the fact that, as it was established from the IR dichroism and DSC studies [32, 33], up to this elongation value, the main energy in the macromolecule network is consumed for the loosening of the soft segments tangle. The influence of the hard segments - effect in which the hydrogen bonding is high,

TABLE 2. Influence of Thickness on the Mechanical Properties of 40 Days Matured Polyurethane Elastomers

Thickness, $\delta$ (mm)	Hardness (Sh <sup>0 A</sup> )	$\sigma^{100}$ (MPa)	$\sigma^{300}$ (MPa)	$\sigma$ (MPa)	EB (%)	R (%)
1	92	6.0	14.1	73.0	600	10
2	92	5.9	13.1	70.0	550	10
4	92	5.8	12.2	65.0	550	10
6	92	5.8	11.1	60.0	550	10

$\sigma^{100}$  = modulus at 100%;  $\sigma^{300}$  = modulus at 300%;  $\sigma$  = ultimate tensile strength; EB = elongation at break; R = residual elongation.



becomes decisive at elongations over about 300% when all the hard segments achieve a parallel orientation towards the stress direction [32, 33].

## CONCLUSION

Postcuring of PU sheets up to 6 mm thickness synthesized with a small -NCO groups excess, (up to  $I = 110$ ), proceeds at room temperature mainly with the assistance of atmosphere humidity during a period of about one month.

The rate of the process, as well as the final mechanical properties, depends on the thickness of PU sheets. The course of the postcure process depends on the competition between the urea and the allophanate group formation. The most enhanced mechanical properties are achieved for thinner films in which the urea groups formation is favored.

The enhancement in the mechanical properties with time is due mainly to the urea groups, and in a small measure, to the allophanate group formation. This consolidation is produced by the intensification of the internal hydrogen bonding produced by the newly formed urea.

Another aspect of possible postcure reactions, which however, is not studied enough as yet, is the role of the atmospheric oxygen on the superficial processes also leading to possible NCO groups consumption both in the thermal cure treatment at 110°C, as well as in the postcure processes. Although, it is known that the atmospheric oxygen produces in time the PUs degradation, it would be possible that oxygen may improve some consolidation of polymer by crosslinking in the first step of the process.

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