Macromol. Symp. **2004**, *216,* 37-46

Non-Isocyanate-Based Polyurethanes Derived upon the Reaction of Amines with Cyclocarbonate Resins

Constantinos D. Diakoumakos, Dimiter L. Kotzev*

New Technologies, Research & Technology Department, Adhesives & Tooling, HUNTSMAN Advanced Materials, Duxford, Cambridge CB2 4QA, United Kingdom
E-mail: konstantinos_diakoumakos@huntsman.com

Summary: Laprolate-803 (L-803) was used as the model cyclocarbonate resin for reactivity and kinetic studies of non-isocyanate-based solventless polyurethanes derived upon the reaction of amines with the 1,3-dioxolan-2-one (dioxolanone) rings of L-803. It was shown that the reaction could undergo either acid-, base- or metal-type catalysis yielding polyurethanes with 100% conversion of the dioxolanone rings at approximately half the time needed for their uncatalyzed counterparts. The activation energy of the reaction of L-803 with diethylene triamine in the presence or absence of a catalyst was determined via Arhenious studies. The reactivity of amines towards the aforementioned model resin was correlated to their chemical structure. A model non-isocyanate-based polyurethane displayed T_g of -1°C (DMA), fast gel time (390 min) at room temperature and good elongation (~70%).

Keywords: cyclocarbonate resins; mechanical properties; non-isocyanate based polyurethanes; polyurethanes; resins

Introduction

Nowadays, processes and materials that are involved or are suspected to be involved in negative environmental effects are under serious revision and alternative ecologically safer solutions are demanded. Cyclocarbonates are a relatively new class of compounds attracting research interest due to their potential use in the preparation of "green" (the highly toxic isocyanates and their predecessors (phosgene) are not involved in the process), porous-free and moisture insensitive polyurethanes. Cyclocarbonates can be synthesized from corresponding epoxy precursors. Network or linear non-isocyanate-based polyurethanes can be formed from the reaction of cyclocarbonate resins and amines[1-10]. No volatile or non-volatile by-products are produced via this reaction resulting to porous-free polyurethanes and an intramolecular hydrogen bond (see Scheme 2) seems to be responsible for lowering the susceptibility of the backbone to hydrolysis

DOI: 10.1002/masy.200451205

resulting in substantial increase of the chemical resistance. The present work focused on the kinetics, and the effect the amines' chemical structures can have on them.

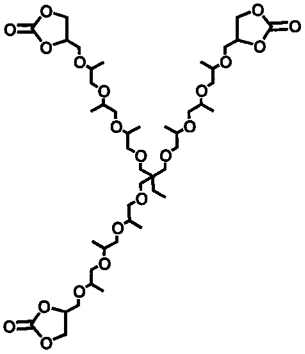
Experimental

Raw Materials

Laprolate-803 (Scheme 1) (L-803, liquid resin bearing 100% 1,3-dioxolan-2-one groups, MW=927) manufactured by *Macromer Ltd.*, Russia was provided by Chemonol Ltd (Israel), Q19262 (4,7,10-trioxa-1,13-tridecanediamine) and Jeffamine D-230 (JD-230) were provided by VANTICO A.G. (now HUNTSMAN Advanced Materials LLC.). Metatin catalysts 702®, 812® and S-26® were obtained by KMZ Chemicals. DABCO-33LV was provided by Air Products. Ethacure-100® (diethyltoluene diamine) and Ethacure–300® were provided by Albemarle. Diaminodiethyldiphenylmethane (DDDM) was provided by Kayahard AA. The rest of the chemicals used in this work (amines, imines, tetrabutyl ammonium bromide, glacial acetic acid, and methanesulfonic acid) were all purchased from Aldrich.

Analytical Methods and Techniques

Attenuated total reflectance fourier transform infrared (ATR FT-IR) spectra were recorded on a Nicolet 510 FT-IR spectrometer. Differential scanning calorimetry (DSC) was carried out on a DSC-2920 (TA Instruments), in air atmosphere at a heating rate of 10°C/min. Thermal mechanical analysis (TMA) was carried out on a TMA-40 (Mettler) at a heating rate of 10°C/min. Thermal gravimetric analysis was carried out on a Mettler TG50 thermo gravimetric analyser equipped with a Mettler M3 thermo balance. The samples were heated from 50 up to 1000°C (heating rate: 20°C/min) in air atmosphere (IDT: initial decomposition temperature where 2% of weight loss was recorded, PDT_{max}: maximum polymer decomposition temperature, Y_{char} @ 500°C and Y_{char} @ 600°C: char yields at 500 and 600°C). The AR-2000 dynamic analyzer (TA Instruments) equipped with torsional rectangular fittings (specimen: 55 mm in length, 10 mm in width and 2 mm in thickness) was used for dynamic mechanical analyses (DMA) (strain: ±1%, frequency 1Hz). Isothermal moisture uptake measurements were carried out at 22°C (acc.: ±2°C) and relative humidity 73% (acc.: ±2%) for 60 days. The mixture of cyclocarbonate resin (L-803) and amine (DETA) reacted stoichiometrically in an aluminium dish placed in a desiccator at ambient temperature for 1 day and subsequently they were put in an oven for 2 days at 60°C. Upon that, the dish containing the polyurethane, was placed in a temperature and humidity controlled chamber and weigh measurements were carried out periodically for 60 days. Gel time measurements at 25°C were carried out on a Michler apparatus equipped with a digital temperature controller (acc.: ±0.1°C). Measurements of reaction's exothermic profiles (temperature vs. time) at room temperature were carried out in a Dewar beaker fitted with a digital thermometer equipped with a K-type probe. Tensile and tear strength measurements at ambient temperature, were performed on an Instron 4467 according to ISO R527/2 and DIN 53356, respectively. Shore hardness D measurements were carried out on a model BS660 power assisted operating stand equipped with DuroProbe model BD-2 (Hampden Test Equipment Ltd., U.K.), according to DIN 53505.

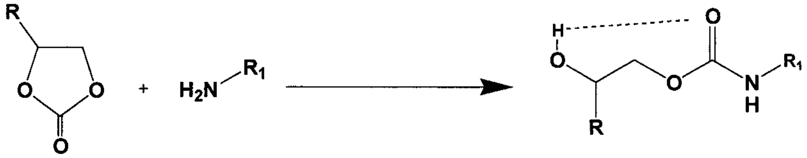


Scheme 1. Chemical structure of L-803.

Results and Discussion

Kinetic Studies and Catalysis

In the present investigation, Laprolate-803 (L-803) was used as a model cyclocarbonate resin for reactivity and kinetic studies of non-isocyanate based polyurethanes derived from the reaction of amines with resins bearing 1,3-dioxolan-2-one rings (cyclocarbonated resins) (Scheme 2).



Scheme 2. Reaction scheme between an amino group and a 1,3-dioxolan-2-one ring.

In the reaction of amines and cyclocarbonated resins there is no detailed study addressing in particular the chemical structure of the amine to its reactivity towards the dioxolanone ring. In addition, and although the reaction proceeds satisfactorily at room temperature, there are no in-depth analyses on the reaction's kinetics and potential catalysis for speeding up relatively slow systems as those where L-803 is the only cyclocarbonated resin involved in the reaction. Therefore, a variety of aliphatic and aromatic di- or poly-amines were reacted in bulk -solventless reactions- under the same conditions in the presence or absence of different catalytic systems (e.g. triethylamine, piperazine, tetrabutyl ammonium bromide, glacial acetic acid, methanesulfonic acid, DABCO-33LV and metatin type substances like the Metatin-702®, -812® and -S-26®) at 25 and 60°C. As a model polyurethane system for evaluating the activation energy (E_a) of the reaction between the dioxolanone ring and primary aliphatic amino groups via an Arhenious study based on FT-IR spectroscopy, L-803 stoichiometrically reacting with DETA (model system) was selected. L-803 resin shows a very characteristic absorption at 1795 cm^{-1} (C=O, stretching) whereas the urethane carbonyl absorbs (stretching vibration) at 1701 cm^{-1}. The decrease in the intensity of the carbonyl of the dioxolanone ring and at the same time the increase in the intensity of the absorption of the urethane carbonyl were attributed to the formation of polyurethane. The increase of the intensity of the absorption at 1701 cm^{-1} was recorded as a function of time for four different reaction temperatures (25, 60, 80, 100°C) in the presence and absence of triethylamine (catalyst). Figure 1, presents the Arrhenious plots for the reaction of L-803 and DETA in the absence and presence of triethylamine after 30 min. of reaction time. In the case where no catalyst was used the activation energy of the reaction was equal to 6.33 KJ/mol. The low E_a of the reaction permits the initiation of the addition-type polymerization to proceed very fast resulting to an abrupt increase of the viscosity of the mixture inhibiting the completion of the reaction of all the dioxolanone rings with amino groups at relatively low conversion. The reaction was completed after 8 days (no absorption at 1795 cm^{-1}) at ambient temperature, whilst 4 days were necessary for the reaction's completion at 60°C. When triethylamine (1% w/w on total reactants' weight) was used as a potential catalyst the activation energy of the reaction was found to be 5.23 KJ/mol. Although, the activation energy of the uncatalyzed reaction is low, the introduction of triethylamine is beneficiary as it contributes to a further decrease of the activation energy by approx. 17.5% and halved the reaction times necessary for 100% conversion at both 25 and 60°C. The relatively low activation energies determined for the reaction may safely lead us to the assumption that the reaction starts as soon as the two reactants come in contact.

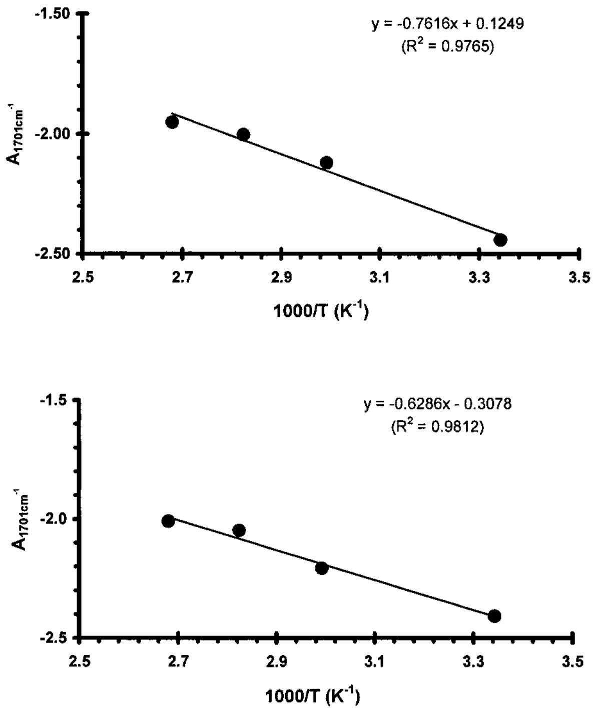


Figure 1. Arrhenious plots for the reaction of L-803 and DETA in the absence (top) and presence. (bottom) of Et_3N as catalyst.

This was also verified with *in-situ* FT-IR studies of a reaction mixture consisting of L-803 and DETA in the absence and presence of triethylamine (Figure 2) as a function of time. The curve shifts towards lower reaction times, when triethylamine was used as catalyst. The same pattern was recorded at 60°C. Different catalysts –as those mentioned here before- were also tested similarly and their effectiveness was assessed via FT-IR spectroscopy based on the decrease of the absorption at 1795 cm^{-1} over a certain time period.

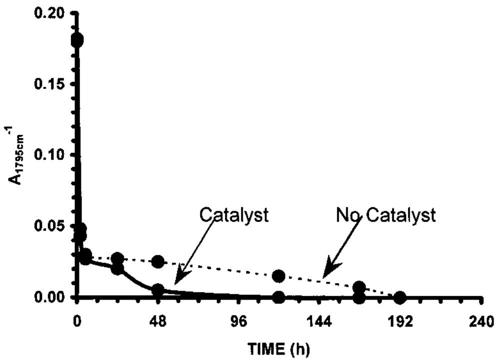
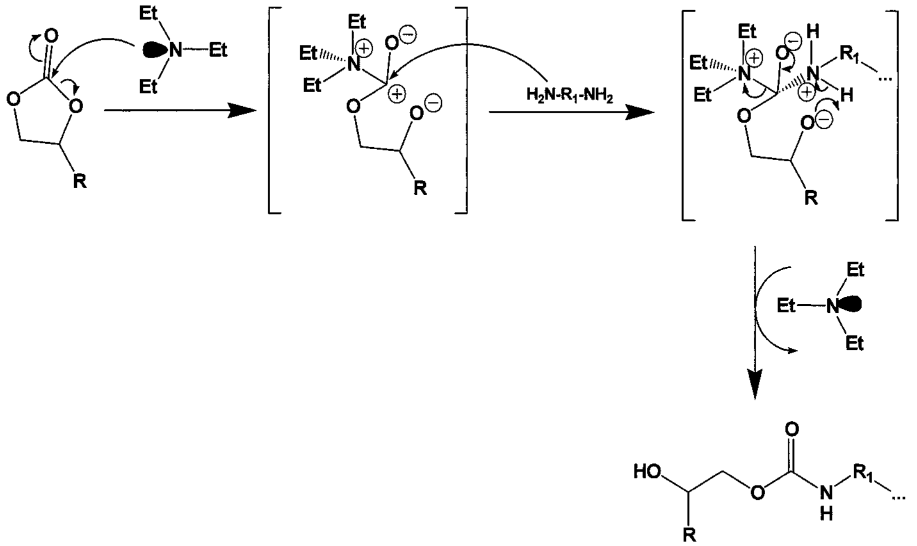


Figure 2. Intensity of the absorption peak at 1795 cm^{-1} as a function of time for the reaction of L-803 and DETA at ambient temperature, in the absence and in the presence of Et_3N as catalyst.

It seems that the reaction can undergo various types of catalysis (e.g. acid or base or metal type catalysis) as the array of the different catalysts tested herein gave evidence that they can catalyze it. From all the substances tested as potential catalysts triethylamine, piperazine, tetrabutyl ammonium bromide, glacial acetic acid, methanesulfonic acid and metatin type substances emerge as the most efficient catalysts providing polyurethanes with 100% conversion of the dioxolanone rings to urethane groups after 3-4 days at ambient temperature and 1-2 days at 60°C.



Scheme 3. Proposed catalytic mechanism in the case of triethylamine (base type catalysis).

Reactivity of Amines

A series of experiments were carried out at ambient temperature ($T_{ambient}$= 22-25°C), involving temperature measurements as a function of time for three different reaction masses (11.62, 17.43 and 22.86 g) of our model system (L-803/DETA). The trend of the exothermic profiles recorded in all the reaction mixtures were the same (Figure 3). The presence of triethylamine did not differentiate either the trend of the curve or the maximum temperature in any of the experiments. The maximum increase in temperature $DT=(T_{max}-T_{ambient})$, of these three reaction mixtures was 10, 15 and 19°C, respectively.

Linear curve fitting analysis (T_{max} *vs.* Reaction mass) provided data for calculating the highest temperature that a given mass of the aforementioned reactants can produce.

$$DT=(T_{max}-T_{ambient})= 0.774\cdot W_{Reactants}+ 1.167 \quad (1)$$

A reaction mass of ca. 170 gr. was the highest reaction mass [much higher than those used to produce equation (1)] that used to verify equation (1) and therefore this is the upper limit of a reaction mass that it was found to comply with the above equation.

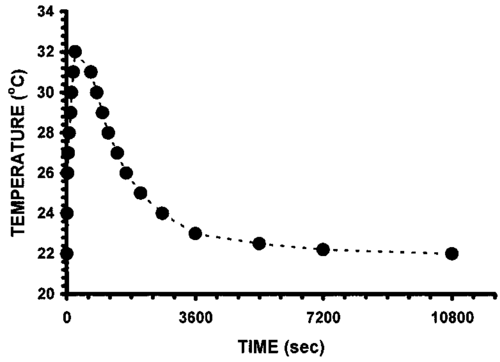
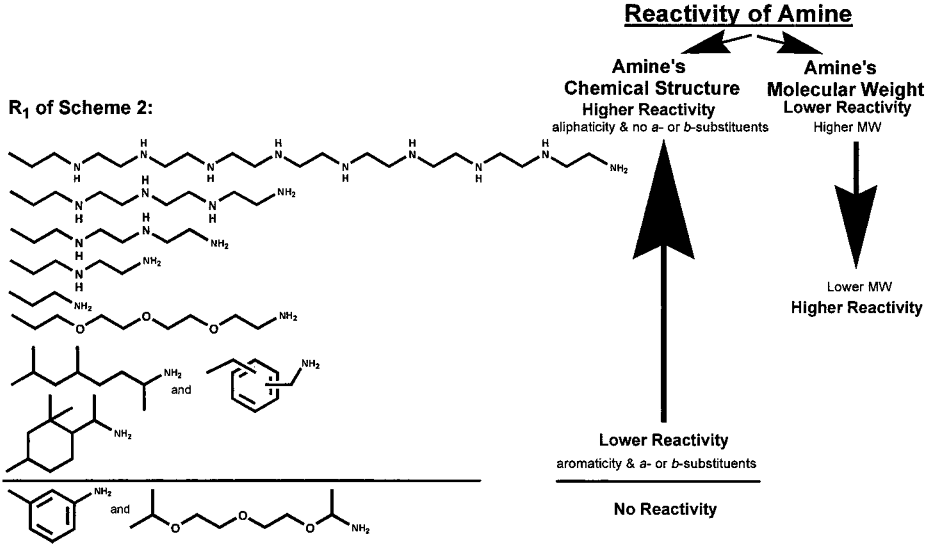


Figure 3. Exothermic profile (temperature vs. time) of a reaction mixture (11.62 g) L-803 and DETA at ambient temperature.

Similar methodology involving reaction masses of the same scale as those used in the case of L-803 and DETA) was also applied in the case of other amines (e.g. TEPA) resulting to equations similar to equation (1). In addition, linear curve fitting analysis taking into account only the mass of the amines (T_{max} *vs.* Amine's mass) can provide comparative measures (slope and T_{max}) related to their reactivity towards L-803. This methodology in combination to reactivity test experiments (L-803 reacted with various amines) assessed via FT-IR studies (recording the changes in the intensity of the peak at 1795 cm^{-1} *vs.* time) helped us to correlate an amine's chemical structure to its reactivity towards L-803 (cyclocarbonated resin). It became evident that the reactivity of the amines towards the L-803 is basically governed by two major parameters: a) its chemical structure and b) its molecular weight. Being more precise, the reactivity of the amine is directly associated to: a) the existence of bulky and/or strong electron withdrawing groups in *a*- or *b*-position in respect to the reactive amino group and b) the co-existence of imino and amino groups (polyamines) preferably positioned along an aliphatic carbon chain. Scheme 4 depicts in detail all our findings regarding the reactivity of various amines in respect to their chemical structures towards L-803 resin.



Scheme 4. Reactivity of various amines towards L-803 resin.

Certain typical properties of a model polyurethane (L-803/DETA) derived upon the reaction of L-803 and DETA (model polyurethane) for 4 days at ambient temperature in the presence of 1% w/w Et_3N are mentioned hereafter and in Figure 4: Gel time: 390 min, (DSC): T_g= -20°C, IDT= 272°C, PDT_{max}= 360°C, Y_{char} @ 500°C= 88%, Y_{char} @ 600°C= 11%, (TMA): T_g= -14°C, Coefficient of thermal expansion (CET)= 55.20×10^{-6}/K (below T_g) and 263.00×10^{-6}/K (above T_g), (DMA): T_g= -1°C, Isothermal moisture absorption: 25.90%, (ISO R527/2): Maximum Tensile strength: 0.48 MPa, Young's Modulus= 16.40 MPa, Maximum Load: 11.40 N, Elongation at break= 72.30%, (DIN 53356): Tear strength= 1.75 N/mm, Average Peel Load= 7.20 N, Maximum Load= 8.70 N, Shore hardness D= 11.00.

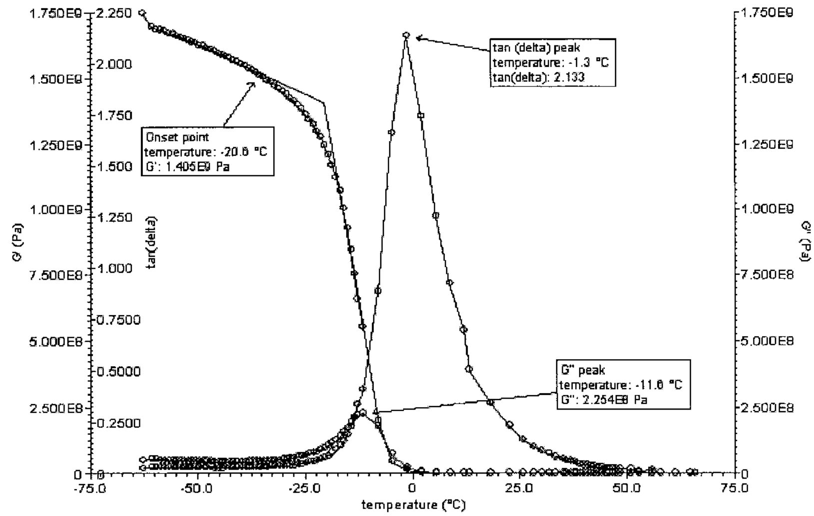


Figure 4. Dynamic mechanical analysis of the model polyurethane.

Conclusion

Cyclocarbonate resins offer a reliable alternative for the preparation of environmentally friendly non-isocyanate based, porous-free and moisture insensitive polyurethanes.

Acknowledgement

The authors wish to thank Professor Oleg Figovski and Dr. Leonid Shapovalov of Chemonol Ltd. (Israel), for providing them with Laprolate-803 (L-803) resin.

[1] A. E. Gurgiolo, W. L. Bressler, J. C. Smith, **1963**, US. Pat. No. 3,084,140.
[2] J. W. Whelan, R. J. Cotter, **1963**, US. Pat. No. 3,072,613
[3] V. V. Fedorova, O. L. Figovsky, I. Kreindlina, E. V. Grigor'ev, **1976**, SU 529197
[4] V. V. Micheev, N. V. Svetlakov, R. M. Garipov, V. A. Sysoev, R. R. Gil'manov, N. G. Gafiatullin, K. Kirova, *Lakokrasochnye Materialy I Ikh Primenenie* **1985**, 6, 27-30.
[5] L. Rappoport, R. D. Brown, **1992**, U.S. Pat. No. 5,175,231.
[6] W. C. Crawford, E. T. Marquis, H. P. Klein, **1994**, U.S. Pat. No. 5,340,889.
[7] O. L. Figovsky, **1999**, *WO 9965969*
[8] O. L. Figovsky, L. D. Shapovalov, N. Blank, **2000**, *EP Pat. No. 1020457*
[9] O. L. Figovsky, L. D. Shapovalov, *Surface Coatings Australia* **2000**, *37*, 14-17
[10] O. L. Figovsky, L. D. Shapovalov, *Macromolecular Symposia* **2002**, 187.