Polyurethanes from crystalline prepolymers

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Abstract

Cast, segmented urea–urethane polymers, obtained from crystalline urethane prepolymers in a reaction with water, were studied. Hitherto the reaction with water was conducted exclusively with liquid prepolymers. If the polycondensation reaction with water is carried out with the prepolymer solidified as a result of its crystallization, rather than the liquid prepolymer, in the cast products the formation of discontinuities in the polymer bulk as carbon-dioxide gaseous phase is eliminated or significantly suppressed. A similar method of cast polyurethane preparation is not known from available literature. Terathane 2000 oligomer was used for prepolymer preparation. The prepolymer was crystallized at various temperatures, and subsequently chain-extended with water. The crystalline polymers thus produced were examined prior to, and after samples were heated to transform the soft-segment crystalline phase into an amorphous state. The effect of prepolymer crystallization temperature and of the chain-extension conditions on the structure of the polymers obtained was investigated. Relations between certain structural features and mechanical properties of the polymers studied were learned. The polymer structure, hence soft-segment crystalline phase content and the degree of phase separation were found to be affected by the prepolymer crystallization point. An analogous effect of crystallization point on the Terathane 2000 oligomer and its prepolymer structures was observed. The effect of prepolymer crystallization point on the crystallizability of hard segments was also revealed. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Cast segmented urea–urethane polymers [1, 2] have their macromolecules built from soft and hard segments [1–3], schematically representable as:

$$[(\square \wedge\wedge\wedge)_x(\square \rule{1em}{0.4pt})_y]_n$$
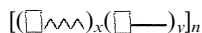
where $(\square \wedge\wedge\wedge)_x$ = soft segment, $x > 0$; $(\square \rule{1em}{0.4pt})_y$ = hard segment, $y > 0$; $\square$ = diisocyanate; $\wedge\wedge\wedge$ = an oligodiol or oligodiamine; $\rule{1em}{0.4pt}$ = a chain-extending agent; and n = the number of segment block in the macromolecule.

Soft segments are formed in a reaction of oligodiols or oligodiamines with compounds containing isocyanate groups. Precursors of these segments may be prepolymers whose molecules are terminated with reactive —NCO groups.

Hard segments of macromolecules are obviously formed in an polyaddition reaction of the prepolymer —NCO groups with the extenders, which typically are low-molecular-weight compounds containing hydroxyl and/or amino groups in their molecule [1–4]. These compounds are often toxic and moreover expensive. In addition, water is a well-known chain extender. However, water reacts with the prepolymer —NCO groups in a polycondensation reaction and is practically only used for polyurethane coatings [3–5]. The mechanism of the reaction of the prepolymer —NCO groups with water is beyond our research.

Prepolymers are usually taken for the reaction in point in their liquid form. Two types of reaction are generally used, polyaddition or polycondensation. The polycondensation reaction is used for making foamed plastics or thin-walled products, mostly coatings with large free areas [3]. Meanwhile thick-walled products from cast, segmented polyurethanes are commercially made exclusively in the polyaddition reaction [1, 2, 6–8].

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The polycondensation reaction of prepolymers with water has notable advantages, such as desirable properties of the urea groups present in the product, energy saving, environmental protection benefits, lowered toxicity, and simpler manufacturing process. During the polycondenstation process, however, next to the polymer, carbon dioxide is formed as a by-product [3], which readily accumulates as a gaseous phase in highly viscous first, and plastic next, reactant mixtures, resulting in defects in the polymer material of the end product. Removal of these defects is virtually unfeasible in view of a high and rapidly increasing viscosity of the reacting mixtures. Thus the polycondensation reaction with the use of liquid prepolymers alone to obtain thick-walled structural castings was entirely unsuitable.

The first information on an efficient use of the polycondensation rection of —NCO groups with water disclosed is the Polish patent [9]. It is based on the results of our previous studies [10]. They allowed us to unambiguously demonstrate that if the reaction with water is conducted with the prepolymer solidified by crystallization, rather than with the liquid prepolymer, the formation of discontinuities as carbon-dioxide gaseous phase in the polymer bulk produced can be eliminated or significantly reduced. The polymers thus obtained are not foamed.

This procedure for cast polymer manufacture is not known from the pertinent available literature. The effect of crystallization conditions and prepolymer chain extension using water as chain extender was examined. Relations between certain structural features and mechanical properties of the polymers obtained from crystalline prepolymers were learnt. The effect of crystallization conditions on the structure and mechanical properties of the polymers of interest were also determined.

Terathane 2000 oligomer was employed for the preparation of the prepolymer [11]. The prepolymer obtained from this oligomer was crystallized at various temperatures and then chain-extended using water under selected conditions. The crystalline prepolymer samples thus produced were studied prior to, and after heating to melt the crystalline phase to transform it into an amorphous state.

2. Experimental

2.1. Materials

Tetramethylene-ether oligodiol (PTMEG), a commercial product Terathane 2000 of an average molecular weight $M_n = 2055$ and hydroxyl number 54.6, a linear diol of the chemical structure $HO(CH_2CH_2\,CH_2\,CH_2O)_nH$, where n averages about 26, was supplied by Du Pont Nemours Co. [11]. 4,4'-Diphenylmethane di-

isocyanate (MDI), a commercial product Isonate M 125, was supplied by Dow Chemical Co. [12].

2.2. Sample preparation

The prepolymer samples were synthesized with mole ratio of MDI/Terathane 2000 equal to 2.05 (for technical reasons the ratio is 0.05 greater than the stoichiometric). All the reactions were carried out in a vacuum reaction vessel equipped with a mechanical stirrer. Terathane 2000 was dehydrated for 1 h at $110 \pm 3°C$ under a pressure of $2–5 \cdot 10^2$ Pa under vigorous stirring. On cooling to $90 \pm 5°C$ MDI was added into the oligomer. The reaction between the oligomer and the diisocyanate was carried on for 40 min at $100°C$ and a pressure of $2–5 \cdot 10^2$ Pa under continous and vigorous stirring and frequent disconnecting of the vacuum.

Subsequently, the prepolymer produced was cast into special moulds heated to ca. $100°C$. The moulds were then allowed to cool to room temperature and then kept for at least 2 days at a specified temperature at which the crystallization process proceeded. The process of chain-extension was performed at $19 \pm 1°C$ with water in crystalline samples previously removed from the moulds. The samples were put into the water. The reaction was performed first at the sample surface, next within the sample. The polymer layer was grown from the sample surface to its centre.

Prior to their crystallization, samples placed on test glasses of polarizing microscope were heated for 30–40 min at ca. $100°C$ to prevent nucleation from occurring in the oligomer and prepolymer.

Samples for the small-angle light scattering (SALS) study were obtained by crystallization of Terathane 2000 oligomer and its prepolymer at specified temperatures on the heating and freezing stage of the microscope.

Samples for the study of the behaviour of the polymer with temperature were in the shape of small cylinders, 14.5 mm in outside diameter, with the wall 2 ± 0.1 mm thick and 20 ± 2 mm high, having smooth and parallel front faces.

Brittle fractures of samples for a scanning-electron microscopic study (SEM) were obtained by cryogenically fracturing ca. 2 mm thick polymer samples (previously frozen in liquid nitrogen). The fracture surfaces were coated with carbon and copper films of a total thickness of 20 nm by sputtering.

Samples for density determinations and for testing mechanical properties were cast in multiple-cell duralumin moulds.

All samples denoted A were subjected to an amorsphization process 1 day prior to examination by heating them for 1.5 h at $50°C$.

2.3. Measurement method

The Terathane 2000 density versus crystallization temperature relation was studied by the hydrostatic weighing technique. The relative error of the method was $\delta\rho = \pm 0.05\%$.

The effect of crystallization temperature on the oligomer and prepolymer structures was studied using a polarizing microscope model MPI 5 of Polish make (PZO) [13] equipped with a Wetzlar heating and freezing stage, and connected to a video camera which allowed the crystallization process to be recorded using a video recorder and an IBM-type computer [14].

The effect of crystallization temperature on the size of the spherulites formed during crystallization process was investigated by the small-angle light scattering (SALS) technique [15]. The recording of the images formed on the matt glass was conducted with a computer-coupled video camera.

The behaviour of samples with rising temperature was examined using a MOM Budapest Paulik–Paulik–Erdey Q-1000 derivatograph equipped with a dilatometric attachment. Results of the measurements were recorded continuously by means of a derivatograph-coupled recorder. The recordings were in the form of curves corresponding to the following temperature functions: temperature changes (T), sample length variations (TD), derivative of the sample length variations (DTD), and derivative of the sample/reference temperature difference (DTA). An analysis of the derivatographic curves allowed the characteristic temperatures (*T*) to be determined, the heat of fusion of the soft-segment crystalline phase (ΔH_{m1}) and the hard-segment heat of crystallization (ΔH_{m2}) to be calculated [17, 18] and the thermal linear expansion coefficient (α) to be evaluated. The studies were conducted at the derivatograph parameters: the temperature range from room temperature to 500°C, heating rate of 2.5 deg/min, paper travel rate of 2 mm/min, DTA sensitivity of 1/1, and DTD sensitivity of 1/10. Arithmetic means of the quantities studied were adopted for the results from at least three samples. Absolute error in the determination of T was ± 2°C; relative error for $\delta\alpha = \pm 3\%$, and for $\delta(\Delta H_m) = \pm 2\%$.

Structure of the surface of cryogenically fractured polymer samples was studied with a scanning electron microscope (SEM) Tesla model BS-300 with the use of secondary-emission electrons [19]. The accelerating voltage was 24 kV, and the sample current was 200 pA. The photographs were taken at a 1000× and 3000× magnification.

Mechanical properties of the polymers were studied by standard testing procedures developed for rubbers [20]. The parameters measured were: tensile strength (R_m), Young's modulus (E), and abrasive wear (ΔV_s). Relative measurement errors were: $R_m = \pm 3\%$, $\delta E = \pm 3\%$, $\delta(\Delta V_s) = \pm 3\%$.

3. Results and discussion

3.1. Oligomer crystallization

Crystallization of Terathane 2000 oligomer was carried out at the following temperatures: −15°, 0°, 10°, 20°, and 26°C. The oligomer crystallinity was assessed on the basis of its density (ρ) knowing [21] that the density is proportional to the crystalline phase content. Results of the measurements are presented in Fig. 1. Below ca. 10°C the crystallization temperature was found not to affect oligomer density, the finding being indirect evidence that it does not affect the crystalline phase content. Not until this temperature is exceeded during crystallization does even a minor rise in temperature bring about a significant drop in density. It can therefore be inferred that at crystallization temperatures lower than ca. 10°C the contents of crystalline structures formed in this oligomer are alike.

Oligodiols are known [22, 23] to crystallize in the form of spherulites. Research done on crystallization of Terathane 2000 oligomer conducted by polarizing microscopy confirmed that it also crystallizes in the form of spherulites. The times of spherulites growth until the completion of the stage I of crystallization (i.e. until the adjacent spherulites come into contact with one another), were nearly identical for the samples crystallized at temperatures lower than 10°C (2 min for the crystallization temperature of −20°C and 2.2 min for 7°C) and over 40-fold shorter compared with the spherulites growth time at a temperature of 18°C (96 min). Based on the Maltese-cross patterns obtained in the polarized-light scattering experiments [15], the size of the spherulites obtained during crystallization at various temperatures could be determined. As shown in Fig. 2, the spherulites radius significantly increases beginning from the crystallization temperature of ca. 10°C, which correlates well with the results presented in Fig. 1. This is also confirmed by microscopic photographs of spherulites taken for the crystallization temperature of −20°C (Fig. 3) and 18°C (Fig. 4). Terathane 2000 crystallizes at the temperatures mentioned in the shape of radial spherulites visibly differing in size. Since Terathane 2000, which is a precursor of the prepolymer in point that contains —NCO groups, does not react with water, as distinguished from the prepolymer itself, the density versus crystallization temperature relation was studied just for the precursor, rather than the prepolymer. An apparently reasonable assumption was there-
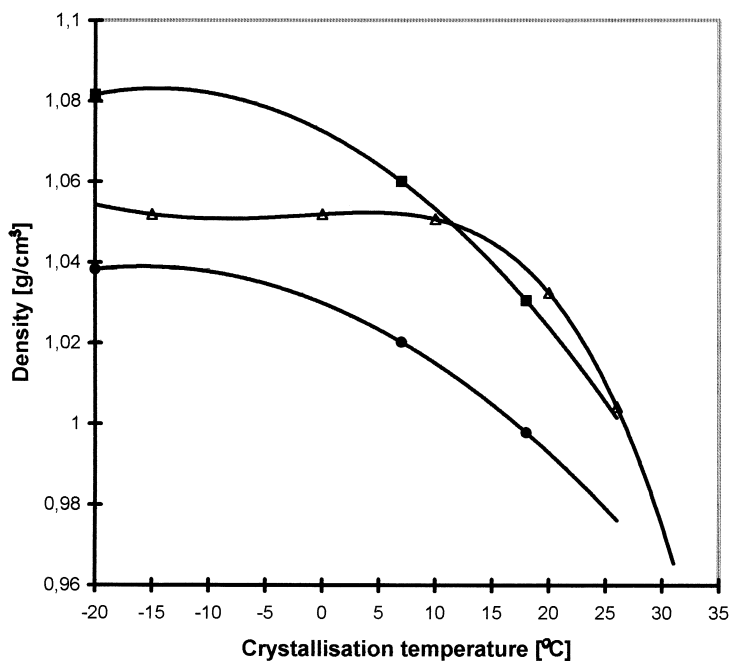
Fig. 1. The effect of crystallization temperature on the density of Terathane 2000 - (Δ), and polyurethaneurea: crystalline - (■), amorphous - (O), obtained from crystalline prepolymer made from Terathane 2000.

fore that there is a considerable analogy between Terathane 2000 and its corresponding prepolymer whose molecules are mostly the Terathane 2000 molecules as regards their crystallization process.

3.2. Prepolymer crystallization

Considering that the crystalline phase of the polymers under study is the same crystalline phase that
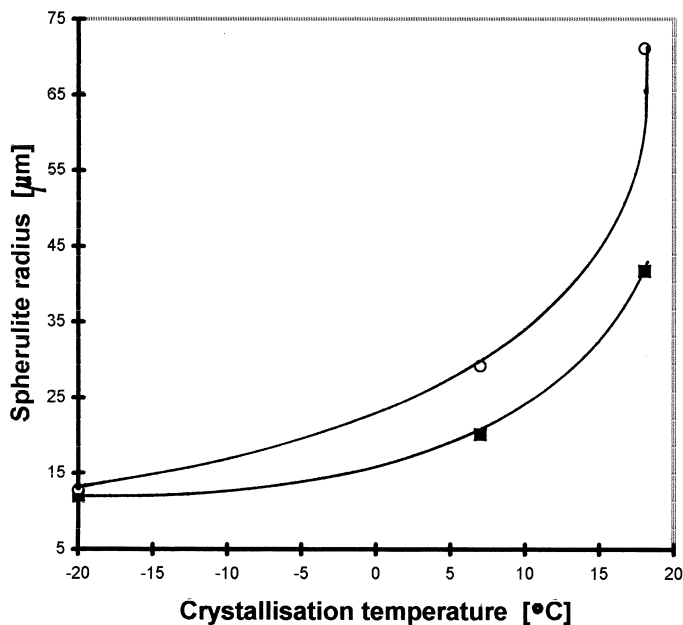

Fig. 2. The effect of crystallization temperature on the size of the spherulites obtained from Terathane 2000 (■) and from its prepolymer (O).

Fig. 3. The spherulitic structure of Terathane 2000 after crystallization at −20°C; 1 cm on the photograph corresponds to 19 mm in reality.

Fig. 4. The spherulitic structure of Terathane 2000 after crystallization at 18°C; 1 cm on the photograph corresponds to 19 mm in reality.

was formed during prepolymer crystallization, the effect of prepolymer crystallization conditions on its structure is identical to the effect on the polymer structure and properties.

Studies on crystallization of Terathane 2000 and its preoplymer, carried out using the polarizing microscope and low-angle light scattering, confirmed an analogy to exist between the crystallization process and the structural features of crystalline Terathane and its prepolymer.

The prepolymer under study also crystallizes in the form of spherulites. However, the time required for stage I to be concluded is greater compared with Terathane 2000. The difference amounts to a mere

1 min at the crystallization temperature of −20°C and attains 107 min at 7°C and equals almost 3 days for 18°C. Thus, the higher the crystallization temperature, the slower the rate with which the prepolymer crystallizes and the greater the difference between the crystallization rate for Terathane 2000 oligomer and its prepolymer. In consequence, there is a more distinct difference in size of spherulites for higher crystallization temperatures (Fig. 2). The higher the crystallization temperature, the slower the crystallization rate for both the oligomer and prepolymer, and the larger size of the spherulites formed. This has a significant effect on a suppressed formation of the crystalline phase in
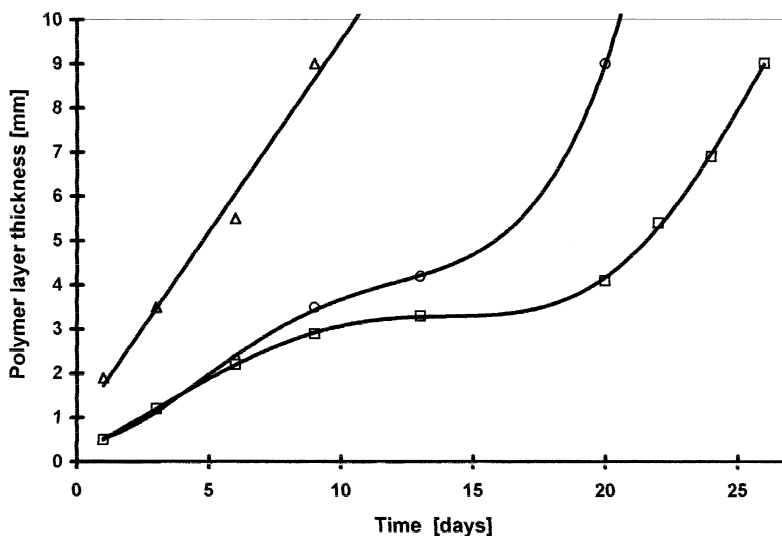

Fig. 5. The effect of prepolymer crystallization temperature on the chain extension process (−20°C (O), 7°C (□), 18°C - (Δ)).

the prepolymer, hence also in the polymer produced in a reaction with water. Furthermore, the difference in prepolymer structure as a result of various crystallization temperatures has a significant effect on the rate of the chain-extending process, determined by polymer layer growth, as shown in Fig. 5. Due to differences in prepolymer structure the rate of water absorption into samples is different. As a result the rate of the polymer layer growth is also different. For example the chain-extending process with water in the prepolymer crystallized at 18°C lasts much shorter, compared with the prepolymer samples crystallized at 7°C and −20°C. The picture of the chain-extending process in the prepolymer crystallized at 7°C and −20°C is fairly similar at the begining. A substantial shortening of time of the chain-extending process that occurs after 20 days in the prepolymer crystallized at −20°C is most likely the result of cracks that were visible with the naked eye. In this way an additional prepolymer surface appeared so that the chain-extending process was shortened. The cracks probably developed due to internal stresses generated in these samples as a result of a sudden prepolymer shrink during very rapid crystallization process at −20°C.

3.3. Polymer crystallinity

3.3.1. Soft Segments

The spherulites formed during prepolymer crystallization are preserved during the polymer chain-extending process. What is more, they represent the soft-segments crystalline phase in the polymer produced. Evidence of this is, among others, observation in polarized light of crystalline polymer samples obtained from crystalline prepolymers as a result of their chain-extending process using water (Fig. 6).

Observations of brittle fractures of polymer samples, both of crystalline ones and following their heat treat-
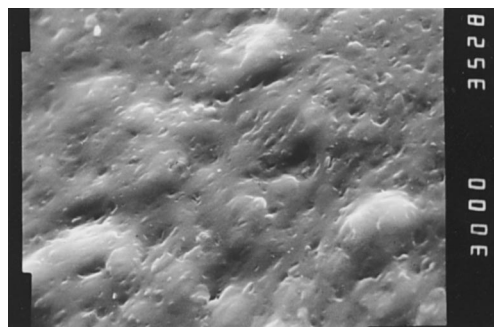

Fig. 7. Brittle fracture of the polymer obtained from the prepolymer crystallized at 7°C, and fractured following the sample heating to convert the soft-segment crystalline phase into an amorphous phase.

ment to transform the crystalline into the amorphous phase, are evidence that the spherical species which develop during the prepolymer crystallization are preserved even after the heat treatment of the polymer soft-segment crystalline phase, as seen in the brittle fractures shown in Figs. 7 and 8. Here again, the effect of crystallization temperature on the size of the spherical species produced has become manifest. The higher the crystallization temperature, the larger and the more regular are the spherical species, as can be seen in Figs. 7 and 8.

A salient feature of the polymers produced from crystalline prepolymers is their density. It stand to reason that density should strongly depend on the crystalline phase content, which depends on the crystallization temperature of the prepolymer. Results of the study demonstrated (Fig. 1) that the polymer density decreases with the rising temperature of prepolymer crystallization, which is equivalent to saying that most likely the crystalline phase content also decreases.

Fig. 6. The spherulitic structure of soft segments of the polymer obtained in a reaction of the prepolymer crystallized at 7°C (1 cm on the photograph corresponds to 5 mm in reality).
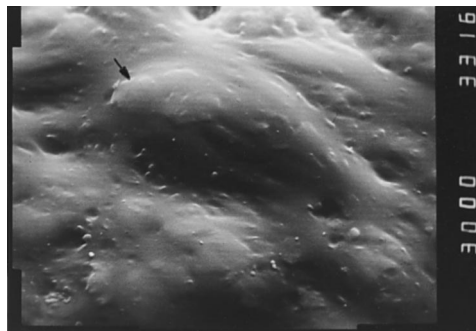

Fig. 8. Brittle fracture of the polymer obtained from the prepolymer crystallized at 18°C, and fractured following the sample heating to convert the soft-segment crystalline phase into an amorphous phase.

The polymer density versus prepolymer crystallization temperature varies, much as it does for the oligomer density versus oligomer crystallization temperature.

The prepolymer crystallization temperature also clearly affects the value of the heat of fusion of the polymer soft-segment crystalline phase (ΔH_{m1}) as illustrated in Fig. 9. As soon as the crystallization temperature of ca. 10°C is exceeded, the (ΔH_{m1}) value significantly decreases, which most likely signifies that this may be due to a decreasing content of the soft-segment crystalline phase in the polymer. These results lend validity to the results of the studies on oligomer and polymer density and on the size of the spherulites in the oligomer and prepolymer.

Based on the foregoing results it may also be expected that the polymer density is affected not only by the different soft-segments crystalline-phase content but also by the differences in polymer structure which consist for instance of a different degree of phase separation obtained as the result of crystallization occurring at various temperatures. A proof of it is the dependence of the polymer density on the polymer crystallization temperature upon heating to transform the soft segments into an amorphous state (Fig. 1). This relation is affected not by the crystalline phase content but so on the amorphous polymer structure. This presumption has been indirectly corroborated by results of the study on the thermal linear expansion coefficients of polymers, as shown from Table 1. The
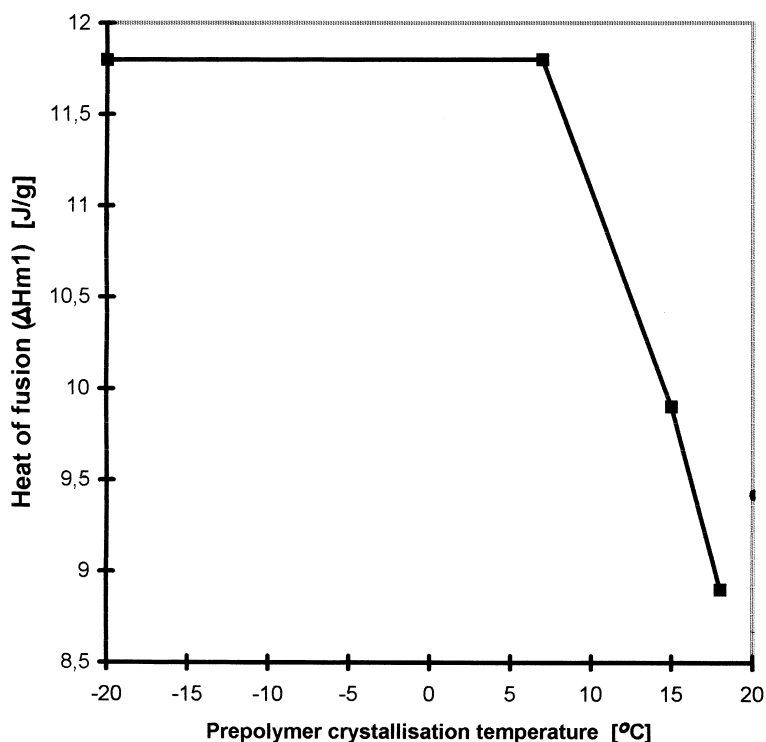

Fig. 9. The effect of prepolymer crystallization temperature on the heat of fusion of the soft-segment polymer crystalline phase.

α_3 coefficient assumes the least value for the lowest, as well as the highest crystallization temperatures, and the highest for a crystallization temperature of 7°C. It may therefore be believed that the greatest degree of phase separation can be expected in the polymer obtained as a result of prepolymer crystallization at 7°C. An indication of it is also the temperature of the onset of hard-segments crystallization (T_5), which is the lowest for the crystallization temperature of 7°C. The latter finding is an indirect proof of the statement that the greater —NCO group segregation among the prepolymer spherulites, the greater is the degree of phase separation which favours crystallization of hard segments. The lower is the degree of phase separation, the more homogeneously mixed are the soft segments with hard segments. Interactions between the soft and hard segments are stronger compared with the soft segments alone, which makes the soft-segment flow point increased. In other words, a lower crystallization temperature of prepolymer below 7°C or higher above 7°C is likely to impair segregation of the —NCO groups among spherulites and, in consequence, lowered degree of phase separation in polymer.

3.3.2. Hard Segments

Hard segments of the polymer under study are formed in a reaction of terminal isocyanate groups (—NCO) with water [3–5]. It was assumed that during crystallization of the prepolymer the terminal —NCO groups tend to become arranged on the spherulites surface and in the soft-segment interspherulitic regions. Thus the hard segments should be formed also on the surface of the soft-segment spherulites surface and/or in the interspherulitic regions of these spherulites. The fact that spherical shapes observed on the surface of brittle fractured samples remain also after heating to transform the crystalline polymer into an amorphous state allows us to suppose that they are surrounded by much more rigid regions of macromolecules capable of forming layers of material which may exhibit stiff properties. In Fig. 8 a kind of irregular-edge layer ("cap" marked with an arrow) can be seen even on the surface of the sphere.

As can be judged from the picture of the brittle fractures, the material starts breaking in the hard layers, i.e. in the layers made up of the hard segments arranged in the interspherulitic regions of the soft-segment and on their surfaces, in the layers of distinguished hardness.

The DTA investigation of polymers demonstrated that at prepolymer crystallization temperatures of 7°, 15° and 18°C, once the soft-segment flow point is exceeded, an exothermal peak appears on the DTA curve which is most likely related to hard segments crystallization. Values of the temperatures of the onset and termination of crystallization (T_5 and T_6) of hard

Table 1
Average values of the linear thermal expansion coefficient (α) and characteristic temperatures (T) and the heat of fusion of the soft-segment crystalline phase and the heat of crystallization of hard segments. α_1 = linear thermal expansion coefficient of the polymer in a viscoelastic state (from room temperature to T_1); α_2 = linear thermal expansion coefficient of the polymer during melting of the soft-segment crystalline phase (from T_1 to T_2); α_3 = linear thermal expansion coefficient of the polymer in a elastomeric state (from T_2 to T_4); T_1 = temperature of the start of melting of the soft-segment crystalline phase; T_2 = peak temperature of melting of the soft-segment crystalline phase; T_3 = temperature of the end of melting peak of the soft-segment crystalline phase; T_4 = temperature of the end of the elastomeric state and the start of soft segments flow; T_5 = temperature of the start of hard-segment crystallization; T_6 = peak temperature of hard-segment crystallization; T_7 = temperature of the end of the hard-segment crystallization peak; T_{go} and T_{gk} = temperatures of the start and the end of hard segments glass transition; ΔH_{m1} = heat of fusion of the soft-segment crystalline phase; ΔH_{m2} = heat of hard-segment crystallization; ΔH_{m1} and ΔH_{m2} values are relative.

T_{cryst} [°C]	$\alpha_1 10^{-4}$ [1/°C]	$\alpha_2 10^{-4}$ [1/°C]	$\alpha_3 10^{-4}$ [1/°C]	T_1 [°C]	T_2 [°C]	T_3 [°C]	T_4 [°C]	T_5 [°C]	T_6 [°C]	T_7 [°C]	T_{go} [°C]	T_{gk} [°C]	ΔH_{m1} [J/g]	ΔH_{m2} [J/g]
−20	1.6 ±0.2	7.6 ±0.6	2.2 ±0.1	34 ±2.5	51 ±1	85 ±5	177 ±5	Not occur	Not occur	Not occur	202 ±10	228 ±10	11.8 ±0.9	Not occur
7	1.5 ±0.1	9.4 ±1.4	2.4 ±0.1	38 ±1	49 ±1	82 ±1	142 ±2	183 ±2	203 ±1	223 ±1	Not occur	Not occur	11.8 ±0.4	0.9 ±0.6
15	1.8 ±0.2	9.8 ±0.8	2.3 ±0.1	40 ±1	49 ±1	81 ±1	158 ±3	192 ±2	213 ±1	229 ±3	Not occur	Not occur	9.9 ±1.1	0.7 ±0.1
18	1.8 ±0.6	8.9 ±0.2	2.2 ±0.1	39 ±1	50 ±1	84 ±1	142 ±10	190 ±2	228 ±1	Not occur	Not occur	Not occur	8.9 ±0.5	1.0 ±0.3

segments and the heat of crystallization of these segments (ΔH_{m2}) are reported in Table 1. For samples of the prepolymer crystallization temperature of $-20°C$ no hard segment crystallization was involved. On the DTA curve merely an inflexion point was observed, characteristic of the glass-transition point (Table 1). The temperatures of the start and the end of glass transition occur within the temperatures characteristic of glass transition of hard segments [3, 24].

The results of studies obtained provide a basis for speculation that at very low temperatures of prepolymer crystallization, e.g. $-20°C$, a very fast crystallization rate is the reason for a clearly worse segregation of the end —NCO groups on the outer spherulites surface. As a result, the hard segments formed in a reaction with water are much less separated from soft segments and they are smaller in number in the interspherulitic regions and on the outer surfaces of soft-segment spherulites. This seems to be the most likely reason why the dispersed hard segments do not form layers on the spherulite surface and are incapable of forming a crystallite.

To elucidate the foregoing suppositions, a study was made on brittle fractures of samples previously heated in the derivatograph dilatometric attachment to a temperature somewhat above the glass-transition point and crystallization temperature of hard segments, subsequently cooled to room temperature. From the photographs taken two of them are shown in Fig. 10 and 11.

The hard domains, from hard segments composed of the prepolymer crystallized at $-20°C$, are visible as white points or spheres in Fig. 10. In this case the degree of phase separation of polymer soft and hard segments is probably too minute, so that the hard segment layers cannot be formed. This is probably the cause of a lack of the ability of hard segments to crystallize.
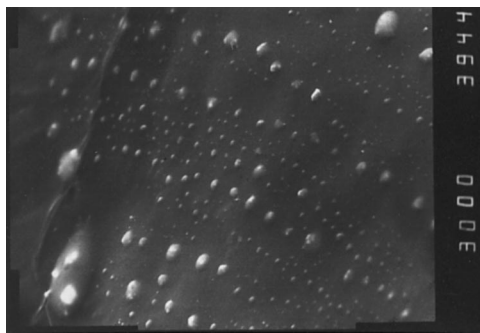

Fig. 10. Brittle fracture of the polymer obtained from the prepolymer crystallized at $-20°C$, and heated above the T_g of its hard segments and cooled to room temperature.
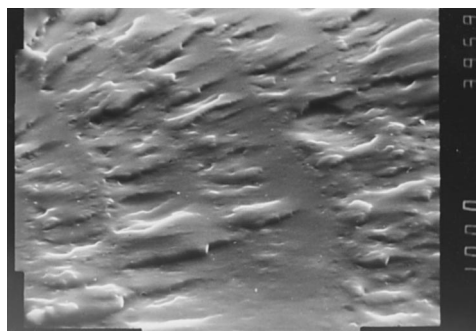

Fig. 11. Brittle fracture of the polymer obtained from the prepolymer crystallized at $7°C$, following hard segments crystallization.

In Fig. 11, which refers to the prepolymer crystallization temperature of $7°C$, the features in Fig. 10 are absent. Here the hard domains form some distinct layers on the surface of previous spherulites. These spherulites become flattened and elongated along the direction of stresses that build up in the cylindrical sample as a result of sample expansion.

For the other prepolymer crystallization temperatures the hard-domain layers are not as continuous as previously, yet they do occur. It will be noted that if the prepolymer samples are crystallized at 15 and $18°C$ hard segments also underwent crystallization.

3.4. Effect of structure on the selected mechanical properties

The effect of structure programmed by the selection of various prepolymer crystallization temperatures on mechanical properties was evaluated for such properties as: Young's modulus (E), tensile strength (R_m), and abrasive wear (Δv_s). Tests were performed on samples containing a soft-segment crystalline phase, as well as samples heated to melt the crystalline phase to transform it to an amorphous state.

The effect of structure on mechanical properties was assessed in two ways. Firstly, the effect of the low-melting soft-segment crystalline phase was evaluated; secondly, the effect of the degree of separation of the soft from the hard segments, which is related to the size of the spherulites formed during prepolymer crystallization, as well as to the way the reactive isocyanate —NCO groups are arranged.

For all the prepolymer crystallization temperatures studied, the polymer containing soft-segment crystalline phase features had high values of Young's modulus compared with the amorphous polymer, as shown in Fig. 12.

Tensile strength is identical for the crystalline and amorphous polymers, as the low-melting soft-segment crystalline phase melted during tensioning under the
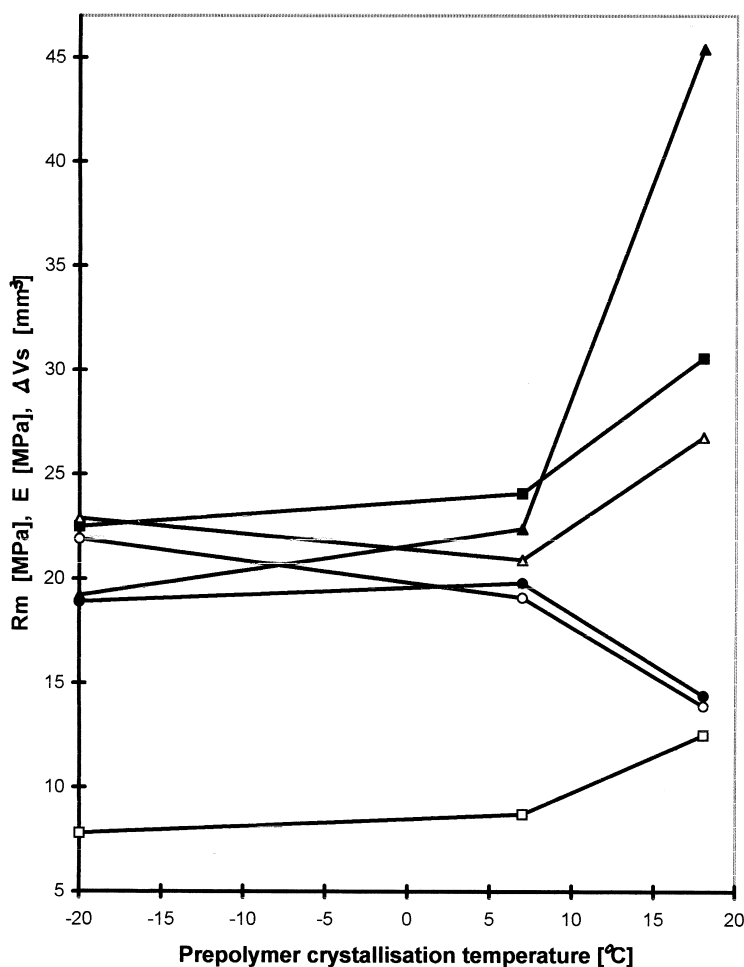
Fig. 12. Selected mechanical properties of the soft-segment crystalline polymer: R_m (●), E (■), and Δv_s (▲) and polymer with vitrified soft segments: R_m (O), E (□), and Δv_s (△) as a function of prepolymer crystallization temperature.

influence of tensile stresses. At −20°C prepolymer crystallization temperatures were observed at slightly lower values R_m for polymer containing soft-segment crystalline phase. It may be due to internal stresses created by very rapid crystallization.

A rise in prepolymer crystallization temperature above ca. 10°C brought about a significant increase in E and Δv_s values which correlate with the increase in a spherulite radius value in Fig. 2. On the other hand a drop in R_m value (Fig. 12) is correlated with the previously discussed variation in oligomer and polymer densities and heat of fusion of the soft-segment crystalline phase with rise in prepolymer crystallization temperature. This refers to the crystalline and amorphous polymer.

Transformation of the low-melting crystalline phase into an amorphous phase of the polymers studied lowers their abrasive wear, except polymer obtained from

prepolymer crystallized at −20°C. That crystalline polymer has lower abrasive wear values than the amorphous one. It is probably caused by expending part of the constant energy used in an abrasive wear method for melting the soft-segment crystalline phase. It is known that if the crystallization temperature is lower, the melting point of the crystalline phase is lower. Polymer soft-segment crystalline phase obtained from prepolymer crystallized at −20°C has the lowest melting point.

It is unexpected that the highest abrasive wear occurs for the polymer obtained from prepolymer crystallized at 18°C. The soft-segment crystalline phase content in that polymer is about 25% lower than in the others, but abrasive wear depends not only on soft-segment crystalline phase content. It also depends among others on the soft-segment spherulite size and form and their melting point as well as the degree of

phase separation. Above five times larger spherulites are obtained in a crystallization at 18°C than at −20°C (see Fig. 2). Probable spherulites obtained at 18°C do not melt quickly during abrasive wear measurement. So the abrasive wear is higher because the spherulites crystalline phase is not flexible.

The degree of phase separation in the polymer obtained from prepolymer crystallized in 18°C is probably low. The lower the degree of phase separation the less flexible are segmented polyurethanes, so that the abrasive wear is higher.

4. Summary

Results are reported for a study on the effect of crystallization temperature on the structure of oligomer Terathane 2000 and its urethane–isocyanate prepolymer as well as on the structure and mechanical properties of the polymers obtained from such prepolymer in their crystalline form.

From the studies with the help of a polarizing microscope a significant analogy was found between the crystallization process and the structural features of crystalline oligomers and their urethane prepolymers. It was observed that as a result of crystallization both Terathane 2000 and its prepolymer afford spherulitic structures, whereas the spherulite radius increases with increasing crystallization temperature for both oligomer and prepolymer. The crystalline phase content determined indirectly from the measurements of density and heat of fusion of the polymer soft-segment crystalline phase decreases as soon as the prepolymer crystallization temperature exceeds 10°C.

Oligomer density and polymer density versus crystallization temperature relations vary analogously. Thereby it is providing evidence for one of the assumption that a significant part of the polymer soft-segment crystallites was formed from the oligomer. Crystalline phase content of that oligomer corresponds to the bulk of the crystallites of the polymer used. The spherulitic structures produced during crystallization of prepolymer remain almost unchanged in the polymer.

On the surface of these spherulites and in the interspherulitic regions of prepolymer hard segments of polymer form and separate to afford hard domains. Hard domains may undergo crystallization in the polymers obtained from the prepolymers crystallized at moderate crystallization rates. Very high rates of the prepolymer crystallization render crystallization of polymer hard segments unfeasible. This for instance refers to prepolymer crystallization at −20°C. These are very likely the conditions that do not favour selection of —NCO groups in the prepolymer interspherulitic regions, which makes formation of separated layers of hard-segment material unfeasible.

The polymer structure controlled by the prepolymer crystallization temperature, including the soft-segment crystalline-phase content and the degree of phase separation, affects polymer mechanical properties. The prepolymer crystallization temperature is higher, as is the Young's modulus and abrasive wear, but the tensile strength is lower.

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