Russian Journal of Applied Chemistry, Vol. 74, No. 5, 2001, pp. 860–863. Translated from Zhurnal Prikladnoi Khimii, Vol. 74, No. 5, 2001, pp. 833–837.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis of Single-Component Urethane Sealants

A. D. Elchueva, N. V. Aristova, I. V. Bortnikov, and A. A. Tabachkov

Kazan State Technological University, Kazan, Tatarstan, Russia

Received October 5, 2000; in final form, February 2001

Abstract—Single-component urethane sealing formulations with aldimines as cross-linking agents were developed. The temperature dependence of the curing time of the sealants was examined. The influence of the –CH=N–/–NCO ratio and of fillers (industrial carbon and chalk) on their physicochemical properties was studied.

Polyurethane elastomers are widely used in various branches of industry. With progress of studies in the field of development of single-component formulations, their performance is improved and the application field is expanded. The procedures used in industry for curing of polyurethane sealants have significant drawbacks. All sealants of this type are two-component; they are not quite convenient in service and require performing certain manipulations directly before use. Their curing is effected with diamines and glycols. Curing of a single-component urethane sealant based on an isocyanate-containing prepolymer results in formation of defects (blisters, cavities) due to release of carbon dioxide on contact of isocyanate groups with atmospheric moisture. The goal of this work was to develop single-component urethane formulations with aldimines as cross-linking agents. Aldimines, when reacting with atmospheric moisture, release active curing agents which react with isocyanate groups without releasing CO_2, so that formation of defects in the cured sealant can be avoided.

Urethane elastomers show considerable promise for practice. Polyurethanes are prepared from compounds containing highly reactive isocyanate groups. Their transformations yield polymeric structures with diverse types of chemical bonds and allow preparation, within the same class of polyurethanes, of materials of widely varying properties.

An important factor determining the physicomechanical properties of polyurethanes, especially at elevated temperatures, is the nature of cross-links in the three-dimensional polymer network, depending on the curing agent used.

Studies of the effect of diamines and water as curing agents in single-component systems on the properties of composites based on various diisocyanates showed [1] that strong intermolecular interaction in polymers results in increased modulus of elasticity and tensile strength. The rigid segments in the chain (bulky aromatic diisocyanates and aromatic amines) also enhance the cohesion strength. Flexible groups (e.g., aliphatic amines) contribute to the elastic properties of the elastomers.

Thus, polyurethanes can be considered as block copolymers [2] with flexible polyether or polyester segments and rigid segments formed by urethane or urea fragments. Flexible segments increase the elasticity and relative elongation at break, whereas rigid segments with enhanced intermolecular interactions increase the hardness, tensile strength, melting point, and glass transition point.

The structure of the three-dimensional polyurethane network is determined by the synthesis conditions, in particular, by the preparation procedure (single-stage or two-stage). When the polymer is prepared by a two-stage procedure via a prepolymer, formation of a more regular network can be expected. Elastomers prepared via prepolymer [3] exhibit higher cohesion strength but lower values of the adhesion strength and modulus of elasticity and are less elastic.

In a two-stage procedure for production of polyurethanes the prepolymers are usually highly viscous, and special equipment is required for their mixing and feeding to reaction vessels without air access. The properties of the final product can largely depend on the accuracy of temperature control and on the storage time and stability of the prepolymer.

The advantage of the single-stage preparation of polyurethanes is the stability of the reaction mixture. With aromatic diamines, an additional advantage is

1070-4272/01/7405-0860$25.00 © 2001 MAIK "Nauka/Interperiodica"

the possibility of dosing these relatively high-melting crystalline substances using standard dosing units. The major problem, however, is to balance the reactivities of the backbone polyol and curing agent to attain the required degree of cross-linking. If both components are diols, it is not difficult, but with amine cross-linking agents it is necessary to add a catalyst accelerating the reaction of the hydroxide with the isocyanate. The advantages of the single-stage procedure are also simpler process and wider range of suitable raw materials.

Analysis of the present state of production of single-component polyurethane elastomers [4] reveals the following trends: improvement of the curing system and development of optimal formulations.

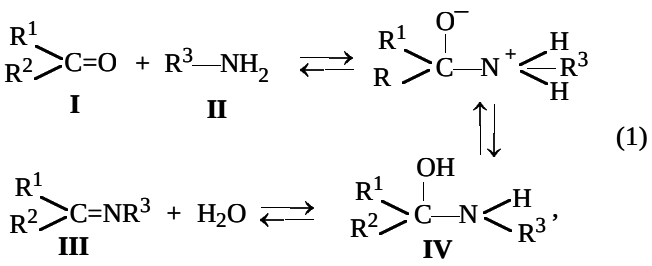
The goal of this study was preparation of single-component urethane formulations with azomethines (Schiff bases) as cross-linking agents. These systems, reacting with atmospheric moisture without release of carbon dioxide, facilitate reaction of the polymer backbone chain with isocyanate groups.

EXPERIMENTAL

In our study we used toluene 2,4-diisocyanate [TDI, TU (Technical Specifications) 6.03331–79), Laprol-5003 polyether (TU 6-05-1513–87), P-803 industrial carbon [GOST (State Standard) 7885–77), and chalk (GOST 842–52). The deformation and strength properties were determined according to GOST 21751–76, and the Shore hardness, according to GOST 263–75.

Aldimines were prepared by reaction of an aldehyde with a diimine in a 2 : 1 molar ratio (see table).

Schiff bases are prepared [5] by condensation of aldehydes and ketones **I** with various amino compounds **II**, resulting in elimination of water and formation of the corresponding azomethines **III**. The kinetic data suggest a two-stage mechanism [Eq. (1)] of formation (and reverse hydrolysis) of azomethines, involving formation of a tetrahedral intermediate, carbinolamine **IV**, which in some cases can be isolated (e.g., reaction of chloral with hydroxylamine) or detected in solution by ^{1}H NMR spectroscopy:



(1)

Initial substances for synthesis of aldimines

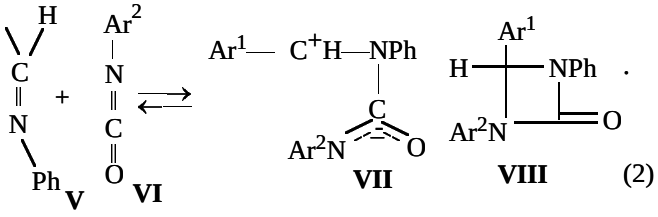
Diamine	Aldehyde	mp, °C
Ethylenediamine	Benzaldehyde	42–44
〃	Nitrobenzaldehyde	145
〃	Furfural	51–52
Hexamethylenediamine	Benzaldehyde	(l)
〃	Nitrobenzaldehyde	86–88
〃	Furfural	43
Phenylenediamine	Benzaldehyde	110–113
〃	Nitrobenzaldehyde	85–90
〃	Furfural	(l)
Diaminodiphenylmethane	Benzaldehyde	121
〃	Nitrobenzaldehyde	172
Diaminodiphenylmethane	Furfural	(l)

where R^1, R^2 = H, Alk, Ar; R^3 = Alk, Ar, OH, OR, NHR, Hal.

Aldehydes and dialkyl ketones smoothly condense with primary amines to give the corresponding Schiff bases, whereas the reactivity of aryl ketones is relatively low, and in this case longer reaction time and Brønsted acid catalysis are required.

Hydrolysis of azomethines to the initial amines and carbonyl compounds is an example of the nucleophilic attack at the C=N bond. This two-stage process involves addition of water molecules to the C=N bond to form a carbinolamine intermediate which subsequently decomposes into the amine and carbonyl compound. The rates of azomethine hydrolysis and formation are pH-dependent.

Cycloaddition of Schiff bases to simple isocyanates **VI** is preceded by reversible formation of zwitter-ionic intermediate **VII** [Eq. (2)] which in some cases can be isolated. The further transformations are determined by the stability of the zwitter-ionic intermediate (i.e., mainly by the steric and electronic effects of substituents in the azomethine molecule) and by the reaction conditions (kinetic or thermodynamic control). On the whole, when the benzylidene moiety of Schiff base **V** contains electron-donor *para* substituents and the reaction is performed at low temperatures (i.e., under conditions of kinetic control), direct ring closure in the zwitter-ion to give [2+2]-cycloadduct **VIII** is favored:



(2)

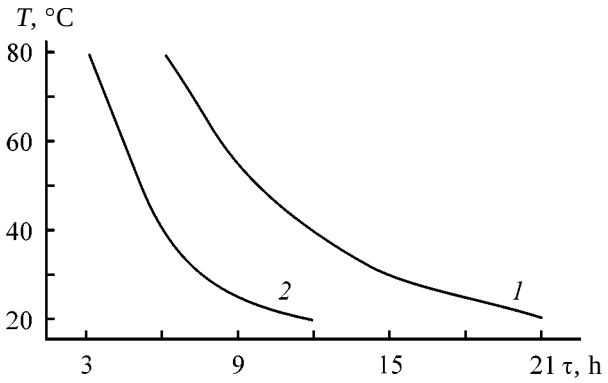


Fig. 1. Correlation between the temperature T and time τ of sealant curing with aldimines based on (*1*) benzaldehyde and (*2*) nitrobenzaldehyde and furfural.

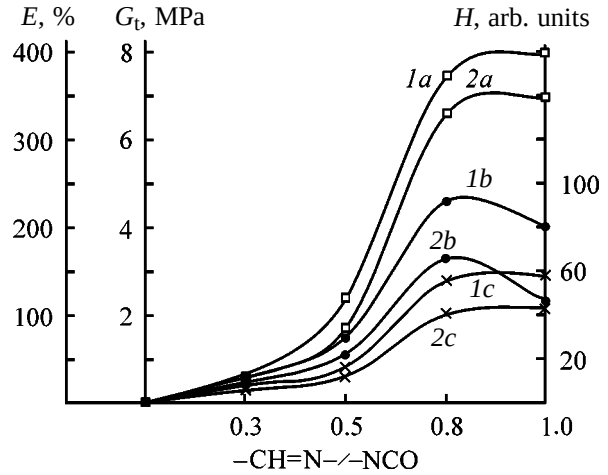


Fig. 2. Influence of the –CH=N–/–NCO ratio on the physicomechanical properties of sealants containing 60 wt parts of industrial carbon, cured with (*1a–1c*) aromatic and (*2a–2c*) aliphatic imines: (*1a*, *2a*) relative elongation E, (*1b*, *2b*) nominal tensile strength G_t, and (*1c*, *2c*) Shore hardness H; the same for Fig. 3.

It was suggested to use Schiff bases for preparing composites from polyisocyanate and aldimine for coatings stable in storage [6, 7]; also, Schiff bases can be used as latent hardeners for low-temperature curing of epoxy oligomers [8].

However, studies by Arbizov and his disciples [9] showed that Schiff bases react with isocyanates only at 100–160°C. Therefore, preparation of cold-curable sealants using the reactions of Schiff base formation is practically impossible. We have studied the hydrolysis of Schiff bases as sealant components.

It is known [10] that aldimines **IX** in the presence of atmospheric moisture are hydrolyzed to the initial compounds: aldehydes and diamines. This reaction, in particular, occurs on a support:

$$R'–CH=N–R''–N=CH–R' + H_2O \rightarrow 2R'–CHO + H_2N–R''–NH_2. \quad (3)$$

The released diamine reacts with the OCN groups of the prepolymer to give a three-dimensionally cross-linked polymer.

Curing of sealants depends on several factors, in particular, on the temperature and structure of substituent R' in the aldehyde molecule (Fig. 1). With increasing temperature, the time of sealant curing decreases. Curing is also accelerated when electron-withdrawing substituents such as NO_2, Br, I, or OCH_3 are introduced into the *para* position of benzaldehyde. These substituents decrease the electron density on the electrophilic center ($–C^+=N–$ carbon atom) and enhance its affinity for water, accelerating the hydrolysis. The amino groups released in the course of hydrolysis react with the isocyanate group even at 0–25°C; as a result, the sealant curing accelerates.

Figure 2 shows the dependences of the physicomechanical properties of sealants on the ratio of the reactive groups –NCO/–CH=N in the oligomeric system. As this ratio is increased, the strength and hardness of the urethane elastomers increase. This is due to the increased degree of cross-linking. The increase in the –NCO/–CH=N ratio to 0.5 has a weak effect on the properties. However, at further increase the strength of the sealants is enhanced, reaching a maximum at the –NCO/–CH=N ratio equal to 0.8–0.85. At the –NCO/–CH=N ratio higher than unity the physicomechanical parameters start to decrease.

The deformation and strength characteristics of sealants are influenced by the structure of the amine moiety in aldimines. For example, the selanats cured with aromatic imines considerably surpass in strength those cured with aliphatic analogs, owing to incorporation of aromatic ring into the polymer structure.

Unfilled sealants are used seldom because of their poor physicomechanical parameters and high cost. To improve the properties and reduce the cost, various fillers are added. In this work we used active (industrial carbon) and neutral (chalk) fillers. Figure 3b shows the dependences of the main physicomechanical parameters of the sealants on the content of industrial carbon and chalk. These data show that, irrespective of the imine type and component ratio, the parameter values as functions of the filler content pass through maxima. The nominal tensile strength and the relative elongation vary in parallel with varying filler content.

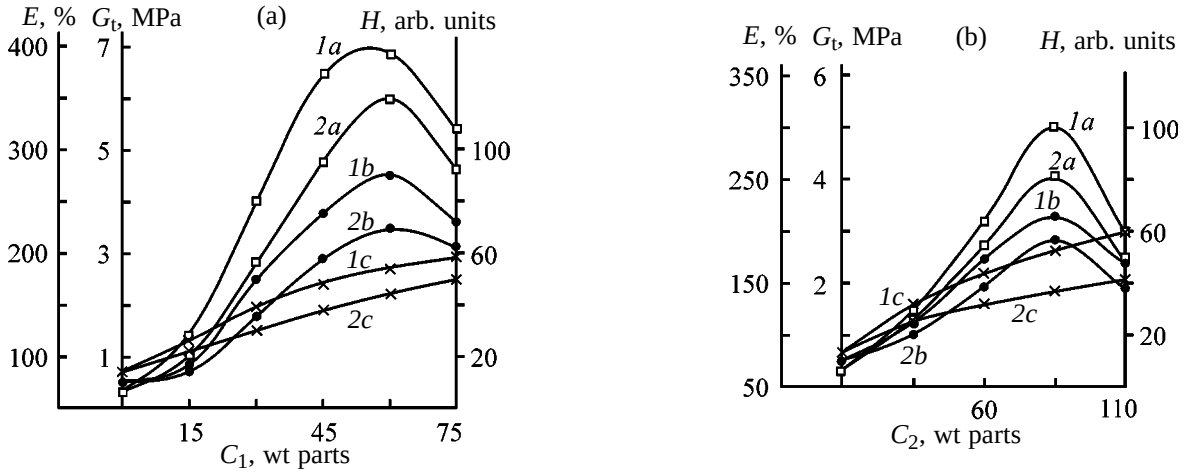


Fig. 3. Influence of the content of (a) P-803 industrial carbon C_1 and (b) chalk C_2 on the properties of sealants cured with (*1a–1c*) aromatic and (*2a–2c*) aliphatic imines.

The hardness of the composites increases monotonically. The physicomechanical properties of polyurethane sealants filled with industrial carbon are considerably better than those of the sealants filled with chalk. However, at high filling (more than 60 wt parts of industrial carbon or more than 90 wt parts of chalk per 100 wt parts of oligomer) the curing becomes complicated because of hindered diffusion. Highly active industrial carbon should be introduced in smaller amounts than chalk; the optimal dosage is 40 wt parts. This filler strongly affects the efficiency of macromolecule binding and formation of the physical network comprising from 60 to 80% of the total content of bonds in the polymer. Replacement of industrial carbon by neutral chalk at the same filler content (60 wt parts per 100 wt parts of prepolymer) decreases the physicomechanical properties of sealants.

CONCLUSIONS

(1) Single-component urethane sealants with aldimines as cross-linking agents were developed.

(2) The effect of temperature on the curing time of sealants was studied. With increasing temperature from 20 to 80°C, the curing time decreases from 12–15 to 2–4 h.

(3) The ratio of the –CH=N– and –NCO groups affects the physicomechanical properties of the sealants, with its optimal value being 0.8–0.85.

(4) The properties of sealants were studied in relation to the filler content. The strength parameters pass through maxima at the following filler content: industrial carbon 60 wt parts and chalk 90 wt parts.

REFERENCES

1. Lipatov, Yu.S., Kercha, Yu.Yu., and Sergeeva, L.M., *Struktura i svoistva poliuretanov* (Structure and Properties of Polyurethanes), Kiev: Naukova Dumka, 1970.
2. Saunders, J.H., *J. IRI*, 1968, vol. 2, pp. 21–22.
3. Rausch, R. and Sayigh, A., *Ing. Eng. Chem.*, 1965, vol. 57, pp. 92–94.
4. *Tematicheskii obzor TsNIITEneftekhim. Seriya: "Promyshlennost' sinteticheskogo kauchuka. Proizvodstvo uretanovykh elastomerov v SShA"* (Topical Review of the Central Research Inst. of Technical and Economical Studies in Petrochemical Industry, Ser.: Chemical Rubber Industry. Production of Urethane Elastomers in the United States), 1979.
5. *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*, Barton, D. and Ollis, W.D., Eds., vol. 2: *Nitrogen Compounds*, Oxford: Pergamon, 1979.
6. US Patent 5 569 706.
7. US Patent 5 523 376.
8. Blagonravova, A.A. and Nepomnyashchii, A.I., *Lakovye epoksidnye smoly* (Varnish Epoxy Resins), Moscow: Khimiya, 1970.
9. Zobova, N.N., Rusanov, G.N., and Arbuzov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, no. 2, pp. 2016–2020.
10. Sorokin, M.F., Onosova, L.A., and Tarasov, A.V., *Zh. Prikl. Khim.*, 1986, vol. 2, no. 8, pp. 17–21.