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CATALYTIC HOT-SETTING OF URETHANE OLIGOMERS

The polyamide compounds as a curing agent (MOCA) are used for curing to produce synthetic elastomers with programmable properties based on oligomers.

It is depermined that MBCA amount in the composition ranges from 11.8 to 19.1 parts by weight per 100 parts by weight polymer depending on the type of urethane rubber. The lifetime of urethane rubber and MOCA during casting at room temperature is about 6–12 minutes.

It is shown that a small amount of a carboxylic acid accelerates the curing reaction and reduces the lifetime of the polyurethane rubber in the molding process at room temperature. It is proposed to use adipic acid as the hardening catalyst, while the lifetime of urethane rubber and MOCA is about 6–12 minutes in a molding process at room temperature, and physical and mechanical properties are substantially unchanged. It allows us to obtain molded articles with given set of properties by free casting.

Key words: polyurethane, curing agent, catalyst, lifetime, adipic acid.

Introduction. Polyurethane is a modern construction material. Due to their peculiar performance characteristics, polyurethanes are widely used as substitutes for different grades of rubber, rubber, metal, and plastic in many branches of industry. Finished polyurethane can be both soft and very hard material. However, wear resistance of polyurethane does not change. Polyurethane products are resistant to atmospheric changes, impact resistant, durable in operation and they possess properties which ordinary rubber cannot have [1].

Polyurethane production is a complex and energy-intensive technological process that takes place by mixing and thermostatic control of two main components: isocyanate and polyol, as well as polyetheramines using fairly expensive equipment. The original stock is produced in Russia, the USA, Italy and Germany.

Practically all existing technological methods of polyurethane processing are used to obtain finished products: extrusion, pressing and casting into molds. The most widely used in industry are molded polyurethane elastomers. Cast molding technology of polyurethane parts allows to obtain products of almost any shape and size, which is impossible for the manufacture of rubber products [2].

Main part. Compounds, the characteristics of which are given in Table 1 were used in our research.

Polyurethane was prepared by mixing prepolymer and a curing agent in the molding machine "Gimatik" 1 in the following order:

– filling tanks for prepolymer and curing catalyst with prefabricated components and the washing tank with the washing composition. The component mass loaded was determined based on the production task;

– determination of the automatically maintained desired temperature for prepolymer (80 ± 5)°C and curing agent (120 ± 5)°C systems. The storage time of the heated prepolymer in the molding machine tank was not more than 24 hours at a temperature from 60 to 80°C;

– prepolymer vacuum degassing, vacuum degassing temperature being (80 ± 5)°C.

Mold filling was monitored visually, casting temperature being (120 ± 4)°C.

Casting time from 2 to 5 minutes depending on the mass of the part.

Curing was performed in the molds at a temperature (120 ± 5)°C for 10–15 min. To complete structurization the cured products were placed in an oven for 1 hour at a temperature (120 ± 5)°C.

The concentration of MOCA was calculated taking into account the specific content of the elastomer urethane groups.

The used amount of MOCA adjusts the degree of cross bonding or chain branches in the final vulcanizate. If the amount of MOCA used is less than the amount required, the excess of isocyanate in the system reacts with a substituted urea group to form a biuret structure, which is a chain branching because it is trifunctional. The higher the biuret groups concentration, the less is the number of hydrogen bonds between the chains. Biuret crosslinks result in increased elasticity modulus and reduced abrasion and wear resistance. With the increase of MOCA concentration towards the calculated amount (20 parts per 100 polymer parts), the final product becomes more linear in structure and maximum resistant to physical factors.

Table 2 shows the polyurethane compositions formulations for the manufacture of semi-finished articles of different weights.

Adiprene L 100 urethane rubber is a liquid urethane prepolymer, which can be cured to a firm rubbery substance by a reaction of isocyanate groups with polyamide compounds. When cured with MOCA curing agent, Adiprene L 100 vulcanizates have a hardness in the range of 88–92 Shore A units.

Table 1

Ingredient characteristics

Components	Material application	Controlled parameters
Adiprene L 100	Elastomer-prepolymer	1. % NCO – 3.95–4.30. 2. Physical form at 25°C – transparent viscous liquid. 3. Brookfield viscosity at 100°C, poise 4.0–6.0
Adiprene L 167	Elastomer-prepolymer	1. % NCO – 6.15–6.55. 2. Physical form at 25°C – transparent viscous liquid. 3. Brookfield viscosity at 100°C, poise – 1.5–2.5
Vibrathane B-600	Elastomer-prepolymer	1. % NCO – 3.95–4.35. 2. Physical form at 25°C – transparent viscous liquid. 3. Brookfield viscosity at 100°C, poise – 3.0–6.0
MOCA	Curing agent	1. Mass content of diazotizating substances, %, not less than 98. 2. Melting point, °C, not lower than 103.
Adipic acid	Catalyst	1. Mass content of adipic acid, %, not less than 99.7 2. Melting point, °C, not lower than 151.0

Table 2

Polyurethane compositions formulations

Rubber and ingredients	Parts by weight per 100 pts. wt rubber	Wt %
Composition No. 1		
Adiprene-L 100	100.0	88.89
MOCA	12.5	11.11
Composition No. 2		
Adiprene L 167	100.0	83.96
MOCA	19.1	16.04
Composition No. 3		
Vibrathane B-600	100.0	89.45
MOCA	11.8	10.55

Upon curing diamine substituted urea groups formed in the chain provide high interacting forces, functioning as “crosslinks”. Apparently, the forces that provide the internal reinforcement, principally are due to the hydrogen bonds between the molecular chains. These bonds are responsible for the diamines cured Adiprene L 100 strength.

MOCA curing agent 4,4'-methylene-bis-(2-chloroaniline) provides the required lifetime of the composition, its curing rate and vulcanizate properties. The lifetime, or the residence time of the Adiprene L 100 and MOCA mixture in the liquid state is about 12 minutes.

The amount of MOCA used adjusts the degree of cross-linking or chain branches in the final vulcanizate. The final product becomes more linear in structure and acquires maximum resistance to physical factors. To accelerate the reaction between MOCA and Adiprene L 100 the adipic acid was used as a catalyst. The polyurethane catalyst composition formulation is shown in Table 3.

Table 4 demonstrates physical and mechanical properties of polyurethane compositions. Adipic acid was used to accelerate the curing of Adiprene L 100, Adiprene L 167, Vibrathane B-600 and MOCA compounds at room temperature.

After one day curing the catalyzed compound is stronger than an uncatalyzed one after seven days curing. The use of adipic acid as a catalyst in an amount of 0.3 pts. wt per 100 pts. wt. Adiprene L 100 reduces the time before demolding from 20 to 7 minutes. In this case, the polyurethane composition lifetime is reduced from 12 to 4 minutes, and the article curing time at 100°C is reduced from 60 to 15 minutes. It is more convenient to dissolve adipic acid in the molten MOCA before adding it to a prepolymer. Although adipic acid melts at 152°C, it is soluble in MOCA at 121°C and is completely miscible with the amine. The mixture was stirred well to avoid undissolved material contained therein. Catalysis with adipic acid reduces the total curing time at any temperature and provides the possibility of obtaining an equivalent cure at a temperature lower than the temperatures employed in applying MOCA only.

When cured with MOCA curing agent Adiprene L 167 vulcanizates have a Shore A hardness equal to 95. An uncured liquid form of Adip-rene L 167 urethane rubber contains a small amount of free toluene diisocyanate (TDI). The lifetime or the residence time of the Adiprene L 167 and MOCA mixture in the liquid state is approximately 6 minutes, depending on the mixing temperature. The amount of MOCA used has little effect on the lifetime of the mixture.

Table 3

Polyurethane compositions formulations with a catalyst

Rubber and ingredients	Parts by weight per 100 pts. wt rubber	Wt %
Composition No. 1		
Adiprene L 100	100.0	88.65
MOCA	12.5	11.08
Adipic acid – catalyst	0,3	0.27
Composition No. 2		
Adiprene L 167	100.0	83.75
MOCA	19.1	16.00
Adipic acid – catalyst	0.3	0.25
Composition No. 3		
Vibrathane B-600	100.0	89.21
MOCA	11.8	10.53
Adipic acid – catalyst	0.3	0.27

Table 4

Physical and mechanical properties of polyurethane compositions

Nominal modulus at 100%, MPa, no less	Nominal tensile strength, MPa, no less	Nominal modulus at 300%, MPa, no less	Nominal elongation at break, %, no less	Shore A hardness, units Shore A	Tear resistance, H/mm, no less	Nominal compression set (100°C, 24 h, (25 ± 5)%), %, no more	Tensile set at break, %,
Composition No. 1without a catalyst							
7.8	34.2	15.6	480	90	20.4	38	12
Composition No. 1 with a catalyst							
8.2	30.8	17.1	370	91	21.2	51	10
Composition No. 2 without a catalyst							
13.1	40.3	20.1	470	95	22.9	33	14
Composition No. 2 with a catalyst							
12.7	41.4	22.4	420	94	23.1	45	10
Composition No. 3 without a catalyst							
7.8	37.8	16.2	430	89	22.8	35	9
Composition No. 3 with a catalyst							
9.1	40.2	16.8	400	91	24.1	42	10

The use of adipic acid as a catalyst in an amount of 0.3 pts. wt per. 100 pts. wt. Adiprene L 167 reduces the time before demolding from 11 to 5 minutes. In this case, the polyurethane composition lifetime is reduced from 6 to 2 minutes, and the product curing time at 100°C is reduced from 45 to 12 minutes. Physical and mechanical properties of the polymer composition No. 2 with the adipic acid as a catalyst are presented in Table 3.

The use of adipic acid as a catalyst in an amount of 0.3 pts. wt per 100 pts. wt. Vibrathane B-600 reduces the time before demolding from 25 to 10 minutes. In this case, the polyurethane composition lifetime is reduced from 10 to 5 minutes and the article curing time at 100°C is reduced from 60 to 15 minutes. Adipic acid is most conveniently dissolved in the molten MOCA before being added to a prepolymer. Catalysis with adipic acid reduces the total curing time required at any temperature and provides the possibility of obtaining an equivalent cure at a temperature lower than the temperatures employed in applying MOCA only.

Conclusion. It has been shown that the use of an adipic acid during the elastomeric compositions curing results in the acceleration of a curing reaction. The time before demolding is reduced by 4–6 minutes. The number of molds required for the manufacture of a given number of cast parts for a certain period of time without deterioration of the product performance properties is decreased 2 times.

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