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Oligomers Solidification Depending on the Nature, Molecular Mass, Type and Reactional Group Containing

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ABSTRACT

The article is devoted to regularity defining of curing oligomers, and prepolymers with hydroxyl and isocyanate groups and double bonds reactive oligomers. The features of the spatial structure of elastic polyurethane based oligomers and prepolymers with the definition of the physical and chemical bonds share, as well as the chain interval length between grid points were researched. The possibility of oligodiendiole curing in the presence of a methacrylate component on the mechanism of radical polymerization was experimentally confirmed. To achieve the objectives rheokinetic method of analysis (rotational viscometer), thermometric and iodometric methods, IR spectroscopy, differential scanning calorimetry were used.

Keywords: Oligodiendiole, Polyisocyanate, Chain branching agent, Polydieneurethane, Coatings.

INTRODUCTION

Currently urethane forming materials and compositions based on them are in demand for the production of sealants, glues, adhesives, waterproofing, sport, and other types of roof coverings. The main range of reactive oligomers of oligodiene nature for such compositions is based on hydroxyl-containing oligomers PDI-1K brand, Krasol LBH 3000 rubbers and PolyBD of European production. Oligomeric rubber PDI-1K is characterized by an insufficient functionality, a relatively high proportion of non-functional and multi-functional molecules, which leads to defects in the vulcanization of elastic polyurethane grid and adversely affects to the elastic-strength properties¹.

From the viewpoint of improving the structure of the elastic polyurethane spatial grid and improve the properties of the oligomeric rubber materials and compositions on their basis their use is reasonable not only for curing the terminal hydroxyl groups of the oligomer, but also double bonds in macromolecules chain. Thus isocyanate chain extending agents for urethane scheme and acrylate compounds for crosslinking macromolecular chains elongated at double bonds can be used. There is reason to anticipate a significant improvement in the properties of complex materials obtained as a result of the combined curing method²⁻³.

Objective of this research phase consists, firstly, in the study of the curing process according to the nature and molecular weight of oligomers; secondly, in the research of the influence of type and content of reactive groups, the type and amount of hardener, elongation and branching agents to process urethane curing mechanism; thirdly, in the research capabilities and features curing oligodiendioles by polymerization mechanism in the presence of methacrylate containing compounds^{4,5}.

These aspects are little-investigated and hardly covered in the scientific and technical information sources, which determines the scientific novelty of the work. Scientific research novelty is also concluded in the fact that oligodiendioles curing by combined method involving double bonds and terminal hydroxyl groups in the presence of an acrylate crosslinker component and a peroxide initiator in combination with an activator of its decay was proposed for the first time.

MATERIAL AND METHOD

For curing compositions based on low molecular weight rubbers PDI-1K and Krasol LBH-3000 polyisocyanate curing agent was used. It is a mixture consisting of 4,4'-methylene diphenylisocyanate in an amount of 81.802%, its isomer 1-isocyanate-2- (4-isocyanatebenzyl) benzene in an amount of 16.170% and a homolog 1-isocyanate-2,4-bis (4-isocyanatebenzyl) benzene in an amount of 2.028%. Mass fraction of isocyanate groups is in the range of 30-33%. Viscosity at 25°C is 134 MPa·s. Ethacure 300 (a mixture of isomers of 3,5-dimethylthio-2,6-toluenediamine and 3,5dimetildio-2,4-toluene diamine), and glycerol were hardeners for prepolymers. The standard methods of the research were used.

RESULTS AND DISCUSSION

As a first step of the research the features of oligomers hardening by the method of rotational viscometry were studied. The basic methodology has been previously worked with compositions based on hydroxyl reactive oligomer mark PDI-1K, characterized by a molecular weight of 3,000. The ratio of isocyanate groups to the sum of the hydroxyl (oligomer of glycerol) at a fixed dose of chain brunching agent and urethane catalyst was varied. Formulations are shown in table 1.

According to breaking of viscosity dependence from time in Fig. 1 it is possible to define the effect of temperature on the nature of the curing. In particular, increasing the curing temperature from 30°C to 50°C leads to an increase in the main phase reaction of urethane in three times (in this case, the ratio of NCO / Σ OH = 1.25).

In table 2 numerical values of the constants curing rate are given.

Also the dependence of activation energy from ratio of reactive groups (table 3) and the dependence of the gelation time of the curing temperature and the ratio of reactive groups (table 4) were defined.

Thus, as a result of research for identifying the characteristics of the curing compositions based on reactive PDI-1K oligomer, it was found that an increase in the content of the polyisocyanate in

Table 1: Formulations of compositions based on reactive oligomer PDI-1K

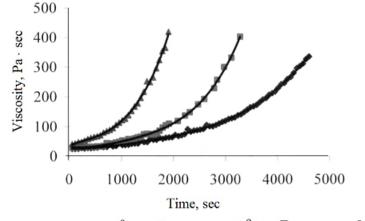
Ratio NCO / Σ OH), mole / mole	0,75	0,9	1,0	1,25	1,5	1,75	2,0
Ingredients of compositions	Ingredients' content, mass.h.						
PDI-1K	100	100	100	100	100	100	100
Polyisocyanate	12,1	14,6	16,2	20,3	24,3	28,4	32,4
Glycerol	2	2	2	2	2	2	2
Tin dibutildilaurinate	0,02	0,02	0,02	0,02	0,02	0,02	0,02

studied temperature range is an increase in the values of the rate constants increase viscosity with a slight decrease in the activation energy of viscous flow.

With the increase of proportion of NCO / Σ OH, in range of 1.25 - 2.0, gelling time decreases. Considering that in the cured elastic polyurethanes besides chemical transverse bonds it is possible to create intermolecular bonds, it is important to properly choose a solvent for detection of special polyurethane net with the Klaff-Gleding method. Toluene is the solvent which has the most optimal thermodynamic relation to investigated

polyurethanes. It was discovered that material sveling in toluene is reversible. Spectral investigation showed no relation between solvent and reactive centers of polyurethane.

Investigation of structural particularities as a result of interreaction of isocyanate and hydroxyl groups on the example of Krasol LBH based cured compositions made it possible to determine that the increase percentage of curing component (polyisocyanate) in composition will bring to growth of general, physical and chemical bonds. (figure 3.10). This fact can be explained by developing of more crosslinked spatial structure due to increase of tough urethane blocks.



Temperature 30°C ■ Temperature 40°C ▲ Temperature 50°C

Fig. 1: Rheokinetic changes depending on the viscosity of compositions based on PDI-1K cure time at different temperatures

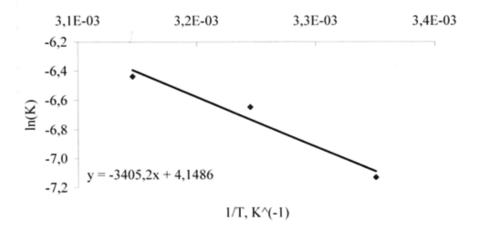


Fig. 2: The logarithm of rate constant with temperature curing dependence

Table 2: Curing rate constant values depending on the temperature for compositions on the basis of PDI-1K at a ratio NCO / Σ OH = 1.25

Temp., K	Constant curing rate, (K _h) c ⁻¹	1/T, K ⁻¹	In(K _h)
303	0,00080	3,30Å-03	-7,1309
313	0,00130	3,19Å-03	-6,6454
323	0,00160	3,10Å-03	-6,4378

Table 3: Dependence of activation energy from ratio of reactive groups

Ratio NCO / Σ OH, (mole / mole)	Activation energy, (kJ / mole)
1,25	28,3
1,5	27,6
2,0	26,9

It is noticed that curves which depict dependence of $M_{\rm c}$ for NCO / ΣOH have decreasing tendency. It is important that with the increase of molecular mass of oligomers $M_{\rm c}$ also increases (figure 3.11). It tells about less crosslink density.

CONCLUSION

There was an investigation of structural particularities of elastic polyurethanes, which are formed by curing of oligomer Krasol LBH based compositions, as a result of interreaction of isocyanate and hydroxyl groups. It was observed that increase of curing component leads to growth of general, physical and chemical bonds. It is explained by the developing of the more crosslinked Table 4: Dependence of the gelation timeof the curing temperature and the ratio ofreactive groups

Ratio NCO / ΣΟΗ), (mole / mole)	Temp., °C	Gelation time, sec
1,25	30	3170
	40	2025
	50	1268
1,5	30	2483
	40	1638
	50	1137
2,0	30	1032
	40	784
	50	585

spatial structure due to increase of tough urethane blocks. It is detected that M_c (length of chain section between joints of spatial connections net) decrease in case of excess of isocyanate groups relating to hydroxyl groups. An important observations is that M_c increases with the increase of molecular mass of oligomers. In other words it tells about less crosslink density of elastic polyurethanes, which has an effect on elastic properties and hardness.

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