



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 oligodiendiol 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: Oligodiendiol, 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

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 swelling 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.

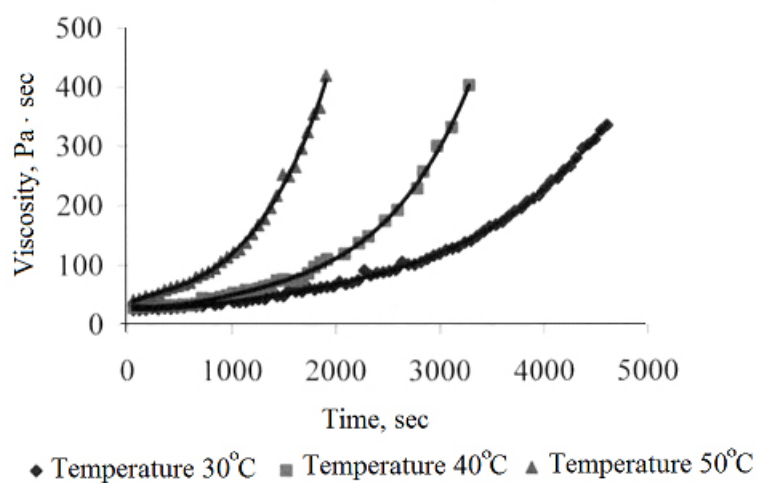


Fig. 1: Rheokinetic changes depending on the viscosity of compositions based on PDI-1K cure time at different temperatures

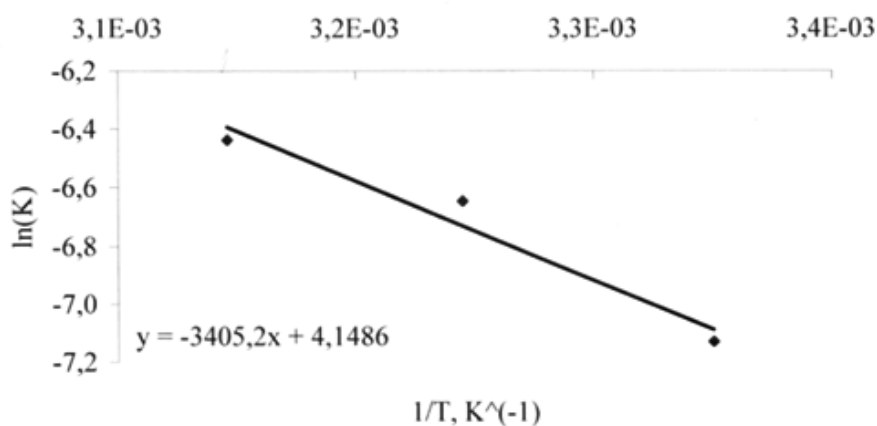


Fig. 2: The logarithm of rate constant with temperature curing dependence

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_p) c ⁻¹	1/T, K ⁻¹	ln(K_p)
303	0,00080	3,30 $\cdot 10^{-3}$	-7,1309
313	0,00130	3,19 $\cdot 10^{-3}$	-6,6454
323	0,00160	3,10 $\cdot 10^{-3}$	-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_c for NCO / Σ OH have decreasing tendency. It is important that with the increase of molecular mass of oligomers M_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 time of the curing temperature and the ratio of reactive groups

Ratio NCO / Σ OH), (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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