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# Properties of Polyurethanes Prepared by Structuring Oligodienediols at Double Bonds and Hydroxyl Groups

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**Abstract**—The curing of oligodienediol with a combined system consisting of a polyisocyanate and a (meth)acrylate-containing compound, which allows it to be structured with the polyisocyanate both at the terminal hydroxyl groups and double bonds due to the (meth)acrylate component, has been studied. The effect of the concentration of the (meth)acrylate component and a peroxide initiator to the degree of cross linking and strength properties of elastomers has been revealed. It has been shown that the participation of oligomer double bonds to form a vulcanization structure, creating the effect of "healing" defects from functional heterogeneity, allows one to increase the degree of cross linking and strength properties of polyurethanes.

*Keywords:* oligodienes, oligodieneurethanes, (meth)acrylates, oligomer curing

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## INTRODUCTION

Increasingly strong requirements, in particular, physicomechanical ones, are being imposed on the properties of elastomers based on hydroxyl-containing oligomeric rubbers used in construction of elastic coatings, which cannot always be satisfied because of the heterogeneity and defectiveness of the vulcanization network of materials obtained by structuring oligomeric rubbers according to the traditional scheme of the urethane formation. This is due to the fact that all known oligomeric rubbers are 10–30% composed of monofunctional and nonfunctional molecular chains, which cannot be considered part of the elastically active part of the network [1–6]. As a result, it is important to search for new ways of structuring such oligomers, including those using double bonds, so as to improve the structure of the vulcanization network and increase the strength properties of oligodieneurethanes.

Structuring an oligodienediol by the terminal hydroxyl groups and double bonds allows one to predict a decrease in defectiveness and an increase in the degree of cross linking of the elastomer due to the involvement in the elastically active part of the network, including nonmonofunctional macromolecules. For cross linking at the double bonds according to the polymerization mechanism, (meth)acrylate-containing compounds can be used [7, 8]. Cross linking of rubber at double bonds by a (meth)acrylate-containing compound can be carried out by the radical mechanism when initiated with peroxides. Activation with amines makes it possible to carry out the process at room temperature [9].

## MATERIALS AND METHODS

The interaction between (meth)acrylate-containing compounds and rubber was determined by means of thermometric studies allowing the temperature of the reaction mixture to be fixed during the structuring of rubber in the presence of a (meth)acrylate compound. NISSO PB G-3000 (Nippon Soda Co) rubber-based compositions 90% of which were double bonds at the 1,2-position and (meth)acrylate-containing compounds, namely, methylmethacrylate (*GOST* (State Standard) *20370–74*), butylmethylacrylate (*TU 2435-025-55856863–2004*), oligoesteracrylates TGM-3 (*TU 6-01-843–73*), MGF-9 (*TU 2226-002-99176106–2012*), and triallylisocyanurate (*TU 6-01-69986*), were studied. The initiator was benzoylperoxide (BP). The activator of BP decay was *N*,*N*,4-trimethylaniline (*TU 6-09-10915–73*).

The process of urethane formation was carried out in the presence of polyisocyanate (PIC, Desmodur 44V20L) with the mass fraction of isocyanate groups varying in the range 30–33%. PIC was introduced in an amount of 12 wt units with respect to 100 wt units of oligodienediol.

The changing temperature of the reaction mixture taken in an amount of 10 mL and placed in glass vials was fixed with a thermocouple and a multimeter in accordance with the procedure reported in [10].

Physicomechanical parameters of elastomeric samples with different content and structure of the (meth)acrylate component and different content of the peroxide initiator were determined in accordance with *GOST* (State Standard) *270–75* using a 5 kN Zwicky rupture machine (Zwick/Roell).

Cross-linking index $\gamma$ was calculated from the equation for the vulcanization of the network formed from a polymer with a random molecular-weight distribution [11]:

$$\gamma = \left(S + \sqrt{S}\right)^{-1},$$

where $S$ is the value of the sol fraction determined after swelling in toluene.

## RESULTS AND DISCUSSION

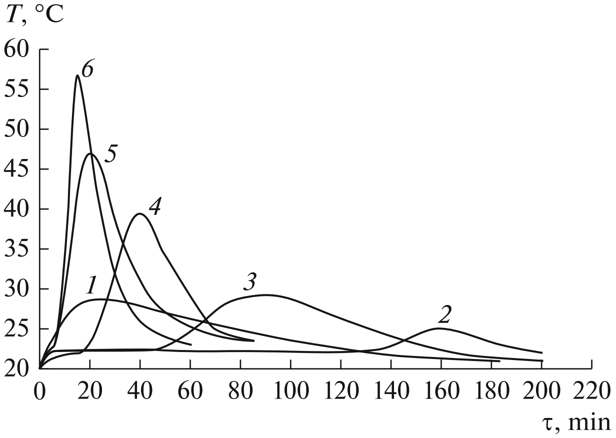

**Fig. 1.** Thermometric curves for curing compositions: (*1*) NISSO PB G-3000 rubber; (*2*) 100 wt units of rubber + 40 wt units of MMA; and (*3*)–(*6*) 100 wt units of rubber + 40 wt units of MMA + 0.5, 1, 2, and 3% of BP relative to the content of MMA, respectively.

Thermograms of rubber curing in the presence of 12 wt units of polyisocyanate, 40 wt units of methylmethacrylate (MMA), and various amounts of BP are shown in Fig. 1. As can be seen from Fig. 1, when rubber is cured only in the presence of polyisocyanate (in the absence of MMA), an insignificant and diffuse temperature peak not exceeding 28°C fixed 20–22 min after mixing the components is observed on thermometric curve *1* according to the pattern of the urethane formation. There is no intense interaction between rubber and MMA in the absence of the peroxide initiator (curve *2*), whereas a very small temperature peak (up to 25°C) is observed on the curve with a time shift up to 160 min due to dilution of the reaction mixture with methylmethacrylate. The introduction of the peroxide initiator into the rubber-(meth)acrylate mixture results in a dramatically increased temperature of the reaction system (up to 29–58°C) and shortened time required to reach the peak (curves *3*–*6*). The sharp increase in the heat release of the system to be cured in the presence of MMA and BP may indicate the possibility of cross linking the oligomer at the double bonds with the parallel homopolymerization of MMA.

The formation of additional bonds during the structuring process is confirmed by an increase in the degree of cross linking of the resulting materials (Table 1). It can be seen from Table 1 that, when oligomeric rubber is cured by the mechanism of urethane formation in the absence of the (meth)acrylate-containing com-

**Table 1.** Effect of composition of the curing system on physicomechanical properties and degree of cross linking of samples

| Ingredient | Ingredient content, wt units | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | composition number | | | | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| NISSO PB G-3000 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| MMA | | | | | 40 | 40 | | | | |
| BMA | | | | | | | 20 | | | |
| TGM-3 | | | | | | | | 20 | | |
| MGF-9 | | | | | | | | | 20 | |
| TAIC | | | | | | | | | | 20 |
| Glycerol | | 3 | | | | | | | | |
| PIC | 12 | 21.5 | 12 | | | 12 | 12 | 12 | 12 | 12 |
| Benzoyl peroxide, wt % of (meth)acrylate component in the composition | | | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| *N*,*N*,4-trimethylanyline | | | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Elastomer properties | | | | | | | | | | |
| Relative elongation at break, % | 350 | 120 | 250 | 0 | 30 | 140 | 150 | 160 | 150 | 200 |
| Relative tear strength, MPa | 0.8 | 2.0 | 0.9 | 0.0 | 0.1 | 5.1 | 1.9 | 3.3 | 2.2 | 2.1 |
| Degree of cross linking | 2.1 | 2.4 | 2.2 | 0.0 | 1.0 | 3.3 | 2.8 | 3.1 | 2.9 | 2.8 |

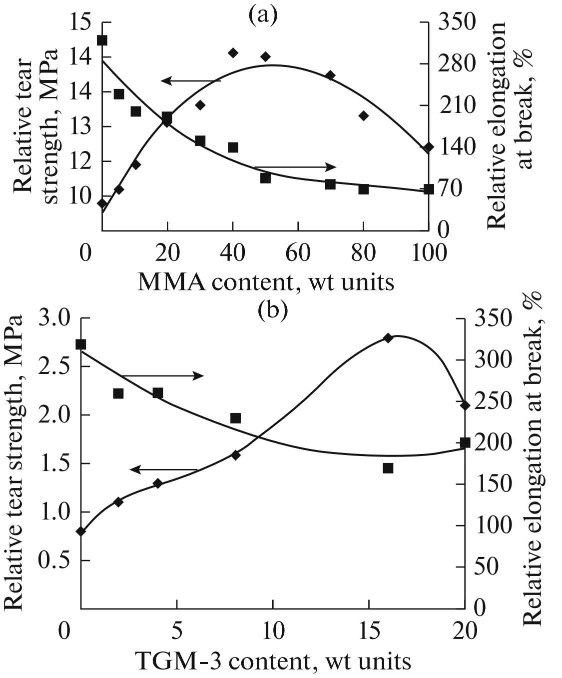

**Fig. 2.** Effect of the content of (a) MMA and (b) TGM-3 on the physicomechanical properties of elastomers.

pound (composition 1), the strength of the resulting elastomer does not exceed 0.8 MPa. When a chain branching agent, namely, glycerol (composition 2), is added, a considerably increased strength and degree of cross linking are observed, which indicates the formation of cross links due to the presence of glycerol. Rubber curing products when using PIC or MMA separately are characterized by low strength and degree of cross linking (compositions 3–5). Curing with a combined system of PIC and MMA in the presence of an initiating system leads to a more than twofold increase in tear strength and an increase in the degree of cross linking (composition 6). Thus, the data listed in Table 1 confirm the effectiveness of combined curing using the mechanisms of urethane formation and radical polymerization, resulting in the increased degree of cross linking due to the formation of cross links at the double bonds. In this case, it is preferable to use MMA or TGM-3 (compositions 6 and 8) as the (meth)acrylate-containing component.

In connection with this, we studied the effect of the amount of the modifying (meth)acrylate component to be introduced and peroxide on the properties of elastomers (Fig. 2): the amount of MMA in the compositions ranged from 5 to 80 wt units, whereas that of TGM-3 was varied from 2 to 20 wt units. The tear strength is an extreme function of the amount of MMA and TGM-3 in the composition. An increase in strength is observed even with the addition of 5 wt units of MMA. The maximum strength level (5–5.5 MPa) is achieved in the range of MMA concentrations from 40 to 60 wt units. For the composition with TGM-3, the extreme character of the function is more pronounced. The maximum level of strength is lower than that for MMA, having an optimum concentration of 16 wt units, but significantly exceeds the strength of the sample when structuring in accordance with the traditional scheme of the urethane formation in the presence of glycerol. The relative elongation decreases monotonically as the concentration of the (meth)acrylate component increases, while remaining at an acceptable level. The extreme character of the tear strength as a function of the amount of (meth)acrylate is apparently due to the depletion of active double bonds in the oligomer with an excess of (meth)acrylate and deterioration of its compatibility with oligodienediol.

The effect of the amount of BP was studied for samples structured by the combined method in the presence of 10, 40, and 70 wt units of MMA (Fig. 3). It is clear from Fig. 3 that the addition of even small amounts of BP (0.1–0.2% of the amount of (meth)acrylate) into the composition results in an increase in the conventional tear strength. The most

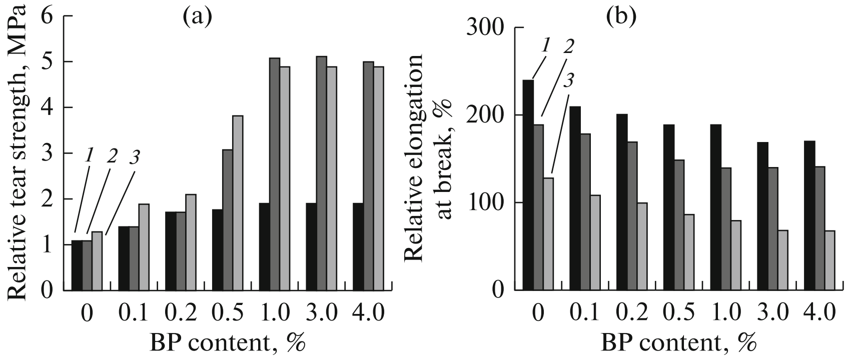

**Fig. 3.** Effect of the content of BP on physicomechanical properties of elastomers at MMA content of (*1*) 10, (*2*) 40, and (*3*) 70 wt units.

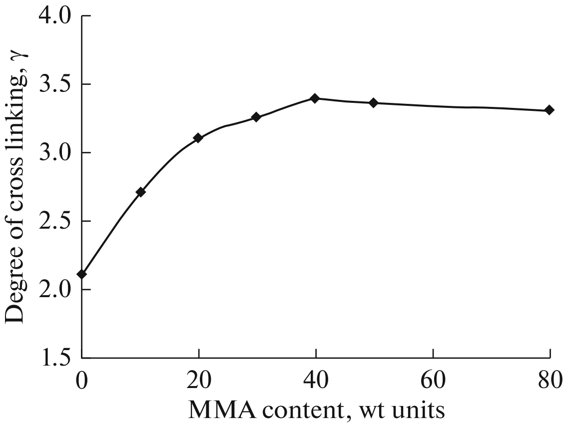

**Fig. 4.** Degree of cross linking of the vulcanization network of elastomers based on NISSO PB G-3000 rubber as a function of MMA content in the presence of BP in the amount of 1 wt % with respect to MMA content.

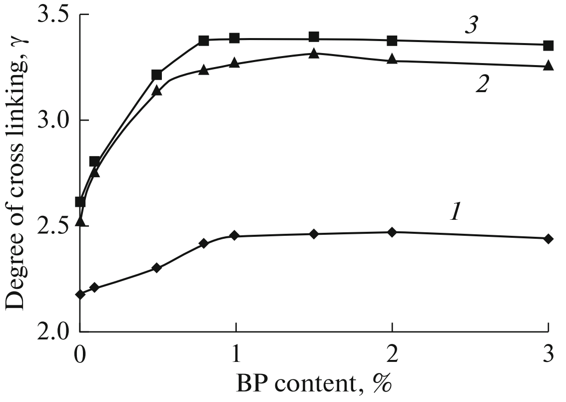

**Fig. 5.** Degree of cross linking of the vulcanization network of elastomers based on NISSO PB G-3000 rubber as a function of BP content at MMA content of (*1*) 10, (*2*) 40, and (*3*) 70 wt units.

significant increase in strength is observed at BP concentrations from 0.5 to 1%; with a further increase in the amount of BP to 4%, the strength remains practically unchanged. However, the intensity of growth and the maximum strength achieved depend on the amount of MMA in the composition. A more pronounced increase in strength is observed at relatively high concentrations of MMA (40 and 70 wt units), providing an increase in strength by four to five times, which is obviously related to the total fraction of the reactive sites in the system. In addition, with a high fraction of MMA in the composition, in addition to interacting with double bonds of rubber accompanied by the formation of a cross-linked structure, it is possible to inoculate and homopolymerize it to form polymethylmethacrylate in the matrix of the structural oligomer to form a “network-in-network” structure [7].

Thus, this study has showed that the preparation of elastomers with a high level of strength parameters requires the amount of the peroxide initiator in the process of combined structuring of oligodenediols to be on the order of 1–2 wt % with respect to the content of the (meth)acrylate-containing modifier.

The revealed character of the dependence of strength properties on the content of the (meth)acrylate component and peroxide initiator correlates with the dependence of the degree of cross linking of the vulcanization network of elastomers (Figs. 4, 5). As can be seen from the presented data, the addition of (meth)acrylate-containing compounds leads to an increase in the density of the cross linking, which indicates the cross linking of rubber at the double bonds with (meth)acrylate. The degree of cross linking depends on the concentration of both MMA and BP reaching the maximum value after the exhaustion of reactive double bonds of rubber, (meth)acrylate, and active radicals.

## CONCLUSIONS

The combined system for curing oligomeric hydroxyl-containing rubber with the participation of double bonds in the formation of the vulcanization structure makes it possible to increase the degree of cross linking and reduce the defectiveness of the network formed by involving nonfunctional and monofunctional macromolecules in the cross-linked structure when they are cross linked through double bonds, creating the effect of “healing” of the defects. Improving the structure of the network and increasing the degree of cross linking can significantly improve the strength properties of elastomers, which is of great practical importance in the construction of formulations when producing polymer compositions.

## ACKNOWLEDGMENTS

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