Frost-resistant polymeric material based on unsaturated polyketone and chlorine-containing epoxy oligomers

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Abstract

Modern technology requires the development of elastic polymeric materials with high frost and oil resistance. In this regard, it is promising to use a new type of reactive oligomers, namely, unsaturated polyketones (UPKs) [1, 2] as a basis for creation of polymeric compositions with enhanced properties. In this work, a new polymeric material was formulated using UPK containing 7.8 wt. % oxygen in the form of C=O groups, chlorine-containing epoxy oligomers, quinol ether as a cross-linking agent for UPK, isomethyl tetrahydrophthalic anhydride as a cross-linking agent for epoxy oligomers, and ionic liquid as a catalyst for curing epoxy oligomers. The developed polymeric material exhibits elastic properties in a wide temperature range and is characterized by an increase in deformation with a decrease in temperature from +50°C to –50°C, as well as by a low swelling capacity (no more than 5.5% at 70°C) in mineral oil. This material is promising for application in a wide temperature range (including low temperatures) in various fields of technology.

Introduction

Liquid oligomers containing functional groups constitute an important class of polymer compounds. They are useful as compatibilizers, plasticizers, and modifiers for a wide range of applications including sealants, coatings, adhesives, rubber goods, tire products, additives to composite materials, etc. The development of new types of functionalized oligomers, improved methods for their synthesis, and materials on their base deserves particular attention.

Earlier, we have shown that the non-catalytic selective oxidation of C=C bonds in diene rubbers by nitrous oxide, N_2O (the so-called ketonization reaction) opens a synthetic route for obtaining a new type of functionalized polymers and oligomers - unsaturated polyketones (UPKs) which contain ketone groups randomly distributed along the polymer backbone [1, 2]. The ketonization with N_2O is applicable to various types of diene rubbers and allows obtaining UPKs with different structure of monomeric units, controllable molecular weight, and specified concentration of carbonyl groups. For example, the composition of UPKs obtained by the ketonization of cis-1,4-butadiene rubbers can be presented by the following formula:

$$CH_2{=}CH\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2)_m\text{-}(CH_2\text{-}CH_2\text{-}C({=}O)\text{-}CH_2)_n\text{-}CH_2\text{-}CHO$$

Due to their adhesive, rheological, and chemical properties, oligomeric UPKs can be used as modifying additives to rubber compounds/vulcanizates, components of epoxy-based materials and adhesive compositions, and in other applications [2-4]. In this work, a new elastic material with high frost and oil resistance was formulated using chlorine-containing epoxy oligomers and UPK obtained by the ketonization of cis-1,4-butadiene rubber.

References

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2. Dubkov K.A., Panov G.I., Parmon V.N., Russ. Chem. Rev., 2017, 86, 510–529.
3. Sidorov O.I., Dubkov K.A., et al., Polym. Sci., Ser. D, 11(2018) 215-224.
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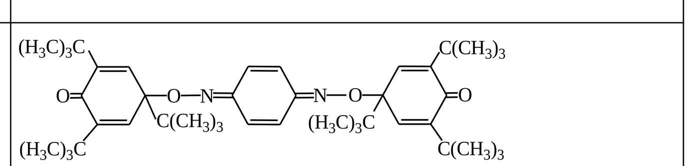
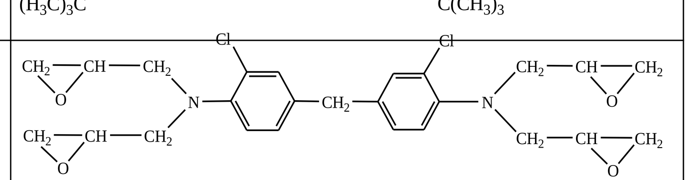
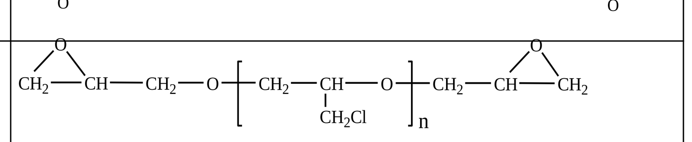
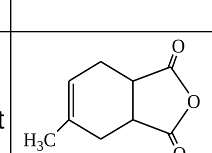
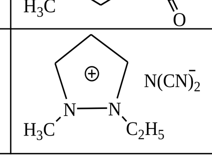
Components of polymeric material based on UPK

#	Components	Function	Formula
1	Unsaturated Polyketone (7.8 wt.% O as C=O groups, Mn = 8100, Mw/Mn = 2.7)	Basis	$CH_2{=}CH\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2)_m\text{-}(CH_2\text{-}CH_2\text{-}C({=}O)\text{-}CH_2)_n\text{-}CH_2\text{-}CHO$
2	EQ-1 quinol ester (melting point > 160°C)	UPK curing agent	
3	Chlorine-containing epoxy oligomer EHD (26-30 wt. % of epoxy groups)	Strengthening component	
4	Chlorine-containing epoxy oligomer UP-655 (20-25 wt. % of epoxy groups)	Active diluent	
5	Isomethyl tetrahydrophthalic anhydride	Epoxy curing agent	
6	1-ethyl-3-methylimidazolium dicyanamide	Epoxy curing catalyst	

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Effect of temperature on the viscosity of oligomers and their mixtures

Compound	Temperature (°C) 25	30	35	40	45	50	55	60	65	70
	Viscosity (η, Pa·sec)									
UPK	27,3	20,6	15,4	11,5	8,9	7,1	5,69	4,7	3,83	3,23
EHD chlorine/epoxy oligomer	—	81,0	38,0	18,7	10,0	5,7	3,4	2,06	1,32	0,89
UP-655 chlorine/epoxy oligomer	—	0,09	0,07	0,05	0,04	0,032	0,025	0,021	0,018	0,025
EHD + UP-655 (2 : 1)	—	2,63	1,64	1,04	0,68	0,46	0,32	0,23	0,17	0,13
EHD + UP-655 (1 : 1)	—	0,80	0,54	0,37	0,26	0,19	0,14	0,11	0,081	0,07
UPK + EHD + UP-655 (100 : 45 : 45)	12,0	8,9	6,44	4,81	3,64	2,80	2,22	1,77	1,42	1,18

- **Viscosity of (EHD + UP-655) composition is lower than that of EHD oligomer**
- **UPK is compatible with a mixture of EHD and UP-655 oligomers**
- **Viscosity of (UPK + EHD + UP-655) composition is lower than that of UPK and EHD**
- **This makes it possible to create a composition with acceptable technological properties**

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Viscous flow parameters for oligomers and their mixtures

Compound	Viscous flow parameters: η_∞, Pa·sec	E_η, kJ/mol
UPK	$2{,}09 \cdot 10^{-6}$	40,6
EHD	$1{,}21 \cdot 10^{-15}$	97,2
UP-655	$2{,}16 \cdot 10^{-8}$	38,2
EHD + UP-655 (2 : 1)	$1{,}56 \cdot 10^{-11}$	64,9
EHD + UP-655 (1 : 1)	$3{,}10 \cdot 10^{-10}$	54,4
UPK + EHD + UP-655 (100 : 45 : 45)	$2{,}21 \cdot 10^{-7}$	44,2

The dependence of viscosity on temperature:

$$\eta_0 = \eta_\infty \exp(E_\eta/RT)$$

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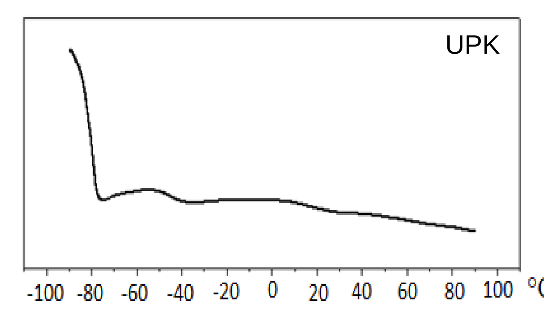
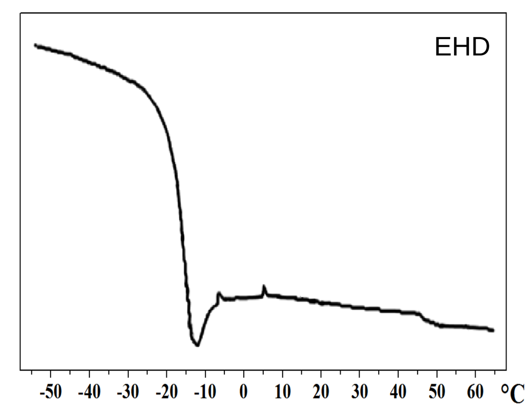
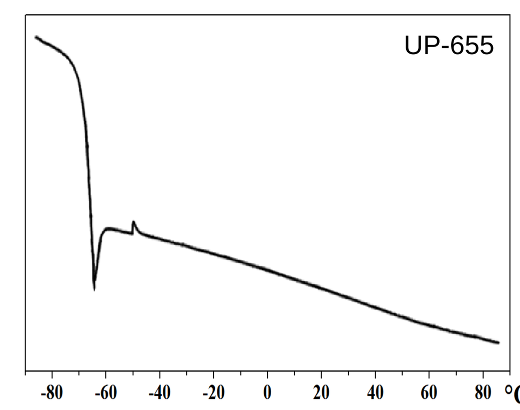
Low-temperature properties of oligomers

Compound	Glass transition temperature, °C
UPK	- 80
EHD	- 19
UP-655	- 70

Thermograms for oligomers







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Mechanical characteristics of the material based on UPK cured with quinol ether

Characteristic	Value
Tensile strength, σ, MPa	0,05
Deformation at break, ε, %	32
Tensile modulus, E10%, MPa	0,225

- Since UPC contains double bonds, it can be cured with quinol ether
- However, the obtained material has low mechanical characteristics

Mechanical characteristics of polymeric material based on UPK and chlorine-containing epoxy oligomers

Characteristic	Temperature, °C: +50	+20	-50
Tensile strength, σ, MPa	0,51	0,56	3,48
Deformation at break, ε, %	16,6	15,1	40,6
Tensile modulus, E10%, MPa	3,27	4,40	17,4

Properties of the developed polymeric material:

- **Elasticity in a wide temperature range**
- **Increase in deformation with a decrease in temperature from +50°C to –50°C**

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Swelling kinetics of polymeric materials based on UPK in non-polar plasticizer (mineral oil) and polar plasticizer (dibutyl phthalate, DBF)

Time, days	Polymeric material: Based on UPK cured with quinol ether		Based on UPK and chlorine-containing epoxy oligomers	
	Plasticizer: mineral oil	DBF	mineral oil	DBF
	Swelling, %			
0	0	0	0	0
0,3	**3,6**	273	**4,2**	83,4
1	**4,8**	—	**5,4**	113
3	**4,9**	—	**5,0**	112
5	**4,7**	—	**5,5**	112
7	—	—	**5,3**	113
10	—	—	**5,2**	116
15	—	—	—	120
20	—	—	—	130
25	—	—	—	136

- **Polymeric materials based on UPK shows low swelling in mineral oil**

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Conclusions

A frost-resistant polymeric material based on unsaturated polyketone and chlorine-containing epoxy oligomers has been created.

The developed material exhibits elastic properties in a wide temperature range. It is characterized by an increase in deformation with a decrease in temperature from +50°C to –50°C, as well as by a low swelling capacity (no more than 5.5% at 70°C) in mineral oil.

This material with enhanced properties can be used as a base for frost- and oil-resistant adhesives and sealants.