Technical Chemistry

Technical Chemistry:
From Theory to Praxis

Edited by

Vladimir N. Strelnikov and Viktor A. Valtsifer

CAMBRIDGE
SCHOLARS
PUBLISHING

Technical Chemistry: From Theory to Praxis,
Edited by Vladimir N. Strelnikov and Viktor A. Valtsifer

This book first published 2011

Cambridge Scholars Publishing

12 Back Chapman Street, Newcastle upon Tyne, NE6 2XX, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-4438-3341-X, ISBN (13): 978-1-4438-3341-7

CONTENTS

INTRODUCTION

This first edition of “Technical Chemistry: from Theory to Praxis” has been compiled of scientific papers written by researchers of the Institute of Technical Chemistry, Ural Division of the Russian Academy of Sciences (City of Perm, Russian Federation). Each of them has contributed to the success of this publication and I would like to thank all of them for their efforts. Prof. Viktor A. Valtsifer has also taken a leading role in shaping the product and, in particular, helping to make it accessible to readers.

This work aims to provide information on some results of our research works, in organic chemistry and in material sciences, to those participating in science-related research and development activities both in Russia and throughout the European continent. International conferences held by the Institute of Technical Chemistry have shown that there is a need for an edition which provides information on the newest results achieved by academic institutions.

Thus, we are very pleased to be able to present this edition. Many of the papers were presented at our last conference “Technical Chemistry: from Theory to Praxis” held in May, 2010. We believe that these papers reflect the research diversity of our Institute and help meet this need.

Finally, we would like to thank Cambridge Scholars Publishing, by courtesy of whom this book was published.

—Prof. Vladimir N. Strelnikov, Dr. Tech. Sci.
Director of Institute of Technical Chemistry

SUMMARY

Over the last decades, significant progress has been made in many areas of material science. Today, there are few technical activities that do not employ materials produced by means of chemical technologies. Almost all industries, almost all consumer products, almost everything we use, can, if analysed, be shown to contain or to deal with products of chemistry. This special edition for the most part contains papers presented at the International Conference “Technical Chemistry: from Theory to Praxis” held on May 18-21, 2010 at the Institute of Technical Chemistry in Perm, Russian Federation, and may therefore be looked upon as the proceedings of this Conference.

This edition is generally intended to provide information on the newest results in solving problems of basic and applied research work in organic chemistry and in material sciences. The extreme familiarity of authors with their subjects enables them to present information in depth and detail, thus giving the most current picture of investigations. The covered subjects include design of new polymeric composite materials and investigations in their properties; synthesis of polymeric sorbents to be used in processes of analysis and concentration of metals; chemistry or porous silica materials; energetic condensed systems etc. Special attention has been paid to the problem of the design of high-strength polyurethanes and to the investigation of physic-chemical properties of polyurethane materials which possess competitive advantages as compared with metals. Results and products in these areas are currently demanded briskly. Furthermore, among the huge amount of books devoted to research works in chemistry, this edition is distinguished by an approach to examination of processes and modifications taking place in materials. This approach consists of special attention by authors to mechanisms of processes and to attempts to quantitatively describe these using known techniques of chemistry.

We therefore expect professionals and students from a wide range of industries and all levels of academia to be interested readers. The list of such readers includes researchers in science of materials, industrial engineers, chemists, and those who teach in universities. Libraries, as it seems to us, will also be interested in acquiring the book.

This book is more than simply a compilation of scientific papers; this is a practical handbook presenting a remarkable opportunity for researchers to work on creation of materials with excellent ordered properties. On the whole, this is an authoritative source for specialists for many years to come.

—Prof. Viktor A. Valtsifer, Dr. Tech.Sci.
Science Deputy Director
Institute of Technical Chemistry

SYNTHESIS AND INVESTIGATIONS IN REACTIVE PROPERTIES OF LATENT EPOXY OLIGOMERS AND DESIGN OF NOVEL HEAT-RESISTANT COMPOSITE CONSTRUCTIONAL MATERIALS ON THE BASIS THEREOF

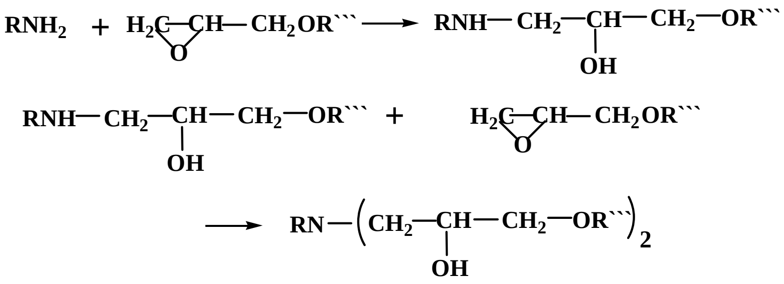
MIKHAIL S. FEDOSEEV, VASILY V. TERESHATOV,
VLADIMIR N. STRELNIKOV
AND LUBOV F. DERZHAVINSKAYA
INSTITUTE OF TECHNICAL CHEMISTRY, URAL BRANCH OF THE RUSSIAN
ACADEMY OF SCIENCES, ACADEMICIAN KOROLEV ST., 3, 614013 PERM,
RUSSIAN FEDERATION, E-MAIL: MSFEDOSEEV@MAIL.RU

Abstract

A new latent epoxy oligomer 4,4´-bis-(glycedylamino-3,3´-dichlordiphenylmetan) was synthesized. The oligomer was hardened at high (140-1600°C) temperatures independently, without hardeners. Heat-resistant polymeric composite materials for constructional purposes on the basis thereof (organo- and carboplastics) were designed and tested.

Introduction

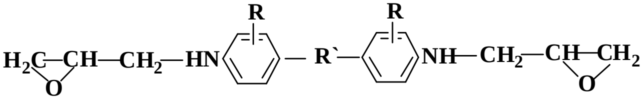
The design of heat-resistant epoxy compounds which harden under the action of various agents is of great interest for different industries. Currently, epoxy compounds comprised of a mixture of epoxy oligomer and latent hardener are well known. The Schiff bases – products of reaction of amines and ketones which, while subjected to high temperature in the presence of water, break down into amine and ketone according to pattern [1]: $R`R``C=NR + H_2O \Leftrightarrow R`R``C=O + H_2NR$ – are known as latent hardeners. The released amine enters into reaction with epoxy groups of oligomer:



Ketone either remains in the compound as a ballast or volatilizes.

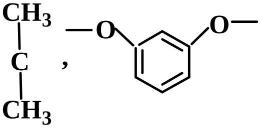
Complexes of boron fluoride with oxygen- and nitrogen-containing compounds [2], e.g. amines, which provide high vitality of compounds at moderate temperatures and decompose at high temperatures into initial boratohydrofluoric acid and amine rapidly hardening epoxy oligomer, have gained the widest acceptance. Tetraalkylphosphonium tetrafluoborate [3] and alkylmethylimidazolium tetrafluoborate [4] are also latent hardeners of epoxy compounds. Their reactivity becomes apparent at high temperatures (190-200°0C). The authors claim that zinc-containing complexes of Lewis acids and tris(halogen)alkylphosphate [5], as per the general formula $[O{=}P(OC_4H_9)_3]2ZnCl_2$, are latent hardeners of epoxy compounds providing unlimited vitality thereof at room temperature. Microcapsulated triphenylphosphine was proposed as a latent catalyst for hardening epoxies by phenolic novolac resins [6]. New thermoreactive polymers made of epoxy resins and benzoxazine on the basis of terpenephenol [7] were produced using latent hardeners. Initial compositions harden at high temperatures (over 180°C). A great deal of latent hardeners of epoxy compounds produced using imidazol and its derivatives are well-known, including adducts of imidazol and isocyanates [8], complexes of imidazol and lactones [9], the product of a combination of 2-ethyl-4-methyl-imidazol and tetrabutylammonium-bromide [10], paste based on acrylic acid, imidazol, water and 1-(2-aminoethyl)piperazine [11], the reaction product of dicinate as per the formula $R\text{-}[OC(=NH)NCH=CHN=CH]_2$ with imidazol [12], compositions based on acid anhydrides, 2-methylimidazol and tertiary amines [13], complexes of imidazols and metal salts [14]. The Ukrainian State Research Institute of Plastic Materials has designed single-use package quick-hardening heat-resistant epoxy adhesives combining long vitality under processing and quick hardening at high temperatures. This has been accomplished through chemical modification of resulting polymers [15].

The mechanism of latent hardeners is based on latent reactivity at moderate temperatures which provides a compound with rather high stability while the compound is produced, stored, and recycled. When hardeners decompose at high temperatures into initial reagents, which are active hardeners of epoxy oligomers, the hardening of composite material and formation of its properties take place. This approach to production of composite materials is of great practical interest. For example, such latent hardeners and catalysts as complex salts of imidazols and metals, isocyanates blocked by imidazols and amines blocked by imidazols, have found application in production of composite materials abroad [16-19]. However, the known latent hardeners are insufficient to produce heat-resistant (up to 300°C) composite materials. This is related to their structure and reactivity, as well as to the structure of resulting reticular polymers while hardened. While developing the “latent” approach to creation of heat-resistant matrix, we propose latent self-hardening epoxy oligomers to be used to produce heat-resistant (up to 300°C) composite materials. The essence of this approach is that the oligomers, while synthesized, contain functional groups capable of involving epoxy group into chemical conversions resulting in formation of reticular polymer. For example, it is common knowledge that tertiary amines are able to initiate homopolymerization of epoxy groups. When they are introduced into epoxy macromolecules, the self-hardening effect of oligomer at high temperatures should be expected. We offer epoxy oligomers containing a secondary amine group with lower reactivity towards epoxy groups as compared with primary amine groups, and exhibiting activity only at high temperatures. This enables epoxy oligomers to be classified as latent oligomers. The epoxy oligomer self-hardening at high temperatures has been synthesized using classic methods of organic and oligomeric chemistry with the general formula:



R — H, CH_3, OCH_3, C_2H_5, OC_2H_5, Cl

R` — O, CH_2,CO, OSO,



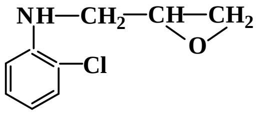
$C(CH_3)_2$, $-O-C_6H_4-O-$

Availability of fragments with different polarities in the structure of an epoxy oligomer molecule opens opportunities to produce epoxy composite materials with adjustable heat resistance and other improved characteristics. Bridge bonds between benzol nuclei (R`) will impact mobility of these bonds and flexibility of chain rather than the scope of intermolecular interaction; this phenomenon will be directly related to heat resistance. For example, higher heat resistance of reticular polymer based on self-hardening oligomer with the O=S=O bridge bond has to be expected. This is confirmed by the fact that glassing temperature of known polymer from epoxy resin based on bisphenol A with SO_2 bridge fragment is higher by 75^0C as compared with CH_2 fragment [20].

Experimental part

4,4’-bis(glycidylamino)-3,3’-dichlordiphenylmethan, the one from the latent self-hardening oligomer group, has been synthesized in collaboration with Dr. Z.G. Leus and Dr. V.N. Averkin, co-workers of the Chimpolymer Research Institute (Tambov, Russia). The oligomer was produced by a reaction of epichlorohydrin and 4,4’-diamino-3,3’-dichrolodiphenyl-methane with subsequent dihydrochlorination by sodium hydroxide. Both stages of the process were performed in ethyl alcohol medium as per the following procedure: 133.5 g (0.5 g-mol) 4,4’-diamino-3,3’-dichrolodiphenylmethane, 95 g (1.03 g-mol) of epichlorohydrin and 150 cm^3 of ethyl alcohol were placed into a four-neck flask fitted with mechanical mixer, thermometer, return cooler and dropping funnel, and boiled for 12 hours (boiling point 82-83°C). When the mixture was cooled to 40-45^0C, solution of 42.3 g (1.05 g-mol) of sodium hydroxide in 55 cm^3 of water was added dropwise to the mixture, while intensively stirred for 30 min. Upon completion of addition, the alkali was held at the same temperature for 1 hr. Then, 150 cm^3 of water-immiscible solvent (toluol, dichloromethane, ethyl-acetate) was poured into the flask. The resulting solution was washed with water three times, 200 cm^3 each washing, to flush out sodium hydroxide. The solvent was distilled and the resulting residue comprised 169 g (89.18% of theoretical quantity) of resin which was a brown transparent viscous fluid with the following characteristics: epoxy group fraction of total mass - 19.68%, NH-group fraction of total mass - 7.1%, saponifiable chlorine - 0.08% with dynamic viscosity 4.35 Pa-sec at 50°C.

It is expedient to investigate reactivity of oligomers of such a structure on model systems which must incorporate structural fragment of the oligomer. For this purpose, we have synthesized N-glycidine-O-chloroaniline monomer as per the general formula:



Synthesis procedure of N-glycidine-O-chloroaniline (NGCA): 64 g (0.5 mol) of O-chloroaniline, 47.5 g (0.51 mol) of epichlorohydrin and 90 cm³ of ethyl alcohol are charged into a flask fitted with a mechanical mixer, thermometer, return cooler and dropping funnel, and boiled for 12 hrs (boiling point is 82-83°C). When the mixture is cooled to 40-45°C, solution of 21.87 g (0.52 g-mol) of sodium hydroxide in 28.5 cm³ water is added dropwise to the mixture, while intensively stirred for 30 min. Upon completion of addition, the alkali is kept at the same temperature for 1 hr. Then, 75 cm³ of water-immiscible solvent (toluol, dichloromethane, ethyl-acetate) is poured into the flask. The resulting solution is washed with water three times, 100 cm³ each, to flush out sodium hydroxide. The solvent is distilled and the resulting residue contains 82.6 g of resin-like monomer with the following characteristics: 19.7% - epoxy group fraction of total mass, 7.09% - secondary nitrogen fraction of total mass, and 0.1% - saponifiable chlorine. Based on results of elemental analysis (C = 59.18%, H = 5.55%, and N = 7.42%) performed on the device (LECO Corporation, USA), the resulting monomer complies with the given formula.

Reactivity of NGCA containing one epoxy group and one secondary amine group in a molecule was investigated by IR-spectroscopy using the IFS-66 spectrometer (Bruker, Germany). Recording conditions were: KBr glasses, 100 scans, and film pressed against the glass. Investigations had uniquely determined reaction of NGCA with aniline, p-aminobenzoyl acid, benzoyl acid, isomethyltetrahydrophthalic anhydride, phenyl-isocyanate and 4,4’-diamino-3,3’-dichrolodiphenyl-methane, and self-hardening of NGCA under the action of catalysts (2-ethyl-4-methylimidazol, and 2,4,6-tris(dimethylaminomethyl)phenol) at 100°C followed by formation of polymeric films. 4,4’-bis(glycidylamino)-3,3’-dichlordiphenylmethan (GACPM), as well as monomer, reacted with all known amine and anhydride hardeners while forming relevant reticular polymers.

Kinetics of hardening of GASPM was investigated by differential scanning calorimetry using the DSC 822^e calorimeter (Mettler-Toledo, Switzerland). The reaction was performed in the dynamic mode in temperature range 20-250°C at the heating rate 5°C/min. The initial

($T_{initial}$) and peak (T_{peak}) temperatures were recorded on thermograms. It has been determined that the GACPM oligomer hardens at 160°C for 4-6 hrs ($T_{initial}$ = 90°C, T_{peak} = 228°C, efficient activation energy E = 95 kJ/mol). With added catalysts (2-ethyl-4-methylimidazol, 2,4,6-tris(dimethylaminomethyl)phenol and 1-methylimidazol), the hardening temperature reduces to 100-110°C.

At moderate temperatures, 20-25°C, GACPM retains its properties for 6 months with unchanged viscosity. Therefore, it may be classified as a latent oligomer.

Glassing temperature of hardened GACPM determined by thermo-mechanical analysis using the UIP-70 device (Russia) is 299-300°C. Polymers with glassing temperatures of such a level are qualified as heat-resistant. Glassing temperature of known polymeric compounds produced by hardening commercial epoxy resins using various hardeners is in temperature range 80-170°C [21, 22]. Taking into account the substantial increase in glassing temperature of GACPM-based polymers, novel heat-resistant epoxy binders without any hardeners were designed. These binders are intended for production of construction-purpose composite materials to be used in the space industry, aircraft engineering and machine building.

We have tested novel self-hardening binders in organic and carbon plastics as compared with standard compositions (Tables 1, 2). Organic plastics produced by “wet winding” procedure were tested at the ISKRA Research and Production Association in Perm. Carbon plastics produced as per the prepreg technology were tested at the Institute of Technical Chemistry (Ural Branch of the Russian Academy of Sciences) and at the Ural Institute of Composite Materials.

Test results of novel heat-resistant epoxy binders have demonstrated an opportunity for their use in production of organic and carbon plastics. Their physic-chemical properties are not inferior to that of standard binders, moreover, their heat resistance and manufacturability even outperform these.

Table 1: Test results of organic plastics

Binder Brand	**Binder Composition**	**Filler**	**Breaking load, N**
UP-2217	UP-610 resin - 60 ED-22 resin - 30 DEG-1 resin - 10 4,4’-diamino-3,3’-dichrolodiphenylmethane - 50	Armos Rusar (aramid filaments)	1520 1650
ESK-1	GACPM oligomer - 70 Ethylacetate - 30	Armos Rusar (aramid filaments)	1540 1760
ESK-2	GACPM oligomer - 70 Ethylacetate - 30 2-ethyl-4-methylimizadol - 1%	Armos Rusar (aramid filaments)	1530 1770

Table 2: Test results of unidirectional carbon plastic

Binder brand	**Binder composition**	**Tensile strength , MPa**			
		25°C	**100°C**	**150°C**	**200°C**
ENFB	EN-6 resin SF-341A resin Furfurylglycidic ether UP-605/3 hardener Ethyl alcohol Commercial-grade acetone	16 0	105	95	90
ESK-1	GACPM oligomer - 70 Ethylacetate - 30	160	160	140	120

Conclusions

1. Novel latent epoxy oligomer - 4,4’-bis(glycidylamino)-3,3’-dichlordiphenylmethan – with epoxy and secondary amine groups capable of reacting to form heat-resistant reticular polymer at high temperatures, has been synthesized.

2. Kinetics of hardening/self-hardening of N-glycidine-O-chloroaniline model monomer have been investigated using IR-spectroscopy and differential scanning calorimetry methods; its reactivity towards various hardeners and reagents has been shown.

3. Novel heat-resistant epoxy binders capable of self-hardening at high temperatures have been designed. The binders are intended to be used in production of construction-purpose composite materials as per existing technologies. Tests of binders in organic and carbon plastics have been performed, it has been ascertained that physic-chemical properties of the binders are not inferior to those of standard binders, moreover, their heat resistance and manufacturability even outperform them.

This work was financially supported by the Ural Branch of the Russian Academy of Sciences (Project “Development of physic-chemical principles for production of heat- and moisture-resistant epoxy polymeric materials with improved elasto-strain characteristics”).

Notes

[1] Sorokin M.F., Schode L.G., Aleksashin A.V. //Khimiya y Khimicheskaya Tekhnologiya (Chemistry & Chemical Technology), 1980, Nr. 7, pp. 900-904.
[2] Sinelnikova M.A., Volkova E.P., Shved E.N. // Problemy Khimii y Khimicheskoi Tekhnologee (Problems of Chemistry & Chemical Technology), 2002, Nr 3, pp. 115-118.
[3] US Patent 6649728 (2002).
[4] Krzysztof Kovalczyk, Tadeusz Spychaj // Polymery. 2003, 48, pp.11-12.
[5] Zinoviev E.G., Efeemov V.A., Koltzov N.I. //Plastmassy (Plastic Materials). 2008, Nr 2, pp. 32-33.
[6] Kim Whan Gun, Yoon Ho Gyu, Lee Jun Young // J.Appl. Polym. Sci. 2001, 81, Nr. 11, pp. 2711-2720.
[7] Kimura Hajime, Murata Youhei, Fukuda Akinori // J.Appl. Polym. Sci. 1999. 74, Nr.9, pp. 2266-2273.
[8] Patent application 59-227925 (1984), Japan.
[9] US Patent 5250638 (1994).
[10] Hadd A.G. // Avail. Univ. Microfilms Int., Order 2620627 from Diss. Abstr. Int. 1996, B.57, 1037.
[11] German Patent 4134081 (1994).

[12] US Patent 4742148 (1987).
[13] Japanese Patent 96157567 (1996).
[14] Broun J, Hamerton J., Howin B. // J. Appl. Polym. Sci. 2000. 75, Nr. 2. pp. 201-217.
[15] Petko O.I., Petko L.K.// Adhesives. Sealants. Technologies. 2007, Nr 2, pp. 6-9.
[16] US Patent 4683283 (1986).
[17] US Patent 6476160 (2002).
[18] Patent application 19927949 (1999), Germany.
[19] Polish Patent 176884 (2001).
[20] Lee J., Neville C. Reference Book on Epoxy Resins. M.: Energia, 1973, 416 p.
[21] Mikhailin Yu.A. Heat-resistant Polymers & Polymeric Materials. St. Petersburg: Professiya, 2006. 463 p.
[22] Deev I.S., Tiunova T.E., Efimov V.A., Mazayev P.Yu. //Plastmassy (Plastic Materials). 2008, Nr. 9, pp.14-17.

INVESTIGATION IN 2,6-DIISOBORNYL-4-METHYLPHENOL AS STABILIZER OF POLYMERS BASED ON OLIGODIENEURETHANEEPOXY OLIGOMERS

MIKHAIL S. FEDOSEEV [1], VASILY V. TERESHATOV [1],
VLADIMIR N. STRELNIKOV [1],
LUBOV F. DERZHAVINSKAYA[1],
ALEKSANDR V. KUCHIN[2], PETR A.SITNIKOV [2],
IRINA YU. CHUKIREVA [2] AND IRINA V. FEDOROVA [2]
[1] INSTITUTE OF TECHNICAL CHEMISTRY, URAL BRANCH OF THE RUSSIAN ACADEMY OF SCIENCES, ACADEMICIAN KOROLEV ST., 3, 614013 PERM, RUSSIAN FEDERATION, E-MAIL: MSFEDOSEEV@MAIL.RU
[2] INSTITUTE OF CHEMISTRY, KOMI SCIENTIFIC CENTRE OF THE URAL BRANCH OF THE RUSSIAN ACADEMY OF SCIENCES, PERVOMAYSKAYA ST., 48, 167982 SYKTYVKAR, RUSSIAN FEDERATION

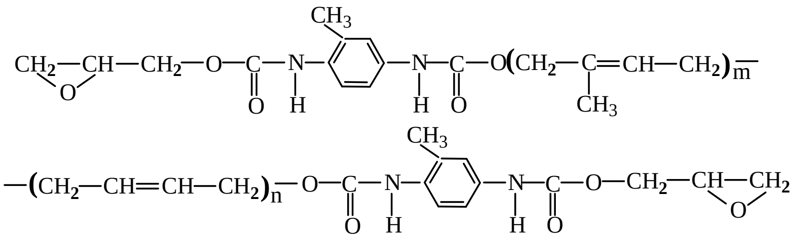
Abstract

2,6-diisobornyl-4-methylphenol was investigated as a thermal stabilizer for polymers synthesized on the basis of PDI-ZAC oligodieneurethaneepoxy oligomer. The stabilizing effect was influenced to a noticeable degree by the nature of the hardener.

Experimental part

It is well known that oxidation is the primary agent of polymeric materials’ ageing. Frequently, it is not only impossible to use, but to process polymers without adding stabilizer. Hydrocarbons and hetero-organic compounds of various classes – phenols, amines, sulfides, mercaptans etc. – are used as stabilizers. Basically, all of them perform two functions: they break oxidation chains through reaction with free radicals, or neutralize instable peroxide compounds through their transformation into relatively stable substances. Phenol compounds like 2,6-diisopropylphenol (Ionol) and amines like phenyl-β-naphthylamine (Naphtham-2), N`-phenyl-N`-isopropyl-n-phenylenediamine (diaphene FP) [1,2] serve as anti-ageing agents for polymeric materials based on unsaturated rubbers (SKI type). Phenol compounds occupy a separate niche in this row due to their high efficiency [3]. As a consequence of closure of a number of enterprises producing domestic stabilizers for chemical resistance, the proportion of imported products, which are often expensive and of low-grade, has increased. Therefore, investigations in the field of synthesis of new anti-ageing agents and assessment of their stabilizing effect on polymers are a vital problem. Terpenephenol compounds which are products of mixed biogenesis combining terpenes/phenols structures appear to be promising as stabilizers. Some terpenephenol compounds used as stabilizers of isoprene rubber (SKI-3) in standard rubber mixtures were investigated in [4]; it was demonstrated that 4-methyl-2-isobornylphenol had the ability to resist ageing. This work investigates stabilizing capacity of 2,6-diisobornyl-4-methylphenol (TF-11), analogous to Ionol, synthesized at the Institute of Chemistry of Komi Scientific Centre of the Ural Branch of the RAS, and described in works [3,5].

Polymeric materials as per the following general formula based on high-molecular weakly-polar oligodieneurethaneepoxy oligomer (PDI-ZAC) were chosen as the object of investigation:



These materials find wide applications in manufacturing products for various purposes [6, 7]. The PDI-ZAC oligomer was hardened using two systems: isomethyltetrahydrophthalic anhydride and 2,4,6- tris(dimethyl-aminomethyl)phenol used as catalysts, and eutectic mixture of 4,4`-diaminodiphenylmethane and μ-phenyleneamine (amine hardening system) (UP-0638). The quantity of added 2,6-diisobornyl-4-methylphenol was 1%

wt. Quantities of Ionol and Naphtham-2 used for comparison were the same.

The stabilizing effect was assessed judging from alterations of physic-mechanical properties of polymers thermally aged (test samples were kept in an oven at 80°C). Physic-mechanical characteristics (rupture stress σ and relative critical strain ε) of test samples formed as blades were determined at 23±2°C and tension rate 0.056sec^{-1} on the Instron 3565 tensile-testing machine (Great Britain).

Table 1. Alterations of physic-mechanical properties of amine-hardened polymers during ageing at 80°C

Stabilizer	Initial		16 days		25 days		55 days	
	σ MPa	ε %	σ MPa	ε %	σ MPa	ε %	σ MPa	ε %
Ionol	3,0	310	2,7	250	2,1	196	1,8	160
TF-11	3,1	330	2,8	260	2,2	220	2,1	200

Table 2. Alterations of physic-mechanical properties of anhydride-hardened polymers during ageing at 80°C

Stabilizer	Initial		16 days		25 days		55 days	
	σ MPa	ε %	σ MPa	ε %	σ MPa	ε %	σ MPa	ε %
Naphtham-2	2,75	270	3,0	260	2,8	270	2,8	265
TF-11	2,65	180	2.7	175	2,75	170	2,75	170

Results of investigations are given in Tables 1 and 2. The data indicate that amine-hardened polymers, while exposed to aging at 80°C for 55 days in the presence of Ionol and 2,6-diisobornyl-4-methylphenol, reduce strength and strain stability by 40 - 50%. Physic-mechanical properties of anhydride-hardened polymers exposed to aging at 80°C for 55 days in the presence of Naphtham-2 and 2,6-diisobornyl-4-methylphenol remain practically unchanged. It should be noted that strain stability of the test sample aged in the presence of 2,6-diisobornyl-4-methylphenol markedly reduces from 265% to 170%. Apparently, this is due to the fact that its hydroxyl groups, while hardened, enter into a reaction with epoxy groups of oligomer. As this takes place, defective chain sections enhancing molecular heterogeneity appear in the polymeric matrix. As a result, this influences properties of polymers. Both pre- and post-ageing investigations of test samples, conducted using the JEOL JSM-6400 scanning electron microscope, confirm this conclusion. In all cases, the ageing of polymers was followed by sensible alteration of surface morphology (Fig. 1-4).

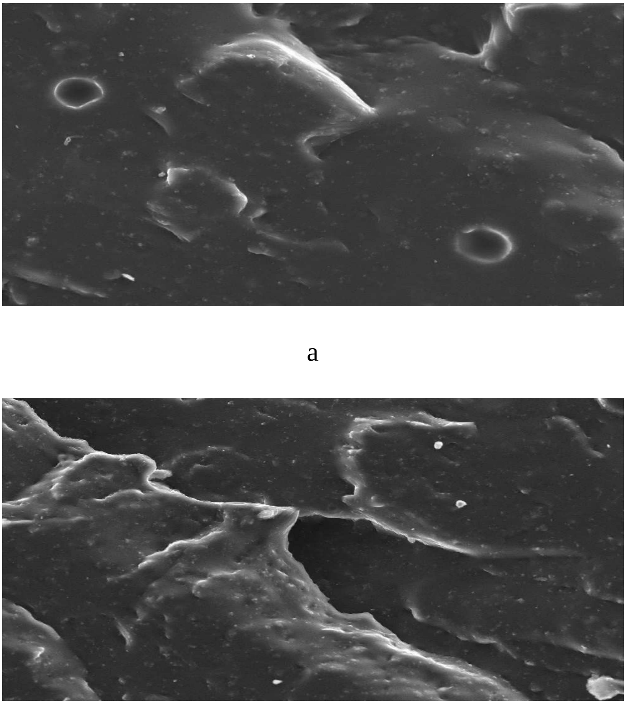
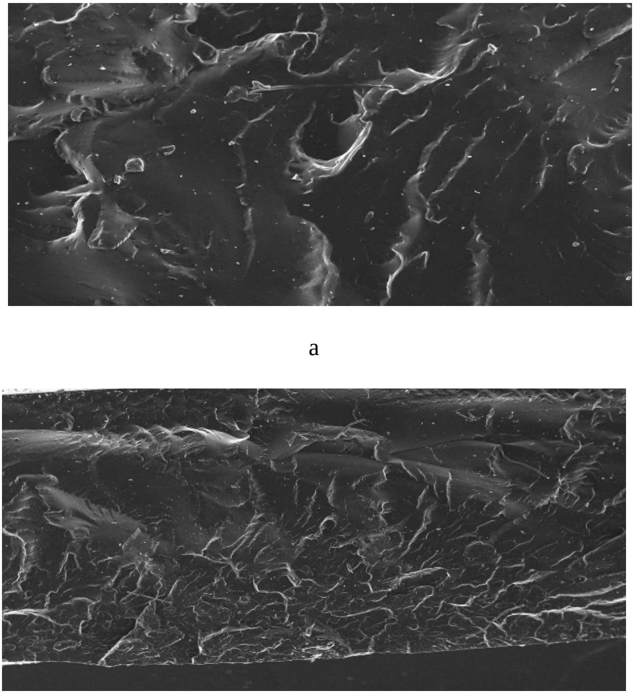


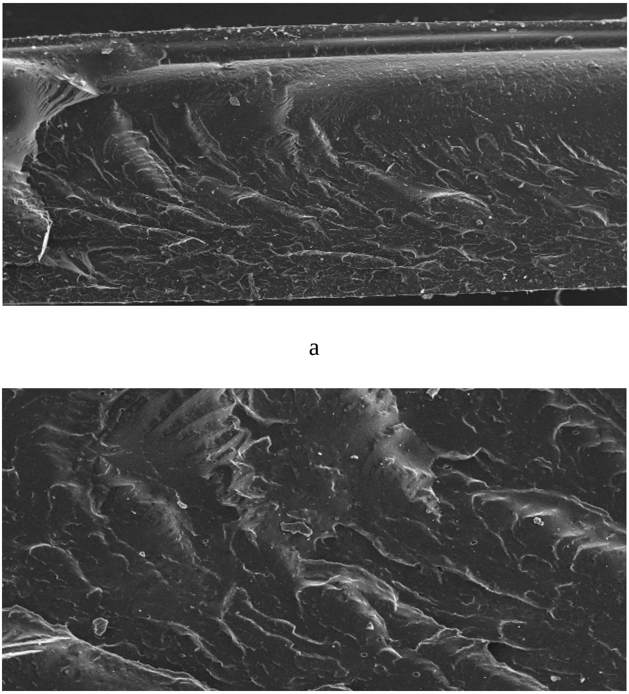
Fig. 1. Surface morphology of amine-hardened polymers aged in the presence of Ionol: a–initial; b–exposed to 80°C for 55 days.



a

b

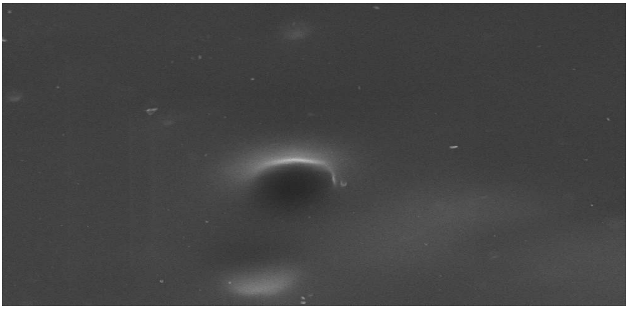
Fig. 2. Surface morphology of amine-hardened polymers aged in the presence of TF-11: a–initial; b–exposed to 80°C for 55 days.



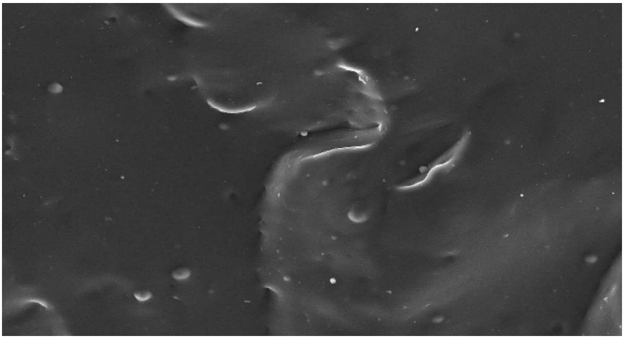
a

b

Fig. 3. Surface morphology of anhydride-hardened polymers aged in the presence of β-naphthalamine: a–initial; b–exposed to 80°C for 55 days.



a



b

Fig. 4. Surface morphology of anhydride-hardened polymers aged in the presence of TF-11: a-initial; b–exposed to 80°C for 55 days.

Conclusions

The 2,6-diisobornyl-4-methylphenol as stabilizer of polymers based on oligodieneurethaneepoxy oligomer PDI-ZAC using amine and anhydride hardening systems has been investigated. The influence of the hardener’s nature on the stabilizing effect in the process of ageing has been demonstrated.

40% reduction of strength and strain of amine-hardened polymers exposed to ageing at 80°C for 55 days in the presence of Ionol and 2,6-diisobornyl-4-methylphenol has been ascertained. Under these conditions, and in the presence of Naphtam-2 and 2,6-diisobornyl-4-methylphenol, physic-mechanical properties of anhydride-hardened polymers remain the same, thus indicating efficiency of said stabilizers in this system.

Notes

[1] Frolikova V.G. // Mir shin (World of Tyres). 2006, Nr. 9, pp. 35-39.
[2] Frolikova V.G., Yalovaya L.I. // Proceedings of the 13th International Practical-Scientific Conference «Rubber Industry. Primary products. Materials. Technologies», M., 2007, pp. 21-22.
[3] Chukicheva I. Yu., Kuchin A.V. // Journal of the Mendeleev Chemical Society. 2004, vol. XVIII, Nr. 3, pp. 21-37.
[4] Novakov I.A., Novopoltzeva O.M., Kuchin A.V., Chukicheva I. Yu., Solovieva Yu. D. // Proceedings of the 3rd International Scientific and Technical Conference «Polymeric Composite Materials and Coatings», Yaroslavl. May 20-22, 2008, pp. 363-364.
[5] Fedorova I.V. // Candidates of science thesis. Institute of Technical Chemistry, Ural Branch of the RAS, 2009.
[6] Gladkikh S.N., Basharina E.N., Naumova L.I. // Adhesives. Sealants. Technologies. 2009. No 9. pp. 26 - 30.
[7] Sidorov O.I., Milekhin Yu.M., Poisova T.P. //Plastmassy (Plastic Materials), 2008, Nr. 12, pp. 47-51.

POLYMERIC MATERIALS BASED ON OLIGODIENEURETHANEEPOXY OLIGOMERS

MIKHAIL S. FEDOSEEV, VASILY V. TERESHATOV
AND LUBOV F. DERZHAVINSKAYA
INSTITUTE OF TECHNICAL CHEMISTRY, URAL BRANCH OF THE RUSSIAN
ACADEMY OF SCIENCES, ACADEMICIAN KOROLEV ST., 3, 614013 PERM,
RUSSIAN FEDERATION, E-MAIL: MSFEDOSEEV@MAIL.RU

Abstract

The hardening process of oligodieneurethaneepoxy oligomer by means of isomethyltetrahydrophtalic anhydride in the presence of catalysts: 2-ethyl-4-methylimidazol and 2,4,6(tris-dimethylaminomethyl)phenol, by means of isoforondiamine and its derivatives, of eutectic mixture of aromatic amines and of an interaction product of aniline with formaldehyde has been investigated via the DSC method in dynamic mode. Physic-mechanical properties of hardened polymers have been ascertained.

Introduction

Polymeric materials based on high-molecular weakly-polar oligodieneurethaneepoxy oligomer (ODEO) find rather numerous applications in the manufacture of multiple-purpose products [1, 2]. In some cases, ODEO is hardened by dinitryloxides using the mechanism of 1,3-dicyclic addition affecting double bonds, but basically as per poly-addition reaction affecting epoxy groups by di- and polyamines, by acid anhydrides and Mannich compounds. However, the achieved level of strength-strain characteristics is moderate. The aim of this work was to design polymeric materials based on ODEO with improved physic-mechanical properties.

Two hardening systems containing liquid hardeners were chosen as objects for investigations in the synthesis of polymers based on ODEO. The first system contained isomethyltetrahydrophthalic anhydride (IMTHPA), maleic anhydride (MA) as well as 2-ethyl-4-methylimidazol, and 2,4,6-tris(dimethylaminomethyl)phenol (TMMP) used as effective catalysts. Amine hardeners – isoforondiamine (IPDA), eutectic mixture of 4,4`-diaminodiphenylmethane and m-phenylenediamine (UP-0638/1), reaction product of aniline and formaldehyde (Polyam) - were chosen for the second hardening system. Efficiency of said catalysts and hardeners had been ascertained in works [3,4,5] upon hardening epoxy oligomers. To reduce viscosity of compounds, plasticizer – 15-20% wt. of dioctylsebacyl (DOS) – was added. To enhance the strength of composite materials, structural modifier 5-10% wt. of glycidylmethacrylate (GMC) and active fillers commercial-grade carbon and schungite powder containing mostly commercial-grade carbon and silica, were used.

The hardening kinetics were studied by means of differential scanning calorimetry (DSC) in dynamic mode at heating rate 5°C/min using the DSC 822^e calorimeter (Mettler-Toledo, Switzerland). Initial ($T_{initial}$) and peak (T_{peak}) temperatures were recorded on thermograms. Thermal effect (Q**)** and effective energy (E) of reaction were calculated. The same device was used to determine glassing temperature (T_g) of test samples. Polymeric compounds were hardened at temperatures resulting from investigations in poly-condensation kinetics of polymeric compounds by the DSC method. Physic-mechanical characteristics (rupture stress σ and relative critical strain ε) of test samples formed as blades were determined at 23±2°C, and tension rate 0.056 sec^{-1} on the Instron 3365 tensile-testing machine (Instron, Great Britain).

Table 1. Hardening kinetics of oligodieneurethaneepoxy oligomer by various hardeners

Hardening system	$T_{initial}$, °C	T_{peak}, °C	Q, J·g^{-1}	E, kJ·mol^{-1}
Isomethyltetrahydrophthalic anhydride 2-ethyl-4-methylimidazol	75	134	30	115
Isomethyltetrahydrophthalic anhydride 2,4,6-tris(dimethylaminomethyl)phenol	82	143	34	118
Isoforondiamine	27 130	81 165	45 17	46.5 116
Polyam	75	140	23	78
Eutectic mixture of 4,4`-diaminodiphenylmethane and m-phenylenediamine (UP-0638/1)	66 102	95 154	20 7	67 76