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DEVELOPMENT OF BIOCIDAL COMPOSITIONS ON THE BASIS OF PVC STABILIZED WITH EPOXY-CONTAINING COMPOUNDS

E.N. Ahmadov[1], Sh.G. Garayeva[1], R.Z. Shahnazarli[2*], G.A. Ramazanov[1]

[1]Sumgait State University, Sumgait, Azerbaijan
[2]Institute of Polymer Materials, Ministry of Science and Education, Sumgait, Azerbaijan

Abstract. The glycidyl ethers of phenyl(benzyl)cyclopropyl carbinol have been synthesized and the compositions on the basis of PVC with use of them as biocidal stabilizers have been developed. The influence of the synthesized epoxy compounds on the critical dissolution temperature of emulsion PVC in the binary mixture consisting of dioctylphthalate (DOPh) and epoxy compounds has been studied and an extreme dependence of the critical dissolution temperature on the quantity of the introduced complex stabilizers has been revealed.
Some physical-mechanical properties of the films made from compositions have been determined and it has been established that the used binary mixtures may be of interest as plasticizing and stabilizing systems for PVC.
It has been revealed that the joint use of the synthesized epoxy compounds and the complex stabilizer (Ca and Zn stearates) in PVC leads to a synergetic effect – the compositions exhibit fungus resistance. It is assumed that the biostability of the made polymer compositions is directly connected with their composition and is appeared as a result of the simultaneous interaction of all components of the composition.

Keywords: *Glycidyl ether of phenyl(benzyl)cyclopropyl carbinol, polyvinyl chloride, composition, thermal stability, fungus resistance, biostabilizer.*

Corresponding Author: *Rita Shahnazarli, Institute of Polymer Materials, Ministry of Science and Education, Sumgait, Azerbaijan, Tel.: +99450546 64746, e-mail: shahnazarli@mail.ru*

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1. Introduction

PVC-based compositions occupy one of the leading places among polymer composition materials. The creation of such composition materials involves the introduction of various additives into the polymer matrix, including fillers, stabilizers, plasticizers, lubricants and other various components (Elgharbawy, 2022; Shahnazarli, 2021; Zolotaryov *et al*., 2013; Mazitova *et al*., 2015; Jubsilp *et al*., 2022). PVC consumes most of all produced polymer additives: approximately 40% or more of most brands of additives for PVC are plasticizers or other additives. Due to the increased requirements in recent years for the selection of formulations for PVC-compositions from a large number of functional additives, the stabilizers are of particular interest in terms of their properties, principles of action and application. As for the polymer materials industry, it

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imposes strict requirements to the biostabilizers (Almeida *et al*., 2023; Stepanova *et al*., 2013; Brostow *et al*., 2018). These requirements include: the high effectiveness of the additive in relation to many microorganisms and activity even at low doses, low toxicity, long service life, storage stability, cost-economy and accessibility. In addition, such additives must be inert in relation to other components of the composition and stable during processing. For this reason, the selection of a biocide as an additive to the polymer is very difficult. Usually, the substances containing sulfur ions and transition metals, such as Cu, Zn, Pb, As, etc., generally have a bio-stabilizing effect. Such compounds are introduced into polymers in pure form or in the form of concentrated solutions in the composition of other additives (for example, in a plasticizer for PVC).

Now, a perspective direction in the stabilization of PVC is the use of substances containing cyclic groups, such as epoxide, cyclopropane, etc., in their molecules, capable of easily reacting with HCl (Bartstein *et al*., 1982; Bashta *et al*., 2016; Smirnov *et al*., 2011; Shikhaliyev, 2017). The introduction of these substances into the composition of PVC compositions provides the satisfactory rheological, physical-mechanical and antifungal characteristics. In addition, the epoxy groups are more reactive than double carbon-carbon bonds, which is an additional advantage, since they are good absorbers of the isolated HCl. The recent investigations showed that the epoxidized sunflower oil in its pure form or in combination with other plasticizers is the good plasticizer and stabilizer for PVC (Bouchoul *et al*., 2017).

The purpose of this work is the synthesis of glycidyl ethers of phenyl(benzyl)cyclopropyl carbinols and the preparation of the biocidal compositions based on PVC with their use as biostabilizers and also the investigation of the fungus resistance of the obtained compositions.

2. Experimental part

Materials

Polyvinyl chloride suspension mark Petvinil-S-39/71 (Petkim, Turkey). The additional purification of the polymer was carried out by multiple washing with ethyl alcohol and diethyl ether followed by vacuum drying (25°C, 10 Pa); ester plasticizer dioctyl phthalate (DOPh) (LG Chemical, Rep. Korea); complex thermostabilizers – Ca stearate ($CaSt_2$) – ACSABCA-3 and Zn stearate $Zn(ZnSt_2)$ – ACSABZN-53 (Akdeniz Chemical products), Turkey); the solvents were distilled and dried according to standard methods before use.

Methods of investigation

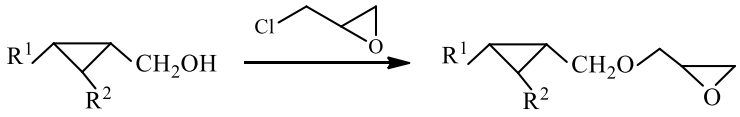
The IR spectra of glycidyl ethers were taken on device IR-Fourier spectrophotometer “ALPHA” of firm Bruker (Germany) in the wave numbers range of 600–4000 cm^{-1} in ZnSe prisms as thin films. The purity of the synthesized compounds was checked by method of gas-liquid chromatography.

The thermal stability of PVC films was estimated by the time of the induction period (the time before the isolation of HCl) on GOST 14041-91 “Plastics. The determination of the tendency to isolation of the hydrogen chloride and other acidic products at high temperature in compositions and products on the basis of homopolymers and copolymers of vinyl chloride. The method congo red” at temperature of 180°C.

The fungus resistance of the compositions was determined on GOST 9.049-91 "Polymer materials and their components. Methods of laboratory tests for resistance to the action of mold fungi". The mass fraction of volatiles was determined on GOST 8728-88 "Plasticizers. Technical conditions".

Synthesis of glycidyl ethers of phenyl(benzyl) cyclopropyl carbinols

Glycidyl ethers of phenyl(benzyl) cyclopropyl carbinols have been synthesized on methodology described in work (Ahmadov *et al*., 2016, 2023) on the scheme presented below:

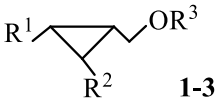


1-3

R^1=$PhCH_2$; R^2=CH_3 (**1**)
R^1=$PhCH_2$; R^2=H (**2**)
R^1=Ph ; R^2=H (**3**)

Some characteristics of glycidyl ethers of phenyl(benzyl)cyclopropyl carbinols are presented in Table 1.

Table 1. Some physical-chemical properties of glycidyl ethers of phenyl(benzyl)cyclopropyl carbinols of general formula:



1-3

Compound code	Glycidyl ethers of phenyl(benzyl) cyclopropyl carbinols			B.p. °C	d^{20}, g/cm^2	n_D^{20}	Yield, %	MW	E.N. %
	R^1	**R^2**	**R^3**						
1	$PhCH_2$	CH_3	Gl*	126-129/44	1.1060	1.5090	78	232	24.56
2	$PhCH_2$	H	Gl	119-122/4	1.1100	1.5180	83	218	26.15
3	Ph	H	Gl	112-182/	1.1206	1.5210	86	204	27.94

*Gl – glycidyl group

PVC films were made by rolling of the compositions containing 40 mass p. of DOPh per 100 mass p. of PVC stabilized with a mixture of epoxycyclopropane (**1-3**) (3.0 mass p.) with Ca and Zn stearates (3.0 mass p.). The components of the composition were thoroughly mixed, gelatinized at temperature of 80°C for 50-60 min. and rolled at temperature of 160°C for 15-20 min.

The critical dissolution temperature was determined by the method described in (Bartstein *et al*., 1982).

The elastic-strength characteristics of the compositions were determined on the "Instron-DX" testing machine on samples cut from PVC-films as standard blades, according to GOST 11262-80 "Plastics. The method of tensile testing".

The heat resistance of the compositions was determined on Vicat device in an air medium on GOST 15088-2014 "Plastics. Method of determination of the softening temperature of thermoplastics on Vicat".

3. Results and discussion

Phenyl(benzyl)substituted epoxycyclopropanes containing ether groups, as experiments showed, are effective stabilizers giving improved exploitation properties and fungus resistance to PVC-based compositions.

Since the dissolving ability of the plasticizer predetermines the viscosity of PVC-composition, we have investigated the influence of the synthesized phenyl(benzyl)substituted epoxycyclopropanes (**1-3**) on the critical dissolution temperature of emulsion PVC in a binary mixture "plasticizer (DOPh) + complex stabilizer (compounds **1-3**)". The obtained results showed an extreme dependence of the critical dissolution temperature on the quantity of the introduced complex stabilizers.

The solubility of PVC in a mixture of DOPh and synthesized phenyl(benzyl)substituted epoxycyclopropanes (**1-3**) has been determined by the thermo-optical method described in (Bartstein *et al*., 1982). The critical dissolution temperature of PVC in a binary mixture containing equal quantities (on 1.5 mass p. per each) of Ca and Zn stearates was compared with its critical dissolution temperature in pure DOPh. It has been detected that compound (**3**) has the lowest critical dissolution temperature in comparison with other epoxy compounds, which indicates good compatibility of the binary mixture with PVC. An increase in the critical dissolution temperature indicates a decrease in the dissolving capacity of the synthesized epoxycyclopropanes (**1-3**). The compound (**2**) has the lowest dissolving capacity, the critical dissolution temperature of which is 136°C.

Table 2. Properties of PVC films plasticized and stabilized with a binary mixture of DOPh to (40 mass p.) and epoxycyclopropanes (**1-3**) (3.0 mass p.)

Name of indices	Compositions on the basis of PVC and compounds 1-3			
	1	**2**	**3**	**DOPh**
Dissolution critical temperature, °C	151	136	139	118
Tensile strength, MPa	19.9	19.7	19.8	19.8
Specific elongation at break, %	222	230	235	233
Modulus at 100 % deformation	121	118	129	122
Thermal stability at 180°C, min	40	45	46	36
Volatiles (at 100°C, 1.0 h under vacuum), %	0.44	0.33	0.21	0.31

For compositions made as films, along with the critical dissolution temperature, some other indices: tensile strength, elongation at break, modulus of elasticity at 100% deformation and thermal stability, presented in Table 2 have been determined. It follows from the data in Table that the thermal stability of PVC films stabilized by binary mixture of DOPh and epoxycyclopropanes **1-3** at 180°C has the close values and is at the level of 40-46 min. The volatility of the composition films is slightly lower than volatility of the films made without the addition of compounds (**1-3**). The obtained results give us reason to conclude that the used binary mixtures may be of interest as plasticizing and stabilizing systems for PVC.

It also follows from Table data that the introduction of the compound **3** in a quantity of up to 0.3 mass p. % reduces the critical dissolution temperature, which is consistent with the theory that the introduction of a small quantity of restrictedly dissolving substances leads to an improvement of the dissolving action of the primary solvents (Smirnov *et al*., 2011). Consequently, in this case, DOPh is activated by a complex

stabilizer, which is a "bad" solvent in relation to PVC. In increase in the concentration of the complex stabilizer in the plasticizer composition to 1.2 mass p., it is observed an increase in the critical dissolution temperature, which indicates a deterioration of the compatibility of PVC with the plasticizer. With an increase in the content of the complex stabilizer, the dissolving capacity of the binary mixture "DOPh+CS" is decreased.

Thus, the used complex stabilizers have a versatile action, which is appeared in increasing the light- and thermal stability and physical-mechanical characteristics of the polymer films. The made compositions show the improved physical-mechanical characteristics, simultaneously these compositions acquire fungus resistance (Table 3).

Table 3. Influence of the complex stabilizers on properties of PVC-compositions

Indicator name	**DOPh 80 mass p.**	**DOPh 70 mass p. + 10 mass p. CP-470***	**Binary mixture, mass p. DOPh:CS = 75:5**
			Compound 3
Breaking strength, MPa	34	35	41
Specific elongation at break, %	180	174	195
Thermal stability at 175°C, min.	26	17	46
Relative loss of whiteness, %	13	24	8.5
Thermal stability at 160°C, min.	46	32	61
Fungus resistance, points	5	3	1

** chlorinated paraffin HP-470 is a transparent oily liquid used in the production of plastisols, PVC pastes, cable plastics, and other polymer compositions.*

It should be noted that the biostability (as well as biodegradability) is one of the important characteristics of the polymer composite materials taken into account at development. In the destruction process of the polymer materials, the microorganisms, for example, fungi, play a basic role. Independently of the type of polymer – whether it is synthetic or natural, the polymer remains a nutrient medium for microorganisms. Therefore, the safety of the polymer materials from the negative effect of microorganisms on them is an actual problem today. In this connection, it is of interest the creation of fungi-stable polymer composition materials on the basis of natural and synthetic polymers.

The epoxycyclopropanes (**1-3**) synthesized by us have been tested as stabilizers in the composition of PVC polymer compositions. However, the compounds (**1-3**) as it has been established, possess bactericidal properties, therefore using them as stabilizers in the composition should give them antimicrobial properties. In Table 4 the results of tests for fungus resistance of various polymer compositions made by us are presented.

Table 4. Fungus resistance of the polymer compositions on the basis of plasticized PVC and epoxycyclopropanes **1-3** (the quantity of DOPh is 30 mass p.)

№	**Polymer composition**	**Fungus resistance in points**	**Suitability estimation**
1	PVC	4	Non-fungus resistant
2	PVC+DOPh	5	Non-fungus resistant
3	PVC+ DOPh+comp. **1** (2.0)	1	Fungus resistant
4	PVC+ DOPh+comp. **1** (2.0)+CS (2.0)	0	Fungus resistant

The polymer composition is considered as fungus-resistant if the degree of growth of fungi on it does not exceed two points. The analysis of the results showed that the polymer compositions possess various resistance to the action of microorganisms. The polymer compositions, including not only epoxycyclopropanes, but also complex stabilizers – salts of transition metals possess the greatest stability.

Among the investigated polymer compositions, there were both fungus-resistant and non-fungus-resistant ones. Consequently, the made polymer compositions can be both biostable and biodegradable (i.e., easily utilizable by means of microorganisms). Contrary to the individual polymer – PVC, the compositions made on its basis with the addition of other components (plasticizer of DOPh, stabilizer **1** and co-stabilizer (Ca and Zn stearates)) were fungus-resistant.

The data presented in Table 4 also indicate that the joint use of the compounds with epoxide groups (**1-3**) and the complex stabilizer (mixture of Ca and Zn stearates) leads to an appearance of synergetic effect and the fungus-resistance compositions have a value "0". It follows from the data in Table 4 that the polymer compositions containing complex of stabilizers show good resistance in relation to microorganisms. It has been revealed that with an increase in the dose of the complex stabilizer, its effectiveness initially increases and then falls. Its optimal quantity is 2.0 mass %.

It can be assumed that the biostability of the made polymer compositions has been directly connected with their composition and is appeared as a result of the simultaneous interaction of all components of the composition. The compositions made from PVC with use of the synthesized epoxycyclopropanes possess high biostability and therefore can be used for creation of materials used in medical practice, agriculture, everyday life and other fields.

4. Conclusion

By the interaction of phenyl(benzyl)cyclopropyl carbinols with epichlorohydrin in the presence of powdered potassium hydroxide, there have been synthesized the glycidyl ethers of phenyl(benzyl)cyclopropyl carbinols, which have been used as biocidal compositions based on PVC.

The solubility of PVC in a mixture of DOPh and synthesized epoxy compounds has been determined by thermo-optical method. Some physical-mechanical properties of PVC films plasticized and stabilized by a binary mixture consisting of DOPh and synthesized epoxycyclopropanes have been determined. It has been shown that the used binary mixtures possess plasticizing and stabilizing properties. It has been established that the compositions made from PVC with use of the synthesized epoxycyclopropanes have high biostability and therefore can be used for creation of materials used in medical practice, agriculture, everyday life and other fields.

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