УДК 541.64:+542.952

ПЛЕНКООБРАЗУЮЩАЯ СПОСОБНОСТЬ КОМПОЗИЦИЙ НА ОСНОВЕ ОЛИГОМЕРОВ ВИНИЛОВОГО И АЛЛИЛОВОГО ТИПОВ

ПЛІВКОТВІРНА ЗДАТНІСТЬ КОМПОЗИЦІЙ НА ОСНОВІ ОЛІГОМЕРІВ ВІНІЛОВОГО ТА АЛІЛОВОГО ТИПІВ

THE FILM-FORMING ABILITY OF THE COMPOSITIONS BASED ON VINYL AND ALLYL TYPE OLIGOMERS

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Изучена пленкообразующая способность композиций на основе α,ω-бис(винил-о-фталатэтиленокси)этилена и гексааллил(бис-пентаэритритсебацинат)диэтиленгликоля. ГАСД синтезировали методом конденсационной теломеризации. ДФТ синтезировали, исходя из этиленхлоргидрина и фталевого ангидрида в присутствии кислого катализатора. Его строение установлено по совокупности данных элементного анализа ИК и ЯМР 1Н-спектроскопии. Приведены физико-механические показатели пленок композиции. Разработана рецептура эмали на основе ДФТ и ГАСД. Установлено, что ненасыщенность пленок композиции и скорость старения уменьшаются с увеличением содержания ДФТ. Предложено использовать композиции на основе ДФТ и ГАСД в качестве пленкообразующих веществ с высокими физико-механическими свойствами.

Вивчена плівкотвірна здатність композицій на основі α,ω-біс(вініл-о-фталатетиленокси)етилену та гексаалліл(біс-пентаеритритсебацинат)діетиленгліколю. ГАСД синтезували методом конденсаційної теломеризації. ДФТ синтезували, виходячи з етиленхлоргідрину і фталевого ангідриду в присутності кислого каталізатора. Його будова встановлена за сукупністю даних елементного аналізу ІЧ та ЯМР 1Н-спектроскопії. Наведені фізико-механічні показники плівок композиції. Розроблена рецептура емалі на основі ДФТ та ГАСД. Розроблено рецептуру емалі на основі ДФТ і ГАСД. Встановлено, що ненасиченість плівок і швидкість старіння зменшуються зі збільшенням вмісту ДФТ. Запропоновано використовувати композиції на основі ДФТ і ГАСД як плівкотвірні речовин з високими фізико-механічними властивостями.

The film-forming ability of compositions based on α, ω-bis(vinyl-o-phthalate-ethyleneoxide)ethylene (DFT) and hexaallyl(bis-pentaerythritsebacate)diethyleneglycol (GASD) has been studied. HASD was synthesized by condensational telomerization. FTD was synthesized based on ethylenchlorhydrinein the presence of an acid catalyst. It's structure is set on a common data EK elemental analysis, and 1H-NMR spectroscopy. Given physical and mechanical properties of the composition films. Studying of oxidative polymerization of DFT showed that it can be used in compositions with oligomeric allyl ethers. For compositions DFT and GASD defined physical and mechanical indicators. It was found that unsaturation of biofilms and the aging rate decreases with increasing content of DFT. Unsaturation of films decreases with increasing of DFT content. The aging rate is also reduced with DFT increasing. A recipe of the enamel based on DFT and GASD has been developed. It is proposed to use compositions based on DFT and GAS as film-forming substances with high physical-mechanical properties.

Ключевые слова: аллиловые эфиры, виниловые эфиры, пленкообразование.
Keywords: allyl ethers, vinyl ethers, film formation

Ability to create new oligomeric materials and coverings on their basis, determines the increased interest in the study of their properties. By the beginning of the twenty-first century (according to expert's estimates), more than 60% of products from the entire range of polymer materials represented in the global market, have been produced with a use of oligomers [1]. The presence in the molecules of oligomers of two or more double links explains use of these compounds in compositions with diverse purposes: to obtain a film-forming material; components for creating laquers, paints and other.

We have previously synthesized α,ω-bis(vinyl-o-phthalate-ethyleneoxide) ethylene (DFT) and investigated it's film-forming ability in a presence of redox systems [2,3], and in a presence of acetylacetonates of transient metals upon UV irradiation [4,5].

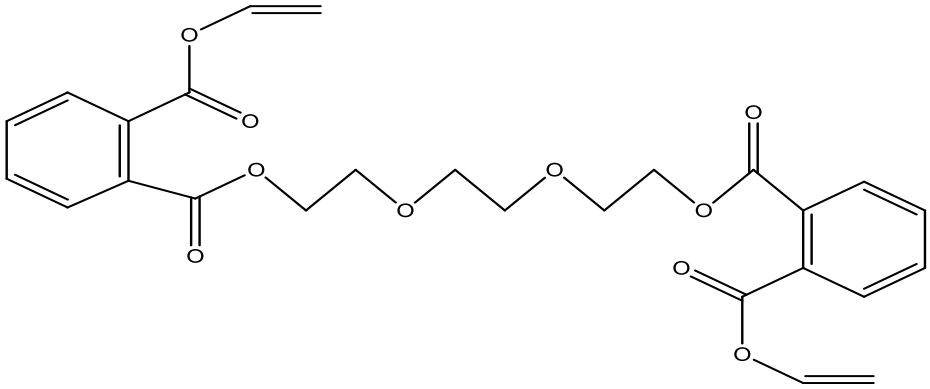
The aim of the study was to investigate the film-forming ability of compositions based on DFT and hexaallyl(bis-pentaerythritsebacate)diethyleneglycol (GASD).

Compared with other oligomeric allyl ethers (OAE) [6], GASD has a low specific functionality, more flexible and long oligomeric chain, which provides high flexibility of coverings and less tendency of internal stresses formation of in the films. Simultaneously GASD molecular functionality is high enough (six double carbon links), and film formation takes place at a high speed in a wide temperature range (292-373 K).

GASD had been synthesized by condensation-telomerization method, physico-chemical parameters were as described in [7].

Multistep synthesis starting from ethylene and phthalate anhydride via an transitional monovinyl-o-phthalate (white crystal substance) which under the action of 3-ethylene glycol in the presence of an acidic catalyst (concentrated sulfuric acid) results in α, ω-bis(vinyl-o-phthalate-ethyleneoxide) ethylene.

The refractive index was 1,5363. The molecular refraction calculated by known formulas - $MR_D10^6m^3$ / mol = 124,1. Density was determined by pycnometric – 1,25 g/cm^3.



The structure of the α, ω-bis(vinyl-o-phthalate-ethyleneoxide) ethylene was established by data set of elemental analysis and IR, and NMR ^1H spectroscopy. IR spectrums were recorded on a IR spectrometer Agilent Cary 660 FTIR and processed in the program "Agilent resolutions pro". 1H NMR spectrum recorded on the device Varian Mercury VX-200 (200 MHz) in DMSO-d_6, internal standard - HMDS (0 m.d.).

The purity of the starting materials and products was monitored by TLC method with highly efficient Sorbfil plates.

In NMR-^1H spectrum of α, ω-bis(vinyl-o-phthalate-ethyleneoxide) ethylene proton multiplet of phenyl rings is located at 7,19-7,68 m.d. Proton triplet of -H_2C-O-CH_2-group - at 3,53 m.d., and a triplet of protons of -CH2-O-C (O)-group - at 4,31 m.d. Doublet of protons of CH_2 = group at 4,53 m.d., and proton triplet of =CH-O-group is located at 2,3 m.d.

Studying of oxidative polymerization of DFT showed that it can be used in compositions with oligomeric allyl ethers.

Polymerization of compositions studied with overcome of the three-dimensional polymer in a films 35 microns thickness in air at 338K, in the presence of a redox initiator system (RIS) consisted of cyclohexanone hydroperoxide 0,55% and 0,1% cobalt naphthenate in conversion to a metal (Figure 1). Content of a three-dimensional polymer in the films was determined by the amount of the gel fraction by gravimetric method.

Based on the results presented in Figure 1, we can say that the induction period (τ_i) for all the compositions, regardless of the components, is more than pure GASD has (curve 1, Figure 1), but less than pure DFT has (curve 5, Figure 1) that satisfies the requirements for the composite materials.

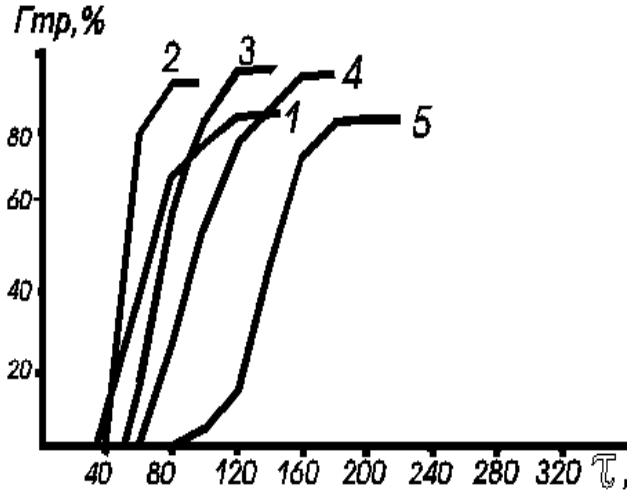


Figure 1 - Polymerization of DFT and GASD compositions at 338 K. The film thickness was 35 microns. The content of DFT, in %: 1-0; 2-20; 3-50; 4-80; 5-100.

Forms of the Curves of the compositions and the average rate of polymerization differ slightly. We can see (curves 2,3,4 Fig.1), that film-formation in compositions is 10-12% higher than the pure GASD (curve 1, Figure 1,) and pure DFT (curve 5 Fig.1) polymerization. The high speed film forming compositions results in a rapid hardening of films (3 h).

For FTD and GASD compositions physical and mechanical properties listed in Table 1 were defined. The relative strength was measured at the balance wheel device ME-3 (State standart #5233-67); Film impact strength was measured by unit U-1 (State standart #4765-73); Coatings flexure was measured on the instrument SH-1 (State standart #6806-73). The conversion of film composition double links was determined by bromide-bromath method after films swelling in icy acetic acid for 72 hours, followed by titration with 0,1N sodium thiosulfate in the presence of starch, which was added at the end of the titration.

Table 1 - Physical and mechanical properties of DFT and GASD films compositions.

Component Content, % wt.		Hardening time of the coating with thickness of 35 microns at 338K, min.	Aging Time coating with thickness of 35 microns at 293K, hours	The conversion of double links, %	Physical and mechanical properties of coatings		
DFT	GASD				Flexure, mm	Impact strength, Nm	Relative strength
0	100	90	24 168 720	70 72 74	2 2 3	5,0 5,0 5,0	0,12 0,13 0,25
20	80	90	24 168 720	60 62 66	1 3 5	5,0 3,5 3,0	0,30 0,39 0,60
50	50	120	24 168 720	69 70 71	1 2 2	5,0 4,0 4,0	0,40 0,45 0,50
80	20	150	24 168 720	78 79 81	3 3 3	4,0 4,0 3,0	0,53 0,53 0,65
100	0	180	24 168 720	88 88 90	5 5 5	4,0 4,0 3,5	0,66 0,66 0,68

Films unsaturation decreases with increasing of DFT amount. The aging rate also decreases with increasing of DFT content. Lower elasticity and resistance to aging with a high content of DFT (80-100%) is due to the more rigid and short oligomeric chain of FTD. We have selected the optimal composition based on DFT and GASD containing 50% of DFT. Films based on DFT and GASD are colorless and transparent, dry well in the air and do not have a sticky surface layer. They are resistant to water, non-polar solvents, but is moderately resistant to alkaline environments.

Compositions based on vinyl oligoester (DFT) and allyl ester have good decorative and protective properties and is recommended DFT as a component of the composite material used in the film-forming substances.

We developed enamel, composed of FTD and GASD (1: 1 by weight). Enamel mixture was obtained by dispersing the components in a laboratory mill, followed by filtration. Enamel receipt is shown in Table 2.

Table 2 - Enamel basis receipt

Components	Content, % wt.	Remark
Titanium oxide (IV)	30,3	Rutile, Z-02
Yellow lead kron	0,9	
DFT	17,2	
GASD	17,2	
colloxyline lacquer	7,8	Mark BB, dissolved in acetone
Alkyd resin	3,9	
Acetone	22,7	
Total	100	

Obtained enamel has all the requirements (enamel PU-126 M Ivory - TU-6-10-1332-78), and some indexes (hardness of coatings, drying time and temperature, resistance to water, gasoline, oils) are above regulations.

Based on this experiment it can be concluded that the compositions based on DFT GASD can be used as film-forming substances having a high hardening rate and physical properties.

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