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Flotator Oxal as the plasticizer for suspension PVC

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Abstract: Flotator Oxal, a mixture of dioxane ethers and alcohols, was studied as a plasticizer for suspension PVC in comparison with the well-known dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DOP). The rheological parameters and gelation ability of the plasticizers were determined, and the values of the storage modulus and tangent of mechanical loss angle in the glassy and rubbery states were measured by the DMA method, and the glass transition temperatures were determined. The deformation-strength properties and rigidity of polymer films were tested before and after light-thermal aging. Oxal was shown to reveal a fairly low viscosity and high gelation properties in relation to PVC. At the same time, its ability to reduce the glass transition temperature and elasticize the polymer in the glassy and rubbery state is somewhat lower than that of phthalate plasticizers. PVC samples plasticized with DBP have the highest resistance to light-thermal aging.

Keywords: phthalates; dynamic viscosity; polyvinyl chloride; DMA method.

INTRODUCTION

Plasticizers play an irreplaceable role in the manufacture of flexible materials based on rigid-chain polymers.[1] Initially, cellulose ethers, poly(vinyl acetate) and its copolymers[2] were used as plasticizable polymers. Currently, the main consumer of plasticizers is the production of flexible PVC materials, such as films, linoleum, artificial leather, awning materials, *etc.*[3]

It is customary to distinguish between internal plasticization associated with the addition of plasticizing fragments into macromolecules of rigid-chain polymers due to covalent bonding[4–6] and external – by introducing special plasticizers without chemical interaction. Among PVC plasticizers, the most common are esters of organic acids (phthalic, adipic, trimellitic, sebacic, azelaic), as well as phosphoric acid.[7,8] To reduce volatility, polymer plasticizers are utilized, in

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particular polyesters.[9] In addition a large group is made up of the so-called secondary plasticizers (extenders), used in conjunction with primary ones. The most common among them are chlorinated hydrocarbons.[3] In recent decades, much attention has been paid to the search for biodegradable plasticizers of various nature,[10–13] which enables a number of environmental protection and health safety problems to be solved[14] and in some cases to combine plasticizing and the antipyretic function of a biodegradable additive.[15]

The most widespread plasticizers based on phthalic acid esters have been used for almost 100 years to change the elastic properties of poly(vinyl chloride).[1] Phthalate plasticizers effectively reduce the pour point and the glass transition temperature of PVC.[6] Nevertheless, there is a permanent search for new plasticizers that, with high efficiency, would have a lower tendency to diffuse onto the product surface, less volatility at elevated temperatures, and a lower cost.[1]

Over the past several decades, the use of a high-boiling by-product Edos (TU 2493-003-13004749-93) as PVC plasticizer has been actively discussed.[16–21] It is formed in the manufacture of 4,4-dimethyl-1,3-dioxane by condensation of isobutylene with formaldehyde. In one turn, flotator Oxal is the by-product of Edos (technical requirements 2452-015-48158319-2009). This product contains about 50 % dioxane ethers and alcohols and about 50 % mixtures of 1, 2 and 3 atomic alcohols.[20]

The successful application of flotator Oxal as a plasticizer in the production of plastisols based on emulsion PVC E was described.[16–18] The influence of Oxal on the properties of composites based on suspension PVC has practically not been studied. Therefore, the estimation of the plasticizing action of Oxal performed in this work seems to be very actual.

EXPERIMENTAL

Materials

Suspension PVC Ongrovil S-5070 was obtained from BORSODCHEM (Hungary). Dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DOP) were purchased from "Ural plasticizers plant" (Russia) and used without purification. Flotator Oxal T-92 (Technical requirements: 20.59.59-029-05766801-2016) was purchased from "Nizhnekamskneftekhim" (Russia), stabilizer Baerostab UBZ 751 – from "Baerlocher GmbH" (Germany).

Film preparation

To study the mechanical and thermophysical properties of the composites, films were produced from PVC melts. The compositions contained 70.2 % PVC, 1.7 % Baerostab UBZ 751 and 28.1 % plasticizer. Dibutyl phthalate (DBP) and di-2-ethylhexyl phthalate (DOP) were chosen for comparison with Oxal. PVC, plasticizer and stabilizer were mixed, then heated for 30 min at 120 °C. The final mixing and formation of the film were performed on rollers at 150 °C for 5–6 min. To achieve a fixed thickness, the films were pressed at 160 °C and 5 MPa for 4 min, followed by cooling in a mold.

Measurements

Rheological tests of plasticizers were carried out in accordance with ASTM D2983-09 on a Brookfield DV-II+ rotary viscometer equipped with Thermosel, in the range of shear rates from 0 to 186 s^{-1} and temperatures 22–45 °C. The size of PVC particles was determined using a polarizing microscope POLAM R-211 (magnification 75.6 times).

DMA was performed on a DMA Eplexor 25N (NETZSCH-Gerätebau GmbH) in the tensile-film mode. The specimens 70.0 mm× 7.0 mm× 0.4 mm were measured from –30 to 80 °C with a frequency of 1 Hz and a temperature ramp of 1 °C min^{-1}. The storage modulus E' and tan δ were recorded as a function of temperature. The glass transition temperature was determined according to ASTM D7028-07(2015).

The tensile strength and elongation at break were measured using a testing machine 2099-P-5 ("Tochpribor", Russia) at 25 °C before and after light-heat aging according to ISO527-2:2012. The length of the films was equal to 170 mm and the stretching speed was 25 mm min^{-1}. The measurements of the mechanical properties of the composite films were made with 5 replicates of each composition.

Accelerated aging was realized in accordance with ASTM G151-19 and D3045-18. Ultraviolet irradiation was performed with mercury-quartz lamps DRT-400, exposure time 36 h at 70 °C. The hardness of films before and after UV light-thermal aging was determined on a PMZh-12 M device. The hardness was assumed to be equal to the load required for deflection of an elementary sample bent into a ring by 1/3 of the diameter. Test conditions corresponded to Gost 8977 (ball weight 0.86 g, sample size 20 mm× 95 mm).

RESULTS AND DISCUSSION

Rheological characteristics of plasticizers essentially influence the technological processing parameters of flexible PVC, especially in the case of using plastisols.[16–18] In this regard, the rheology of the product Oxal was studied in comparison with the most common phthalate plasticizers: dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DOP) (see Experimental). The values of dynamic viscosity were measured in the shear rate range 0–186 s^{-1}. All plasticizers studied were found to behave like Newtonian liquids.[22] The simulation of temperature semilogarithmic dependencies (Fig. 1) according to the Frenkel–Eyring Equation:[23]

$$\eta = \frac{N_{\mathrm{A}}\hbar}{V} e^{\frac{-\Delta S^{\#}{}_{\mathrm{VF}}}{R}} e^{\frac{\Delta H^{\#}{}_{\mathrm{VF}}}{RT}} \tag{1}$$

where η is the viscosity, V the mole volume, $\Delta S^{\neq}{}_{\mathrm{VF}}$ and $\Delta H^{\neq}{}_{\mathrm{VF}}$ the changes in activation entropy and enthalpy, respectively, of viscous flow, allowed the flow activation parameters to be calculated, which together with the viscosity at 25 °C are presented in Table I.

An analysis of these data indicates a slightly lower viscosity of Oxal (25 °C) than that of DOP, but higher than that of DBP. The free activation energy, $\Delta G^{\neq}{}_{\mathrm{VF}}$, of viscous flow follows the same trends. Simultaneously, the ratio of the activation parameters of Oxal are completely different than those of the phthalate plasticizers (Table I) – lower enthalpy and practically zero entropy of activation. This testifies to differences in the flow mechanism of the studied fluids. It is known that the value of $\Delta H^{\neq}_{\mathrm{VF}}$ is associated with the size of the molecule or its fragment involved in the momentum transfer in viscous flow.[24] Therefore, the activation enthalpy of DOP is slightly higher than that of DBP. Thus, a low Oxal value indicates a weaker effect of temperature on the viscosity (Fig. 1) and a smaller volume of the momentum transfer element.

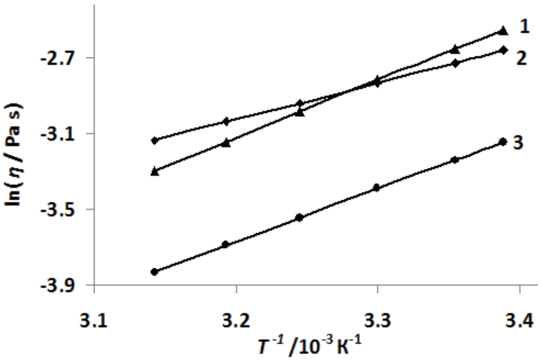

Fig. 1. Temperature dependence of the logarithm of the dynamic viscosity for plasticizers: 1 – DOP, 2 –Oksal, 3 – DBP.

TABLE I. Rheological parameters of the considered plasticizers

Plasticizer	η / mPa s (γ = 27.9 s^{-1}, t = 25 °C)	$\Delta H^{\neq}_{\mathrm{VF}}$ kJ·mol^{-1}	$\Delta S^{\neq}_{\mathrm{VF}}$ J·mol^{-1}·K^{-1}	$\Delta G^{\neq}_{\mathrm{VF}}$ kJ·mol^{-1} (t = 25 °C)
DOP	70.5	25.1	29.8	16.2
Oxal	65.4	16.1	0.2	16.1
DBP	39.4	23.9	30.7	14.8

One of the most important properties of a plasticizer is its gelation ability for a given polymer.[6] The combination of suspension PVC with plasticizers begins with their mechanical mixing and is accompanied by swelling of the polymer particles and an increase in the particle size.[3] The ratio of the size of the swollen PVC particles to the size of the initial particles allows the effective absorption of the plasticizer during hot mixing to be evaluated and, consequently, its gelation properties (Table II).

TABLE II. Average particle size of PVC and swelling degree after combining with plasticizer at 120 °C within 30 min

PVC composite	Average particle size, µm	Swelling degree of the PVC particles
Initial PVC	79.6	1
PVC + DBP	143.9	1.81
PVC + DOP	104.1	1.31
PVC + Oxal	149.0	1.87

According to the data in Table II, the gelation properties of Oxal is at the level of DBP – one of the most effective PVC plasticizers.[3,6] Thus, significant absorption at the mixing stage allows “dry” blends based on suspension PVC and Oxal to be produce, which could be used in calender and extrusion technological schemes.

The main function of the primary plasticizer is to lower the glass transition temperature and increase the elongation and softness of the polymer compositions.[6] The most informative method for evaluating the plasticizing effect is dynamic mechanical analysis (DMA), which permits fundamentally important physical-mechanical and thermo-physical parameters to be measured. In this regard, the temperature dependences of the storage modulus (Fig. 2a) and the tangent of the mechanical loss angle tan δ (Fig. 2b) were obtained by the DMA method. The values E' in the glassy and rubbery states, as well as the glass transition temperatures t_g corresponding to the maxima on the curves tan $\delta = f(t)$ are presented in Table III.

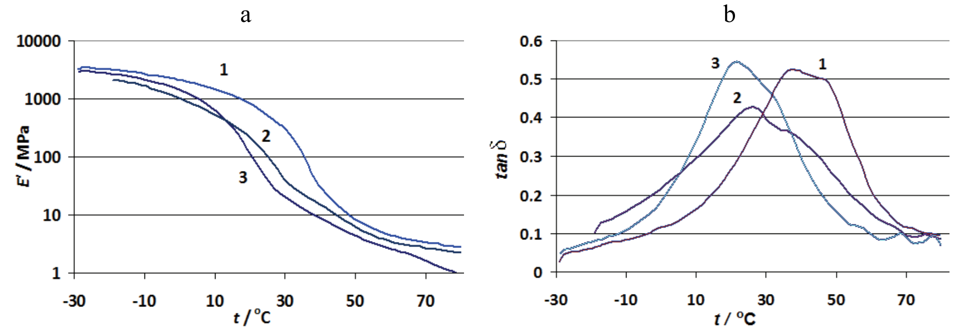

Fig. 2. Temperature dependences of the storage modulus E'(a) and tan δ (b) of PVC composites with plasticizers: 1 – Oxal, 2 – DOP, 3 – DBP.

TABLE III. Efficiency of PVC plasticization; Plasticizer content: 28.1 %

Plasticizer	t_g / °C	Δt_g / °C	E'/ MPa at –8 °C	E'/ MPa at 60 °C
Without plasticizer	80	–	–	–
DBP	20.9	–59.1	2087	2.6
DOP	24.9	–55.1	1513	3.4
Oxal	32.9	–47.1	2620	4.5

Analysis of these data shows that the rigidity of PVC films plasticized with Oxal are higher than those of phthalate plasticized films both in the glassy and in the rubbery state (Table III). At the same time, the efficiency of elasticization of the latter in different relaxation states is different. Thus, DOP provides greater elasticity to the glassy polymer, while DBP provides highly soft for rubbery PVC. The efficiency of plasticizers, estimated by the decrease in the glass transition temperature (Δt_g) of the plasticized polymer relative to the original polymer, decreases in the series DBP > DOP > Oxal simultaneously with a lowering in the modulus (Table III) in the rubbery state.

Along with the characteristics of plasticizers presented above, the deformation and strength parameters of plasticized samples and their behavior during accelerated aging are essential. Therefore, in this work, the tensile strength, elongation, and hardness of plasticized PVC films before and after light-thermal aging (see experimental part) were measured. The results of these tests are listed in Table IV.

TABLE IV. Deformation and strength properties of PVC films before and after light-thermal aging

Composite	Properties before aging			Properties after aging		
	Tensile strength, MPa	Elongation %	Hardness cH	Tensile strength, MPa	Elongation %	Hardness cH
PVC+DBP	22.7	220	18.1	22.3	190	23.2
PVC+DOP	25.6	280	16.3	23.4	243	24.1
PVC+ Oxal	33.7	215	55.9	28.6	143	89.4

The data (Table IV) showed a higher rigidity and lower elasticity (elongation) of PVC films plasticized with Oxal, in comparison with those phthalate plasticized. The highest resistance to accelerated light-thermal aging was demonstrated by the samples plasticized with DBP.

CONCLUSIONS

The dynamic viscosity of flotator Oxal was shown to be lower than that of di-(2-ethylhexyl) phthalate (DOP), but higher than that of dibutyl phthalate (DBP). Analysis of the activation parameters of the flow indicates a weaker dependence of the Oxal viscosity on temperature compared to the phthalate plasticizers. Size estimation of PVC particles swollen in the studied plasticizers revealed the high gelation ability of Oxal comparable with that of DBP.

A comparative study of the plasticizing effect by dynamic mechanical analysis (DMA) showed that the lowering the PVC glass transition temperature under plasticizing (Δt_g) decreases in the series DBP > DOP > Oxal, simultaneously with a decrease in the storage modulus in the rubbery state. The data on the mechanical properties exhibit a higher rigidity and lower elasticity of PVC films plasticized with Oxal, in comparison to those with phthalate plasticizers. The highest resistance to accelerated light-thermal aging was demonstrated by the samples plasticized with DBP. Thus, the complete replacement of phthalate plasticizers with Oksal makes it impossible to obtain materials with similar working properties.

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ИЗВОД

ФЛОТАЦИОНИ РЕАГЕНС „ОКСАЛ“ КАО ПЛАСТИФИКАТОР ЗА СУСПЕНЗИЈУ PVC

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Флотациони реагенс „Оксал“, мешавина етара на бази диоксана и алкохола, проучаван је као пластификатор за суспензију PVC у поређењу са познатим дибутил-фталатом (DBP) и ди-2-етилхексил)-фталатом (DOP). Одређени су реолошки параметри и способност желирања пластификатора, мерене су вредности модула сачуване енергије и тангенса угла механичких губитака у стакластом и гумоликом стању методом динамичко-механичке анализе (DMA) и одређене температуре остакљивања. Својства отпорности на деформацију и крутост полимерних филмова тестирани су пре и после излагања светлости и температури. Показало се да „Оксал“ показује прилично низак вискозитет и висока својства желирања код PVC. Истовремено, његова способност да смањи температуру остакљивања и еластичност полимера у стакластом и гумоликом стању је нешто нижа од способности фталатних пластификатора. PVC узорци пластифицирани помоћу DBP имају највећу отпорност на старење после излагања светлости и температури.

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