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New Polyfunctional Modifier of Water Dispersions of Polar Polymers

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Introduction

Water dispersions of polymers present great practical interest due to such factors as their low toxicity, reduced fire hazard and price which is ascribed to the absence of harmful, combustible and expensive solvents in their composition. Besides the viscosity of water dispersion materials is easily controlled by simple water dilution, and it is possible to use polymers with high molecular mass and low acid number. At the same time water dispersions can have some negative implications connected with their latent instability during preparation and utilization. This is why it is effective to use in their compositions polyfunctional water soluble and surface active modifiers which can also be used as plasticizers.

In this aspect the plasticizer EDOS, a mixture of 1,3 dioxane derivatives, presents a special interest. As opposed to traditional plasticizers of polar polymers such as the esters of phthalic acid, EDOS is a low toxic, relatively cheap, partially water soluble one, while being similar in chemical composition to nonionogenic surfactants, as it is based on linear and cyclic formals of dioxane alcohols.

Experimental Part

EDOS is a mixture of 1,3 dioxane derivatives with the formal of 4–methyl-4–hydroxyethyl-1,3–dioxane [1] as the main component. For comparison dibutylphthalate (DBP) was tested. Most experiments were performed with polyvinylacetate (PVA) water dispersions with viscosity in the range of 11-25 sec.

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As investigation methods inverse gas chromatography (IGC), determination of surface stress (SS), critical concentration of micelle formation (CMC), limit absorption (LA), molecular square (MS) and surface activity (SA) were used.

Measurements by IGC method were carried out by gas chromatography with helium as the carrier gas and chromaton as the solid carrier. As sorbates benzene, ethanol, methyl ethyl ketone, nitromethane, pyridine, octane, nonane and decane were used. The research object of IGC method was an immovable polymeric phase and correlation between its properties and sorbates was established. Each of the above mentioned sorbates is capable of one type of intermolecular interactions (IMIs). The IGC method permits to estimate a contribution of each different type of IMIs, [2] depending on water dispersion composition.

Surface stress was determined by measurement of the break force of a platinum ring from the surface of liquid-air separation line by means of DU-NUE instrument.

Critical concentration of micelle formation was determined as the concentration corresponding to the bending of the curve of surface stress vs. plasticizer concentration.

Limit absorption, Gm, was defined as proportional to the tangent of the linear section of the dependence of surface stress with plasticizer concentration (Fig.1), according to the Gibbs equation:

$$G_m = (-1/RT)\cdot[d\sigma/d(\ln c)],$$

where c = CMC, Gm is constant and equal to G_∞, σ is the surface stress, R the universal gas constant, T the absolute temperature.

The area occupied by one plasticizer molecule (S_o - molecular square) in a saturated monomolecular adsorption layer was defined by the formula:

$$S_O = \frac{1}{G_\infty \cdot N},$$

where N_A = Avogadro number ($6{,}02 \cdot 10^{23}$ mol $^{-1}$).

The surface activity G was defined as the slope of isotherm linear section of surface stress with plasticizer concentration (c) approaching zero:

$$G = -\left(\frac{d\sigma}{dc}\right), c \rightarrow 0$$

Results and Discussion

EDOS is effective for water dispersions of polyvinylacetate (PVA), copolymers of butadiene with vinylidenchloride (CBV), and polyacrylates (PA) [1,3].

EDOS possesses colloid solubility in water and water solutions of surfactants [1]. For this reason it causes a twofold decrease of the plasticization process time for PVA dispersions as compared to phthalates. As a result both energy and labour consumption in plasticized PVAD production decrease what gives preference to EDOS use from economical point of view.

This effect is also connected with the higher polarity of EDOS, as established by inverse gas chromatography method through calculation of conditional polarity factors (PF) (Table 1).

Table 1. Polarity factors of binary PVA – plasticizer systems.

Composition (mass fraction)	Type of IMIs				
	Hydrogen	p-donor	Orientation	acceptor	Donor
PVA	5.0	1.5	2.0	2.7	0.65
EDOS	4.1	1.5	2.6	4.7	2.8
DBP	2.7	1.9	1.8	3.1	1.7
PVA-EDOS (100 / 20)	5.5	1.5	3.6	3.0	0.7
PVA-DBP (100 / 20)	5.3	2.1	3.5	3.2	0.8

The latter are higher for EDOS than for DBP with the exception of the p–donor factor (Table 1).The larger p-donor factor of DBP can be ascribed to the presence of the phenyl ring in DBP, which is pertinent to namely this type of IMIs [4]. The larger contribution to the overall conditional polarity factors of plasticized PVAD are hydrogen and acceptor links. Hereby both the above-mentioned plasticizers affect orientational intermolecular interactions to a greater extent.

The value of hydrogen intermolecular interactions in EDOS is closer to PVA as compared to DBP (Table 1). This is one of the reasons of better compatibility of our plasticizer with PVA water dispersions. Indeed, due to absence of chemical interactions between the components, hydrogen bonds play an important role in plasticized water dispersion materials.

EDOS provides better adhesion properties to PVA and PA dispersions and CBV impregnating compounds as compared to DBP. This is ascribed to the presence in EDOS composition of a large quantity of electronegative oxygen atoms and hydroxyl groups able to form hydrogen bonds with atoms of water and polymers.

On the basis of surface stress isotherm analysis [5] we established that EDOS possesses ability to micelle formation as well as surface activity. EDOS decreases surface stress of water dispersions of PVA as well as other polar polymers (Fig 1). It plays the role of a nonionogenic surfactant and possesses colloid-chemical properties comparable with oxiethylnonylphenol (neonol) (table 2). This effect depends on plasticizer composition, method of dispersion production as well as the type of emulgator used [5]. At the same time phthalates do not reveal any surface activity, therefore causing problems with the stability of their water dispersions.

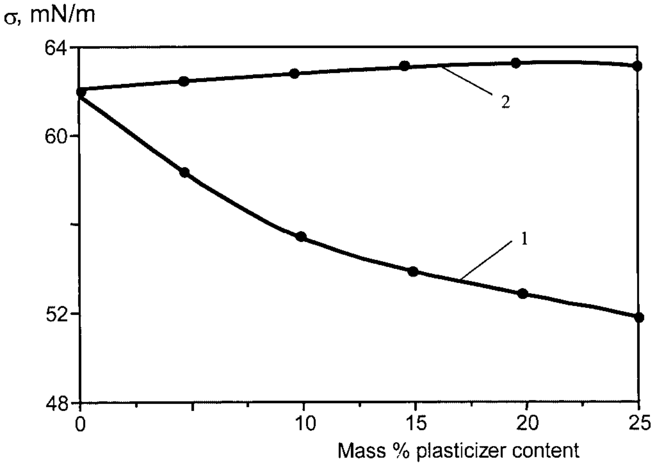

Figure 1. Dependence of surface stress from plasticizer content in PVAD.
1 - EDOS; 2 - DBP.

Table 2. Colloid-chemical properties of EDOS as compared to oxiethylnonylphenol.

Parameters	EDOS	Neonol
CMC, mol/l	0.37	0.10
Limit absorption, 10^6 mol/m^2	2.9	1.8
Molecular square, m^2/mol	0.57	0.36
Surface activity, nm^2/mol	1.2	1.3

EDOS, similarly to the esters of phthalic acid, plays the role of a plasticiser in water dispersions of PVA, CBV and PA. Its use decreases glass transition temperature (Fig 2.). This effect is less evident in the case of EDOS use for PVA dispersions as opposed to DBP. However, it increases with the growth of the content of EDOS' main component – a symmetric formal of 4–methyl-4–hydroxyethyl-1,3–dioxane. Lesser plastification effect is obtained in the case of 4–methyl-1,3–dioxolane. Indeed the 1,3 dioxolane derivatives are less effective plasticizers due to lesser flexibility of the 5-member ring as compared to the 6-member rings in the case of 1,3 dioxanes.

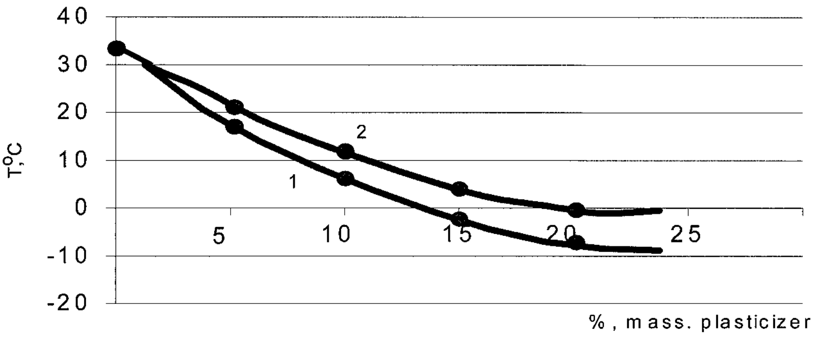

Figure 2. Dependence of glass transition temperature from the content of plasticizer. 1 - DBP, 2 - EDOS.

At the same time, thanks to its surface activity properties, EDOS increases the stability of water dispersion materials and decreases the probability of coagulum creation as well as critical concentration of micelle formation [5]. Besides, due to the presence of components with hydroxyl groups (dioxane alcohols) EDOS improves the adhesiveness of PVA and PA water dispersions as well as CBV latexes. Such increase reaches about 30-70 % (measured as the minimum load at which two PVA or PA-coated stripes of lenderine, a nitrocellulose-impregnated cloth, separate) depending on the content of dioxane alcohols in EDOS composition. It also correlates with plasticizer concentration and achieves its maximum with EDOS content of 10-20 mass % (calculated as the solid residue) (Table 3).

Table 3. Characteristics of PVA dispersions with 15 % mass fr. of different types of plasticisers.

Properties	Unplasticized	EDOS	DBP
Adhesiveness, N/m	0.60	1.20	0.75
Compatibility with plasticizer at 25^{0}C, hours	----	1.5	3.5
Glass temperature, ^{0}C	32	3	-2
Particles size, μm	1.6	1.9	1.75
Viscosity, sec.	17	29	22

So EDOS performs as a polyfunctional modifier in water dispersions of polar polymers. It decreases the polymer glass transition temperature as a plasticiser, and improves adhesiveness as an adhesion-active additive, also reducing surface stress at the phase separation boundary as well as the probability of coagulation processes as a nonionogenic surfactant. By comparison, DOP performs only the first of the above mentioned functions and is less compatible with water dispersions.

Besides, EDOS improves economical and safety-environmental properties of water dispersion materials of different polar polymers and plays a role as a thickener, increasing dispersion viscosity.

EDOS is industrially produced in Russia in three grades and is more than twice cheaper than DBP.

Conclusions

For water dispersions of polar polymers EDOS possesses the following advantages over DBP and other phthalates:

- lesser toxicity (3 danger class of EDOS compared to 2 danger class of DBP);
- colloid water solubility, providing better compatibility with water dispersions and significantly decreasing plasticization time;
- surface activity, increasing stability of water dispersions;
- good adhesive properties;
- possibility of manufacture from by-products of isoprene synthesis, the latter serving as a raw materials;
- possibility of composition control by changing processing conditions of by-products of isoprene synthesis.

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