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THE INFLUENCE OF POLYSTYRENE MODIFIER AND PLASTICIZER NATURE ON THE PROPERTIES OF POLY(VINYL CHLORIDE)

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Abstract: Poly(vinyl chloride) (PVC) has been modified by dissolution of polystyrene modifier in diesterphthalate plasticizer, followed by dispersive mixing with PVC. The effects of the kind of modifier and plasticizer used on the wetting of PVC by the plasticizer have been evaluated. The degree of plasticizer migration out of the material and the effects of the migration on mechanical and thermophysical properties of modified materials have been determined.

Keywords: poly(vinyl chloride), migration, plasticization, modification, polystyrene, ABS plastic.

1. Introduction

Products made of plasticized PVC are widely used in different branches of industry. Such products with necessary elastic-plastic, strength and thermo-physical properties are of great importance [1]: window profiles, pipes, hoses, cables, coatings, *etc.* As per S. Patrick [2] it is possible to directionally control the technological and operational properties of materials plasticized by PVC within a wide range by their combination with other thermoplastics. Some of the authors [3] have found that among procedures of modified materials obtaining the thermoplastic preliminary dissolution in the plasticizer followed by introduction of fine-dispersed PVC is the most rational and economically grounded method. PVC modification by thermoplastic polymers from plasticizer solution allows distributing the polymer-modifier in PVC volume uniformly. This method allows controlling the necessary properties without technological process complication.

Diesters of phthalic acid are widely used as plasticizers for the production of elastic materials based on PVC [2, 4]. They have high affinity with PVC,

considerable plasticizing ability and high boiling temperature. Moreover, in accordance with the last investigations, they are non-toxic [6, 7]. It should be also noted that these plasticizers are capable to dissolve a series of thermoplastic polymers, such as suspension and impact-resistant polystyrene (PS) or acrylonitril butadiene styrene (ABS) plastic.

There are several kinds of polystyrene modifiers. Our goal was determination of the influence of the kind of modifier on the technological (wettability, compatibility, degree of plasticizer migration) and performance (elasticity, plasticity, surface hardness, heat resistance) properties of plasticized PVC.

2. Experimental

PVC polymers of Lacovyl PB1156 type, PS suspension, ABS plastic, and purified plasticizers such as dibutylphthalate (DBP), di-2-ethylhexylphthalate (DEHP) and diisononylphthalate (DINP) were used.

The thermoplastic-modifier was preliminary dissolved in the plasticizer. PVC was combined with modifier solution in the drum mixer. Then the composition was gelatinized for 1 h at 363 K and rolled or extruded at 418 K.

The wetting angles were measured using spreading drop method. A drop of modifier was applied over horizontal PVC basis and then the geometric sizes were determined using digital technique.

The degree of plasticizer migration was determined in 2B-131 oven according to the change of samples mass for 16 h at 363 K. The sample thickness was 1 mm.

The surface hardness by conic flow point was determined at 293 K using Heppler consistometer. The steel cone was pressed in the polymer sample under the loading of 49 N for 60 s. Lip angle was 58°08'.

The elastic-plastic properties were determined using hardness meter of TSHR76 model (ISO 7619). The samples were as flat parallel plates. The steel ball of 5 mm diameter was pressed in the sample for 30 s under the loading of 10 N.

Tensile strength and elongation at break were determined in accordance with standards using tearing machine TIRA Test 2200.

3. Results and Discussion

During PVC plasticization by plasticizers of different nature, in particular diesters of phthalic acid, the phenomena connected with components compatibility play the key role [3-5]. The introduction of polystyrene modifier preliminary dissolved in the plasticizer increases PVC wetting by the plasticizer and improves the components compatibility (Fig. 1) and technological effectiveness of compositions preparation. The wetting value increases in the row of plasticizers as follows: DBP–DINP–DEHP. While using the plasticizers mixture the wetting angles is averaged. The introduction of polymeric modifier in the amount of 2 wt % decreases the wetting angles regardless of plasticizer nature. In other words, the wetting of PVC surface increases, which is connected with the thermo-dynamic properties changing due to the molecular interaction.

For the plasticizers of linear structure: DBP and DEHP the extreme dependence of wetting angles on PS content is observed with the minimum values at 1.5–3 wt % and at 4–6 wt %.

The character of PS effect on the angle of PVC surface wetting by the mixture of DBP and DINP plasticizers is different: it decreases with the increase of polymer content. The reason is the increase of components compatibility in such systems.

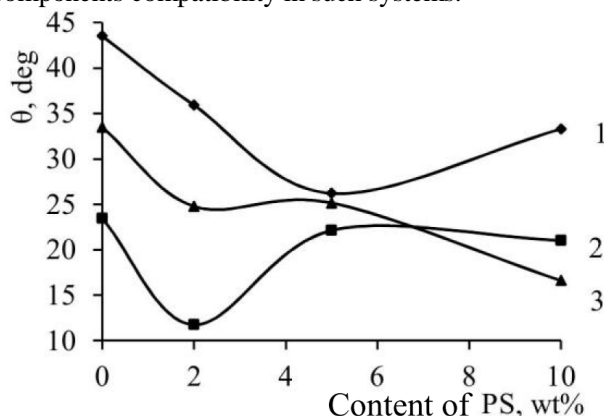


Fig. 1. Effect of PS suspension content on the angle of PVC surface wetting by plasticizers: DBP (1); DEHP (2) and DBP:DINP = 1:1 (3)

At the same time while using ABS plastic the wetting angle increases with the increase of modifier content (for mixture DBP+DINP, Fig. 2).

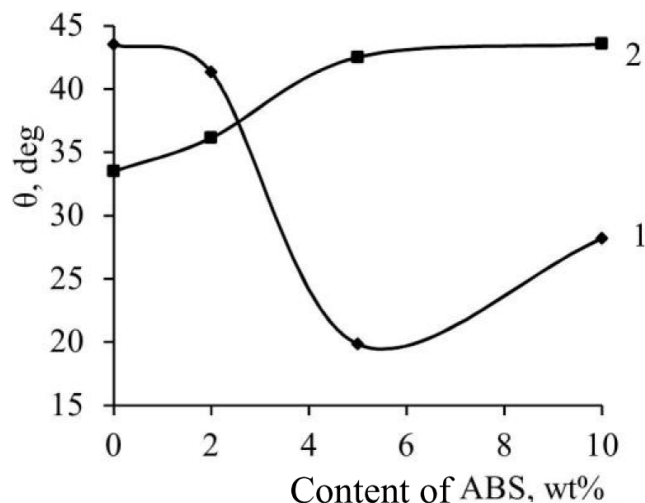


Fig. 2. Effect of ABS plastic content on the angle of PVC surface wetting by plasticizers: DBP (1) and DBP:DINP = 1:1

The increase of ABS content in DBP has the similar effect observed while using PS – the extreme dependence with the minimum values at 4–6 wt % of polymer. It means that while DBP using the effect of polymeric modifier on the components compatibility is of the same type irrespective of modifier nature.

The effect of polymeric modifier nature and amount on the adhesion was investigated using different plasticizers (Fig. 3).

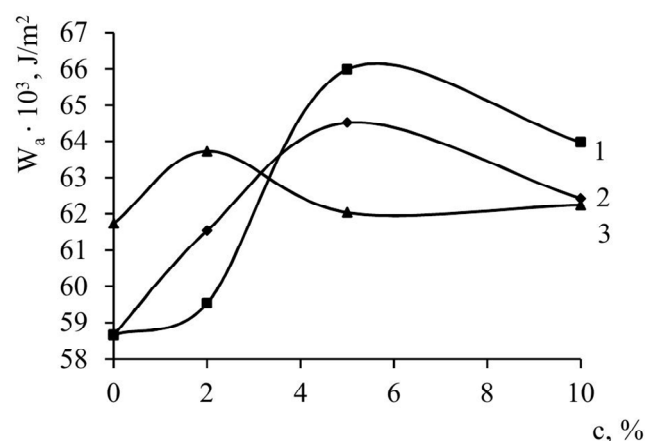


Fig. 3. Effect of polymer-modifier content on the adhesion between PVC and plasticizer: DBP (1, 2); DEHP (3); PS (1, 3); ABS (2)

Regardless of the modifier nature the maximum adhesion is observed at modifier amount of 5 wt % while

using DBP. In the case of DEHP these values are less (2 wt %). The compositions with DBP have higher values of adhesion.

The peculiarities of PVC surface wetting by investigated plasticizers indicate the essential effect of polymeric modifier on PVC and plasticizer compatibility; probably they are connected with the change of thermodynamic characteristics leading to the change of molecular interaction between the components, first of all with the participation of macromolecules.

The quantitative estimation of polymer-containing ternary system is based on the assumption [8] that macromolecules packing may be the reason of their mutual repulsion. At the same time the polymeric mixture viscosity is lower than values of pure components calculated in accordance with additivity rule. If there is an interaction between polymers, the macromolecule associates of both types are formed and viscosity increases. The data on viscosities were quantitatively interpreted in accordance with the model [8, 9]. The estimation of interaction between different macromolecules was carried out on the basis of comparison between parameters of molecular interaction determined from experimental data on viscosities ($b_{12\text{exp}}$) and theoretically calculated data ($b_{12\text{theor}}^*$). The theoretical parameter was calculated according to the formulas:

$$b_{12}^* = (b_{11}b_{22})^{1/2} \quad (1)$$

where $b_{11} = K_{x1}[h_1]^2 \quad (2)$

$$b_{22} = K_{x2}[h_2]^2 \quad (3)$$

The experimental parameter $b_{12\text{exp}}$ was calculated according to the equation:

$$h_{\text{spec.blend}} = [h]_1 C_1 + [h]_2 C_2 + b_{11} C_1^2 + 2b_{12\text{exp}} C_1 C_2 + b_{22} C_2^2 \quad (4)$$

where $[\eta]_1$ and $[\eta]_2$ – characteristic viscosities of the individual polymers; C_1 and C_2 – concentrations of first and second polymers in the mixed solution. Defined in this manner was the following value:

$$\Delta b_{12} = b_{12\text{exp}} - b_{12\text{theor}}^* \quad (5)$$

Thus Δb_{12} allows to consider the prior interaction between dissimilar macromolecules, *i.e.* the presence of mixed associates in the solution (positive value) or between the similar ones, *i.e.* the presence of homoassociates (negative value).

Fig. 4 represents the dependence of Δb parameter on polymer concentration in the solution, their ratio and plasticizer nature.

It should be noted that the most essential interactions in PVC-PS-plasticizer system are observed at

polymer low concentrations in the plasticizer solution and at the small amount of one polymer relative to another. In the compositions with PVC content of 90–95 % the values Δb is positive. This fact testifies to the attraction between dissimilar macromolecules of PVC and PS and existence of mixed associates and hence, to greater compatibility between system components. At the same time the nature of diesterphthalate plasticizer have minor effect on PVC and PS compatibility in the solution.

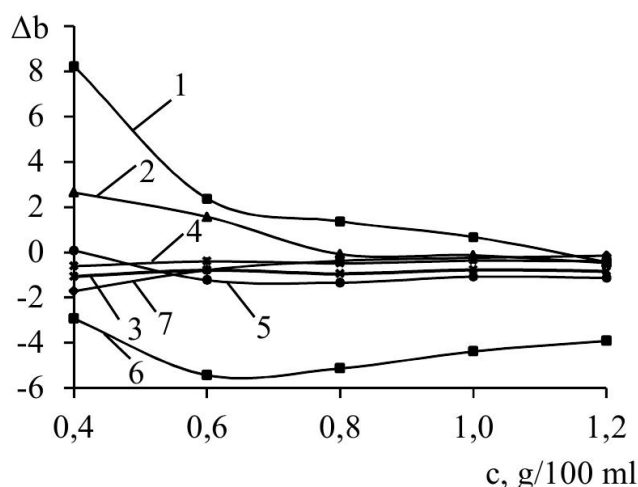


Fig. 4. Dependence of compatibility parameter Δb on polymer concentrations in the solution and plasticizer nature: DEHP (1–6) and DBP (7). PVC:PS (w/w) ratio: 0.95:0.05 (1); 0.90:0.10 (2); 0.80:0.20 (3, 7); 0.50:0.50 (4); 0.20:0.80 (5); 0.05:0.95 (6)

During PVC plasticizing by diesters of phthalic acid, namely DBP and DEHP, the phenomena connected with thermodynamic compatibility play the key role. In this work the compatibility is characterized by wetting of PVC surface by plasticizers and compatibility parameter. These factors have considerable influence on the release (migration) of plasticizer from poly(vinyl chloride) plasticates during exploitation of products on their basis and, therefore, on their properties.

The release of plasticizer is a negative factor affecting the final properties of polymer materials [10]. We studied kinetic regularities of plasticizer release depending on its nature and nature of polymer-modifier (Fig. 5).

The introduction of polymeric modifier into plasticized PVC decreases the plasticizer migration, especially for more elastic materials.

The lowest values of migration degree are observed for DINP and the highest ones – for DBP. Obviously it is connected with the molecular weight of plasticizer and its affinity with PVC. At the same time the increase of plasticizer content in PVC increases the migration degree.

The effect of polymer-modifier on migration degree of plasticizer is observed most of all at high values of plasticizer content.

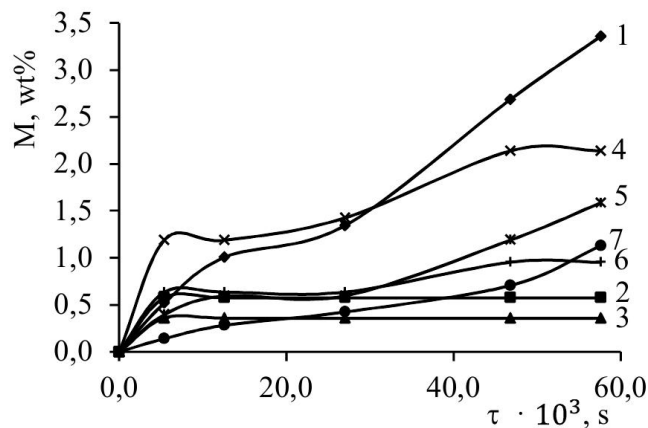


Fig. 5. Kinetics of plasticizer release from PVC materials depending on plasticizer nature: DBP (1, 5, 6); DEHP (2, 7); DINP (3); DBP:DINP (w/w) = 1:1 (4) and polymeric modifier: ABS (5); PS (6, 7). Plasticizer content is 23 %, modifier content is 2.1 %

From the standpoint of plasticized PVC use the physic-mechanical properties, especially elastic-plastic and thermo-physical ones, together with technological characteristics, are important factors.

The highest value of hardness (95.5 %) is observed for plasticized PVC based on DINP (Table 1). Obviously it is connected with specific interactions between components and their effect on composite morphology. While using DBP and DINP the hardness essentially decreases (49.6 %) but elasticity is almost the same.

It should be noted that elasticity of PVC materials increases with the increase of modifier content. The hardness increases as well. It is observed most of all at high content of plasticizer. Thus, for the compositions based on DBP the increase of PS content by 1.5 times increases the hardness from 13.08 to 19.60 MPa and elasticity from 48.3 to 84.6 %. The same regularity is observed while using ABS plastic as the modifier.

The increase of modifier content allows to support elastic properties of plasticized PVC at high level (elasticity is 80–84 %) even at the considerable (by 4 times) increase of plasticizer content.

Table 1

Effect of plasticizer and modifier nature on strength properties of PVC

PVC	Composition, wt parts					Elastic-plastic properties			Vicat softening point, K
	Plasticizer			Polymer		Hardness H , MPa	Elasticity S , %	Plasticity P , %	
	DBP	DEHP	DINP	PS	ABS				
100	30	–	–	–	–	7.1	42.5	57.5	~295
100	–	30	–	–	–	62.2	40.6	59.4	313
100	–	–	30	–	–	95.6	68.4	31.6	325
100	15	–	15	–	–	93.5	49.6	50.4	313
100	30	–	–	–	2.8	22.2	52.5	47.5	309
100	30	–	–	2.8	–	13.1	48.3	51.7	308
100	30	–	–	4.2	–	19.6	84.6	15.4	–
100	90	–	–	13.4	–	6.3	80.1	19.9	–
100	120	–	–	17.6	–	4.6	81.3	18.7	–
100	–	30	–	2.8	–	101.2	59.0	41.0	311

Table 2

Effect of filler based on PS and ferrum oxide on the operational properties of PVC composites

Composition, wt parts			σ , MPa	ε , %	F , MPa
PVC	DBP	Filler			
100	30	0	7.3	15	39.1
100	30	5	12.9	11	52.6
100	50	0	5.3	108	34.8
100	50	5	4.6	102	13.6
100	50	50	2.2	58	19.8

Notes: σ – tensile strength, MPa; ε – elongation at break, %; F – surface hardness, MPa.

Such peculiarities of elastic-plastic properties of modified PVC are connected with reduction of plasticizer molecules mobility under the influence of polymeric modifier and formation of dense fluctuating network in the presence of polystyrene macromolecules. At the same time the nature of plasticizer and polymeric modifier also affects the thermo-physical properties of plasticized PVC, which are estimated by Vicat softening point. The increase of softening temperature is observed while using plasticizers in the row DBP–DEHP–DINP. The DBP+DINP mix averages the softening temperature values. Polystyrene modifier increases softening temperature of plasticized PVC based on DBP by 15–20 K.

It should be noted that using polymer-inorganic composite based on polystyrene and Fe_3O_4 with 30 % DBP as the modifier increases tensile strength and hardness (Table 2). The converse is observed at plasticizer content of 50 %. Such peculiarities of modified PVC are connected with the change of interphase layers characteristics [11], mutual influence of plasticizer and filler on PVC morphology, different nature of interaction, and different swelling index of polystyrene in plasticizer with its possible dissolution and distribution in PVC matrix.

4. Conclusions

The physical modification of plasticized PVC by PS suspension or ABS plastic with preliminary dissolution of modifier in diesterphthalate plasticizer and compatibility with PVC allows to uniformly distribute the modifier, increases the compatibility between components and decreases the migration of plasticizers from the matter volume.

The introduction of polystyrene modifier allows to directly control the elastic-plastic properties of plasticized PVC and increases the surface hardness, tensile strength and Vicat softening point.

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ВПЛИВ ПРИРОДИ ПОЛІСТИРОЛЬНОГО МОДИФІКАТОРА Й ПЛАСТИФІКАТОРА НА ВЛАСТИВОСТІ ПОЛІВІНІЛХЛОРИДНИХ ПЛАСТИКАТІВ

***Анотація.** Проведено фізичне модифікування полівінілхлоридних пластикатів, яке включає попереднє розчинення полістирольного модифікатора в діестерфталатному пластифікаторі з подальшим суміщенням з дисперсним полівінілхлоридом. Встановлено і обґрунтовано вплив природи полістирольного модифікатора і діестерфталатного пластифікатора на змочуваність полівінілхлориду пластифікатором, ступінь його мігрування з об'єму матеріалу, а також на пружно-пластичні, міцнісні та теплофізичні властивості модифікованих матеріалів.*

***Ключові слова:** полівінілхлорид, міграція, пластифікація, модифікація, полістирол, ABS пластик.*

