Modification of PVC-compositions for Linoleum

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Abstract. Nowadays, modification is one of the most effective methods of enhancing quality of building compound materials and broadening the scope of their application. Polyvinylchloride (PVC) linoleum is manufactured and used massively in construction industry. The plasticizer EDOS is applied as one of the components of this composite material, it represents the mixture of derivatives of 1,3-dioxane distinguished from other traditional plasticizing agents by its lower cost and toxicity. At the same time, this plasticizer, due to its lower heat stability and higher fugitiveness, requires incorporation of special types of modifying additives into the linoleum composition. Those additives reduce its migration from flooring material during its production and maintenance. In this view, reactive compounds with epoxy and cyclocarbonate groups able to form hydrogen and chemical bonds with the EDOS plasticizer are of certain interest. The authors proposed the method of modification of PVC-compound materials by application of epoxidized soybean oil with conversion of epoxy groups in a modifier (%) 53, 75 and 90. For analysis the authors have chosen cyclocarbonate Laprolat-83 of domestic industrial manufacturing. Using the standard and advanced high-information physical and chemical methods, the authors have researched the properties of epoxidized soybean oil, the processes of migration of the plasticizer EDOS from PVC-paste and PVC-linoleum, miscibility of plasticizer with modifying agent. The composition formulation has been optimized. The implemented research has resulted in reducing migration of volatile substances from PVC-paste and linoleum, achievement of additional flexibilizing effect, enhancing modulus of elasticity and wearing property, shrinkage reduction and improvement of sanitary and hygienic properties of linoleum.

1. Introduction

Throughout the last few decades polyvinylchloride (PVC) linoleum has established its position on the domestic market of flooring materials. Selection of PVC linoleum is rather wide as it’s produced by both Russian and foreign manufacturers [1,2].

Due to its high demand on the flooring market, development of effective methods of modification of PVC-compositions with the purpose of intended modification of their performance, sanitary-hygienic, processing and economic properties of linoleum, received utmost priority.

In recent times, EDOS is widely used as a plasticizer for PVC-composite materials for linoleum. It’s distinguished from traditional plasticizer additives – phthalate esters – by its lower cost and toxicity [2].
At the same time, due to its lower heat stability and higher fugitiveness, effective use of this plasticizer requires introduction of special types of modifying agents which enable reducing its migration from flooring material during production and maintenance.

In this, the use of reactive compounds with epoxy and cyclocarbonate groups [3,4] forming hydrogen and chemical bonds with plasticizer EDOS is of certain interest. Thus, epoxidized soybean oil is well known as a stabilizer and plasticizer of PVC-composite materials.

2. Materials and methods
For linoleum manufacturing, the following components were applied: paste plastic emulsion PVC-resin, grade PVC-E-6250-Zh (GOST 14039-78), reinforcing material - micro marble (TU 5716-001-99242322-2007), plasticizer EDOS – the mixture of 1,3-dioxane (TU 2493-003-13004749-93). As a modifying agent, there were applied specially synthesized [7] cyclocarbonates of epoxidized soybean oil with fractional conversion of epoxy groups into cyclocarbonate equal 55, 75, and 90% correspondingly (CCESO-55, CCESO-75, CCESO-90). As a comparison, the following industrial additives have been used: additives with epoxy and cyclocarbonate functional groups – Laprolat-803 (tricyclocarbonatepropyl ether of polyoxypropylene triol) with functionality 3 (TU 2226-034-10488057-2003), epoxidized soybean oil (ESO).

Linoleum abrasion has been determined by means of the drum-type machine MIVOV-2 according to GOST 11529-86; variation of linear dimensions of roll materials has been valued according to GOST 7251-77. Migration of plasticizer from PVC-paste and linoleum has been determined in compliance with the European standard EN 664 1994. Dynamic mechanical analysis was carried out with the use of appliance NETZSCH DMA 242 at frequency of 1 Hz in argon atmosphere with the gas flow rate of 50 ml/min in the temperature range from -80 up to 100°C.

3. Results and Discussion
Cyclocarbonates of epoxidized soybean oil (CCESO) have flash-point higher than 200°C i.e. they are more thermally stable than plasticizer EDOS. Moreover, the compounds containing cyclocarbonate groups are able to interact with ether bonds [4,5] in EDOS molecule.

The main problem of obtaining cyclocarbonates on the base of epoxidized vegetable oils limiting their industrial production is long processing time and relatively high pressure required for reaction behavior.

Due to this factor and high viscosity coefficient of CCESO, the authors researched cyclocarbonates with incomplete transformation of epoxy groups into cyclocarbonate ones as modifying agents. This technique allows lowering viscosity coefficient of CCESO, their synthesis time, and then power consumption related to their production and cost.

CCESO are miscible with plasticizer EDOS and can form homogeneous mixtures with lower fugitiveness and higher flash-point [1].

Due to its relatively high fugitiveness, plasticizer EDOS can migrate to the surface of PVC roll materials during production and maintenance. This factor adversely affects performance properties of flooring materials [8].

Quantitative assessment of miscibility of plasticizer and polymer is estimated, according to the references [9], with the use of solubility parameter ($\delta$). Nowadays, there exist few theories of solubility. At present time, HSP-theory (Hansen Solubility Parameters) [9] is considered to be the most credible. It takes into account the influence of three parts of interaction on solubility such as polar ($\delta_p$), interaction on expense of hydrogen bonds ($\delta_h$) and dispersive one ($\delta_d$).

Using the additive method of calculations, we’ve defined gram-molecular volume and partials of solubility parameter for EDOS compounds according to the formulas 1-4:

$$\Sigma \Delta V = \Sigma n_i \Delta V_i, \text{ m}^3/\text{mole}$$

$$\delta_p = (\Sigma n_i \Delta V \delta_{pi}^2 / \Sigma \Delta V)^{1/2}, (\text{MJ/m}^3)^{1/2}$$

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\[ \delta_h = \left( \sum n_i \Delta V \delta_h^2 / \sum \Delta V \right)^{1/2}, \text{(MJ/m}^3\text{)}^{1/2} \tag{3} \]
\[ \delta_D = \left( \sum n_i \Delta V \delta_D^2 / \sum \Delta V \right)^{1/2}, \text{(MJ/m}^3\text{)}^{1/2} \tag{4} \]

where \( n_i \) – quantity of \( i \)-functional group in molecule.

The values of \( \Delta V \delta_p^2 \), \( \Delta V \delta_h^2 \), \( \Delta V \delta_D^2 \) and \( \Delta V \) corresponding atom groups are set out in Table 1.

### Table 1. Values of partials of solubility parameter of functional groups

| Functional group | \( \Delta V \cdot 10^6 \), m\(^3\)/mole | \( \Delta V \delta_p^2 \cdot 10^6 \), MJ/mole | \( \Delta V \delta_h^2 \cdot 10^6 \), MJ/mole | \( \Delta V \delta_D^2 \cdot 10^6 \), MJ/mole |
|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| CH\(_3\)-         | 33.5                            | 0                               | 0                               | 4710.15                         |
| -CH\(_2\)-        | 16.1                            | 0                               | 0                               | 4940.42                         |
| -CH<             | -1.0                            | 0                               | 0                               | 3433.18                         |
| -C\(_\xi\)        | -19.2                           | 0                               | 0                               | 1465.38                         |
| -O-              | 3.8                             | 2093.40                         | 1884.06                         | 0                               |
| -O-(cycle)       | 3.8                             | 2512.08                         | 1884.06                         | 0                               |
| -OH              | 10                              | 2930.76                         | 21143.34                        | 7410.64                         |

Table 2 represents the values of partials of solubility parameter of PVC [9].

### Table 2. Partials of Hansen solubility parameter of PVC and solubility radius

| Polymer | \( \delta_D \) (MJ/m\(^3\))\(^{1/2} \) | \( \delta_p \) (MJ/m\(^3\))\(^{1/2} \) | \( \delta hb \) (MJ/m\(^3\))\(^{1/2} \) | R |
|---------|---------------------------------|---------------------------------|---------------------------------|---|
| PVC     | 18.40                           | 6.60                            | 8.00                            | 3.00 |

For PVC dissolving capacity is described by the radius \( R=3 \) (MJ/m\(^3\))\(^{1/2} \) [2] limited by the solvents of the given polymer. Solubility parameter of PVC is the centre of this area.

It’s proved that migration of volatile components from plasticized EDOS-paste on the base of emulsion PVC in modification by all researched reactive additives is decreased noteworthy (table 3). This could be explained by lowering fugitiveness of EDOS when cyclocarbonates and ESO are introduced as this particular parameter determines migration on the present stage of linoleum production [2].

### Table 3. Modifying-agent effect on migration of plasticizer EDOS from PVC-paste

| Migration,% | 3.9 | 3.7 | 3.3 | 3.4 | 4.0 | 4.1 |
|-------------|-----|-----|-----|-----|-----|-----|

*Note: content of modifier 5 pts. wt. for 100 pts. wt. of PVC.

At that, the use of laprolat L-803 has the most insignificant effect and the use of CCESO with the degree of conversion 55-75%— the maximum (lowering migration for 15-20%). ESO has intermediate antimigration effect in terms of value.
Based on these data, unique correlative correspondence between the value of antimigration effect and the content of cyclocarbonate (CC) or epoxy groups in modifiers is not observed. Thus, concentration of CC-groups in laprolat L-803 and CCESO-75 is virtually the same while effectiveness of their influence on EDOS-migration differs fundamentally.

It is evident that viscosity of modifying agents and structure of a polymer backbone (steric factors) has certain effect. Thus, laprolat has a more branched molecule than cyclocarbonates of epoxidized soybean oil which can hinder its interaction with EDOS-plasticizer. CCESO-90 has lower antimigration effect due to higher viscosity and lesser miscibility with PVC-paste.

As compared with CCESO, ESO has lesser impact on migration of EDO from PVC-composite materials. Apparently, cyclocarbonate groups in modifying agent interact with plasticizer EDOS more actively than epoxy groups regardless of their position in a polymer backbone [9]. In our opinion, it points to importance of the role of functional groups nature as compared to modifiers’ viscosity in lowering migration of plasticizer.

Migration of EDOC from linoleum is significantly lower than from PVC-paste, however, its decrease is greater when modification is applied [1,2]. Apparently, it is connected with the fact that a large portion of volatile components of plasticizer has already migrated during the process of thermally induced gelation of the paste and their residual amounts have been extracted on the surface of PVC-linoleum. It is necessary to take into account that during the linoleum production stage migration of EDOS to the surface is limited by plasticizer’s diffusion. Evidently, interaction of EDOS with modifiers has greater influence on this factor.

Table 4. Performance properties of PVC-linoleum plasticized by EDOS and modified by CCESO

| Type of modifier | CCESO-90 | CCESO-75 | CCESO-55 | No modifier added |
|------------------|----------|----------|----------|-------------------|
| Abrasive resistance, mcm | 27.7 | 25.5 | 24.6 | 29.6 |
| Shrinkage, % | 0.015 | 0.01 | 0.01 | 0.02 |

*Note: the content of modifier is 5 pts. wt. for 100 pts. wt. of PVC

Using DMA it was proved that both laprolat and cyclocarbonates of epoxidized soy oil have flexibilizing effect on a polymer [10]. This becomes evident in lowering temperatures of all fixed relaxation transitions (figure 1).

It is notable that these effects are higher in the case of application of CCESO-75 than laprolat. This can be ascribed to a greater length and flexibility of molecular backbone of cyclocarbonates on the base of soybean oil.

Both types of the researched cyclocarbonates can enhance dynamic modulus of PVC-compounds in the broad temperature range. In our opinion, this could be explained by forming physical and hydrogen bonds between cyclocarbonates and PVC and their probable chemical interaction with EDOS [5,6].

It is well known that in the systems ‘PVC - modifying agents’ with oxygen-containing groups, bonding energy between HC-CL and COOR is 1.5 times as high as the energy between groups HC-CL of neighbouring molecules of a polymer.

For PVC-compounds modified by laprolat in the area of α-relaxation (relaxation transition) the higher values of mechanical loss tangent are observed as compared to application of CCESO-75 or non-modified compound. This can be ascribed to a higher level of molecular motion of PVC-compounds containing L-803 attributed, apparently, to the presence of ether links in the structure of laprolat [10].
Figure 1. Temperature dependences of dynamic modulus (1) and mechanical loss tangent (2) of PVC-compounds modified by 5 pts. wt. of CCESO-75

4. Conclusion
Thus, application of CCESO-75 as a modifying agent with optimal functionality allows reducing migration of EDOS from PVC-paste and linoleum on its base, has flexibilizing effect, lowers shrinkage and improves abrasive resistance of this flooring material. In equal measure sanitary and hygienic properties of linoleum are also improved as cyclocarbonates are produced on the base of renewable plant raw materials.

References
[1] Gotlib E, Kozhevnikov R, Miloslavskij D, Sokolova A and Shajkhutdinov R 2014 Modifikaciya PVH kompozicii dlya izgotovleniya linoleuma ciklokarbonatami epoksidirovannyh rastitel'nyh masel [Modification of PVC-compounds for Linoleum Production by Cyclocarbonates of Epoxidized Vegetable Oils] J Vestnik KGSU 17 no 8 pp 139-140
[2] Gotlib E, Kozhevnikov R and Sadykova D 2015 PVH linoleum: klassifikaciya, sposoby proizvodstva, analiz rynka, receptury, svojstva [PVC-linoleum: Classification, Production Methods, Market Analysis, Formulation, Properties] Kazan KNITU p 135
[3] Doll K and Erhan K 2005 The Improved Synthesis of Carbonated Soybean Oil Using Supercritical Carbon Dioxide at a Reduced Reaction Time J Green Chem 7 pp 849–854
[4] Tayde S, Patnail M, Bhagt S and Renge V 2011 Epoxidation of Vegetable Oils: a Review IJAET 2 4 pp 491–501
[5] Meier M, Metzger J and Schubert U 2007 Plant Oil Renewable Resources as Green Alternatives in Polymer Science. J Soc. Rev. 36 pp 1788–1802
[6] Sharma V and Kundu P 2006 Addition polymers from natural oils – A Review J Prog. Polym. Sci. 31 Is. 11 pp 983-1008
[7] Gotlib E, Miloslavskij D and Akhmetzyanova R 2013 Ciklokarbonaty na osnove epoksidirovannyh rastitel'nyh masel [Cyclocarbonates on the Base of Epoxidized Vegetable Oils] J Vestnik KGTU 16 Is 9 pp 138-141
[8] Kerimov E 2007 Ocenka potrebitel'skih svojstv i konkurentosposobnosti PVH linoleumov s primenieniem funktsional'no-stoimostnogo analiza: avtoref. dis. …kand. tekhn. nauk p 19

[9] Miloslavsky D, Gotlib E, Figovsky O and Pashin D 2014 Cyclocarbonates Based on Vegetable Oils  *Int. letters of Chemistry, Physics and Astronomy* **8** pp 20-29.

[10] Gotlib E, Kozhevnikov R and Miloslavkij D 2016 Dinamicheskie mekhanicheskie svojstva PVH kompozicij, plastificirovannyh ciklokarbonatami [Dynamic Mechanical Properties of PVC-compounds Plasticized by Cyclicarbonates] *Izvestiya Komi nauchnogo centra UrO RAN* **2(28)**