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POLYMERIC MATERIALS BASED ON REACTIVE FUNCTIONAL OLIGOMERS

Purpose. Research of structural characteristics of the alkyd resins and materials based; addition to structure alkyd resin diene/vinyl liquid rubbers and oligomers with various functional groups allows receiving polymeric materials of the various structural organization and the increase physicochemical parameters.

Methodology. A films modified polymeric alkyd materials have been characterized by methods of IR-spectroscopy where devices Tensor-37 (Bruker, Germany).

Findings. Have been received modified polymeric film-forming materials with high protective properties by interaction alkyd resin and synthesized oligomers. It is proved, that at presence in structure alkyd 3÷5 % diene/vinyl oligomers result in substantial increase of parameters of impact resistance, elasticity and adhesion to a metal surface.

Originality. First established of interrelation of influence, it is proved, that at presence in structure alkyd 3÷5 % diene/vinyl oligomers result in substantial increase of parameters of impact resistance, elasticity and adhesion to a metal surface.

Practical value. These materials can be recommended for using as protective coatings for energy and chemical equipment, autoindustries and the objects of domestic facilities.

Keywords: oligoisoprene, oligostyrene, radical polymerization, modification.

Introduction. At present, significant progress has been research on the synthesis of polymeric materials based on reactive oligomers with terminal functional groups. The changing nature of the functional groups in these oligomers can vary their physicochemical properties and, therefore, extends the possibilities of their use in various industries. Were carried out to develop methods for the synthesis of oligomers with terminal functional groups (amide, hydroxyl, epoxy, urethane, acrylate) [1–3]. As the monomers used isoprene, styrene, acrylate, aliphatic isocyanates and polyols nature. Synthesis oligodiene / oligovinyl with terminal amide and hydroxyl groups were carried out in methanol by free radical polymerization initiation 2.2 azo-bis-isobutiroamide [4–7]. Product yield was 25 – 80%, depending on the nature of the initial monomer. By physical modification of alkyd resins functionalized oligomers of these formulations have been developed polymeric film-forming materials (PPM) [8, 9]. It is proved that the increase in rates of adhesion and impact strength with the introduction of the MRP is 3 – 5% (by weight) of modifying-oligomers in the alkyd resin. Products based on them are characterized by adhesion to the surfaces of various materials, high dielectric properties, hardness and resistance to corrosion and water, as well as a sharp change in temperature.

Setting objectives. The aim of this study was to develop methods of modifying the industrial alkyd resins functionalized by oligomers, and obtaining on their basis of coatings with improved physical-mechanical properties.

Results of investigations. Synthesis and properties of the functional oligomers.

Chemical modification of the structure of vinyl and diene oligomers, is a promising method to create complex materials with improved properties. In most cases, this approach determines the need for additional steps or even the specific processes of chemical activation of macromolecular chains, which leads to the creation of oligomers with the respective functional groups.

Oligoisoprene / oligostyrene with amide terminale groups. Amide terminated oligomers of both isoprene and styrene as well as their cooligomers were synthesized by a free radical polymerisation in methanol using ABIA as initiator. Firstly, 0.75 g (0.0039 mol) of initiator (ABIA) was dissolved in 10 ml of methanol, and then this solution was mixed with 40 ml of styrene monomers (0.3997 mol). Chemical reaction was carried out for 10 hours in an autoclave at continuous stirring and at temperature $90 \pm 0.05^\circ\text{C}$. The final products of the reaction were dried from the solvent and unreacted monomers under vacuum conditions. The monomers of styrene and isoprene were taken at different combinations, and the functionality of the synthesized oligomers was varied by the ratio of monomers to initiator. The chemical structures of the synthesized oligomers of isoprene and styrene are presented in Fig. 1 (A) and (B) respectively. The samples abbreviation and their chemical compositions are given in Table 1. A product yield of the oligomers varies in the range of 30 – 80 % and depends on the ratio of the monomers to initiator.

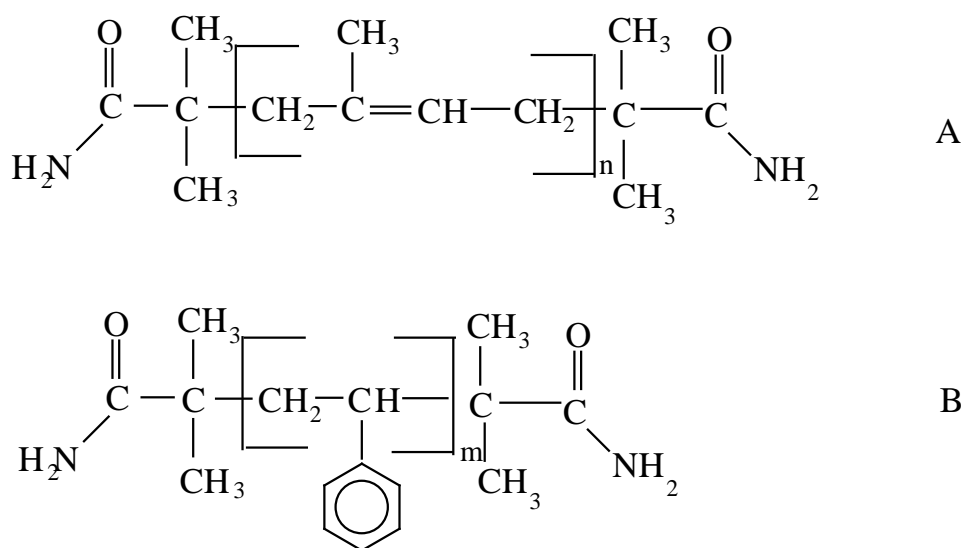


Fig. 1. The chemical structures of the synthesized oligomers of isoprene (A) and styrene (B).

The structural features of the original reagents and products of the reaction was studied by infrared spectroscopy with Fourier-transform on a spectrophotometer "Tensor-37" (f. Bruker, Germany), spectral range of $600 - 4000 \text{ cm}^{-1}$.

FTIR-spectra of the initiator ABIA (Fig. 2, spectrum 1) showed characteristic intense bands of stretching vibrations around $3150 - 3450 \text{ cm}^{-1}$ NH_2 (max. $3188, 3401, 3429 \text{ cm}^{-1}$) stretching vibrations of $\text{C}=\text{O}$ (max. at 1671 cm^{-1}) and deformation vibrations of $1500 - 1600 \text{ cm}^{-1}$ NH_2 (max. $1574, 1629 \text{ cm}^{-1}$) of the amide group ($-\text{CONH}_2$). The bands of deformation vibrations CH , CH_2 , CH_3 groups are showed around $1300 - 1500 \text{ cm}^{-1}$ and $600 - 900 \text{ cm}^{-1}$.

Table 1.

Characteristics of the synthesized oligomers: number average molecular weight (Mn) and polydispersity index (Mw/Mn), content of amide groups, and functionality (f) of the oligomers

| Samples code | Mn (g/mol) | Mw/Mn | Amide content (%) | f | Yield (%) |
|--------------|------------|-------|-------------------|------|-----------|
| OI (50:1) | 3400 | 3,09 | 2,48 | 1,92 | 45 |
| OI (100:1) | 4200 | 2,78 | 2,10 | 2,00 | 40 |
| OI (200:1) | 9700 | 1,79 | 0,88 | 1,94 | 31 |

The IR spectra (Fig. 2, spectrum 2) of synthesized OI terminated amide groups demonstrated the bands of stretching vibrations NH_2 with max. $3467, 3408, \text{cm}^{-1}$, absorption bands characteristic of the $\text{C}=\text{O}$ (max. $1675, 1643 \text{ cm}^{-1}$ amide I) and NH_2 (max. 1605 cm^{-1} , amide II) of the amide group ($-\text{CONH}_2$). The appearance of a large absorption bands at $2900\text{-}3200 \text{ cm}^{-1}$ for the CH_2 groups are demonstrated.

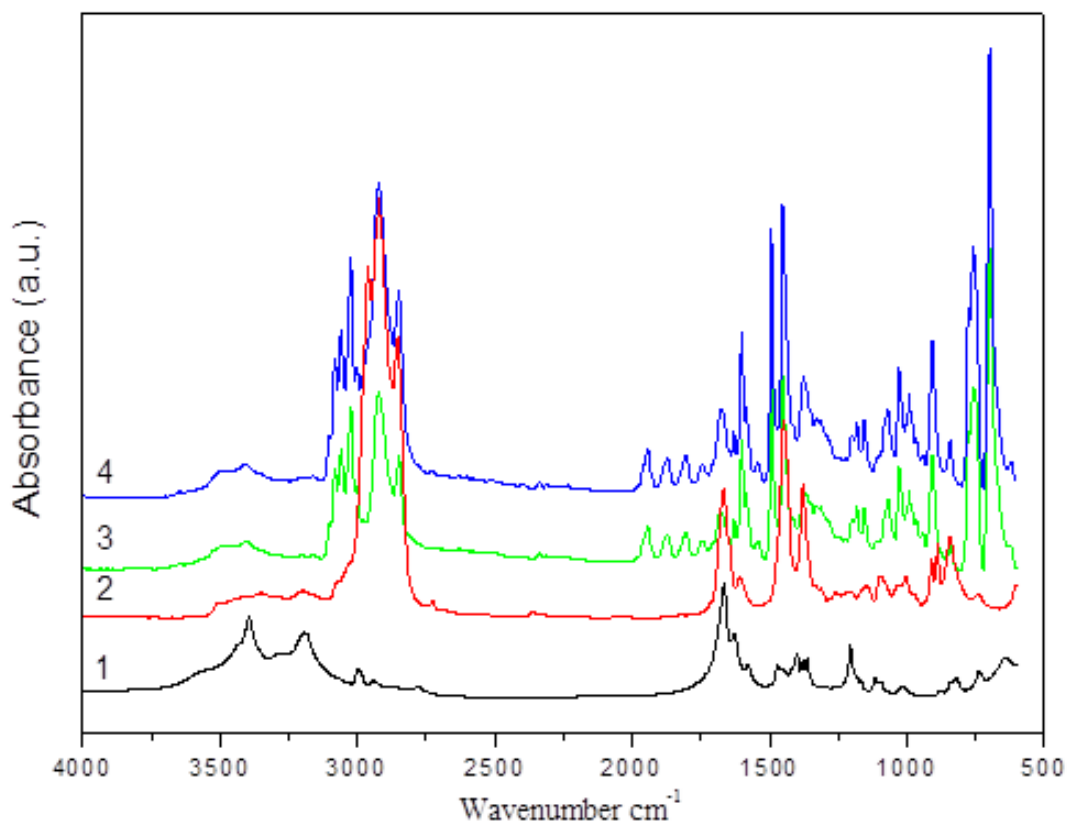


Fig. 2. Fragments of the IR-spectra for: ABIA – (1), OI – (2), OS – (3) and CO – (4).

The IR spectra (Fig. 2, spectrum 3) of synthesized OS with amide groups a showed absorption bands broad characteristic of the NH_2 end groups (max. $3481, 3408, \text{cm}^{-1}$), absorption

bands characteristic of the bands of stretching vibrations of C=O linkages (max. 1671, 1628 cm⁻¹ amid I) and NH₂ at (max. 1577 cm⁻¹, amide II) of the amide group (-CONH₂).

The IR spectra (Fig. 1, spectrum 4) CO with amide groups are observed characteristic bands of stretching vibrations of NH₂ (max. 3474, 3411 cm⁻¹), stretching vibration of C=O (max. 1678, 1631 cm⁻¹ amid I) and NH₂ bending vibrations (max. 1581 cm⁻¹, amide II) of the amide group (-CONH₂).

IR spectra copolymer of isoprene with styrene (Fig. 1, spectra 3 and 4) is showed the bands of deformation vibrations (1800 – 2200 cm⁻¹) and stretching vibrations (3000 – 3200 cm⁻¹) of the CH groups phenyl ring.

Thus, the presence in the IR spectra of OI, OS, and CO with the terminal amide groups of absorption bands characteristic of amide groups, indicate the formation of oligomers of the proposed structure.

Applications. Have been received modified polymeric film-forming alkyd materials with high protective properties by interaction alkyd resin (varnish PF-060) and synthesized functional oligomers with amide groups. It is proved, that at presence in structure alkyd 5 % oligomers result in substantial increase of parameters of durability at impact, elasticity and adhesion to a metal surface.

Table 2.

Comparative physicochemical parameters of the synthesized polymeric film-forming material and industrial analogue PF-060

| Parameter | Industrial analogues PF-060 | Polymeric film- forming materials |
|---|--------------------------------|--------------------------------------|
| Drying time of film to degree 3, at 20±5 °C, hour | 27 | 24 |
| Hardness, point | 0,38 | 0,43 |
| Adhesion, (Method of trellised cuts), point | 2 | 1 |
| Shock strength, κGs | 20 | 50 |
| Elasticity, mm | 1 | 1 |
| T _g , °C | 18,94 | 13,30 |
| ΔC _p , Jg/K*grad | 0,270 | 0,296 |

It was determined that obtained materials are significantly better then industrial analogues by their physical chemical and protective properties, especially anticorrosion stability [10, 11]. So, these materials can be recommended for using as protective coatings for energy and chemical equipment, auto industries and the objects of domestic facilities.

Conclusions. Thus, the inclusion in the base polymer matrix a structural fragment of functional oligomers (various amounts) forms a systems with new desired properties. Found a significant increase in sensitivity of the compositions, degree of the structure forming (estimated by determining the hardness), a significant improvement in adhesion to the base of the application layer. This allows you to create new composite materials with controllable properties and to extend the capabilities of these materials for application in instrument manufacture, microelectronics as a protective coating of printed circuit boards and chips in the printing industry in the manufacture of label production, packaging, securities.

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**ПОЛІМЕРНІ МАТЕРІАЛИ НА ОСНОВІ РЕАКЦІЙНОЗДАТНИХ
ФУНКЦІОНАЛЬНИХ ОЛІГОМЕРІВ**
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Мета. Дослідження структурних характеристик алкідних смол і матеріалів на їх основі; додавання до структури алкідної смоли дієну / вінілу рідких каучуків або олігомерів з різними функціональними групами дозволяє отримувати полімерні матеріали різної хімічної природи та підвищують фізико-механічні показники.

Методологія. Модифіковані плівки полімерних алкідних матеріалів були охарактеризовані методами ІЧ-спектроскопії на приладі Тензор-37 (Bruker, Німеччина).

Результати. Були отримані модифіковані полімерні матеріали з високими захисними властивостями при взаємодії алкідної смоли і синтезованих олігомерів. Доведено, що при наявності в структурі алкідних смол 3÷5 % дієн / вінілових олігомерів істотно збільшуються показники ударної міцності, еластичності і адгезії до металевої поверхні.

Наукова новизна. Вперше встановлено взаємозв'язок впливу наявності в структурі алкідних смол 3÷5 % дієн / вінілу, що призводить до істотного збільшення показників ударної міцності, еластичності і адгезії до металевої поверхні.

Практична цінність. Ці матеріали можуть бути рекомендовані для використання в якості захисних покриттів для енергії і хімічного обладнання, автоіндустрії та об'єктів побутових приміщень.

Ключові слова: олігоізопрен, олігостирол, радикальна полімеризація, модифікація.

**ПОЛИМЕРНЫЕ МАТЕРИАЛЫ НА ОСНОВЕ РЕАКЦИОННОСПОСОБНЫХ
ФУНКЦИОНАЛЬНЫХ ОЛИГОМЕРОВ**
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Цель. Исследование структурных характеристик алкидных смол и материалов на их основе; добавление к структуре алкидных смол диеновых / виниловых жидких каучуков или олигомеров с различными функциональными группами позволяет получать полимерные материалы различной структурной организации и увеличивать физико-механические параметры.

Методика. Модифицированные пленки полимерных алкидных материалов были охарактеризованы методами ИК-спектроскопии на приборе Tensor-37 (Bruker, Germany).

Результаты. Полученные модифицированные полимерные пленкообразующие материалы с высокими защитными свойствами путем взаимодействия алкидной смолы и синтезированных олигомеров. Доказано, что при наличии в структуре алкидных смол 3÷5 % диеновых / виниловых олигомеров происходит значительное увеличение параметров ударопрочности, эластичности и адгезии к поверхности металла.

Научная новизна. Доказано, что при наличии в структуре алкидных 3÷5 % диеновых / виниловых олигомеров наблюдается значительное увеличение параметров ударной вязкости, эластичности и адгезии к поверхности металла.

Практическая ценность. Эти материалы могут быть рекомендованы для использования в качестве защитных покрытий для энергетического и химического оборудования, автоиндустрии и объектов бытового назначения.

Ключевые слова: олигоизопрен, олигостирол, радикальная полимеризация, модификация.