Section 7. Chemistry

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ANTICORROSIVE COATINGS BASED ON COOLIGOMERS MODIFIED BY AN AMIDE GROUP

Abstract. Modern oligomer technology is focused on developing a new generation of oligomer materials with specific functional properties, showing promising applications in various cutting-edge fields. A key aspect in achieving this objective is the advancement of film-forming material production techniques that enable the creation of films and coatings possessing exceptional mechanical, electrical insulation, adhesion, and thermal characteristics. This approach to polymer material development opens up new prospects for the creation of advanced technical solutions. Films and coatings made from these materials can find applications in diverse fields such as electronics, aviation, medicine, the automotive industry, and others, where high functionality and reliability are prerequisites.

Keywords: Corrosion resistance, surface treatments, chemical modification, coating formulations, polycondensation, epoxy-phenolic oligomers, polyimide copolymer.

Modification of oligomers with the aim of obtaining materials with improved not only physicochemical but also physicomechanical properties is possible through the introduction of various functional groups. These groups include metilol, carboxylic, hydroxyl, amine, amide, epoxy, and others. The presence of functional groups in oligomers enhances their elasticity, resistance to aqueous environments, and frost resistance, and contributes to achieving improved dielectric properties.

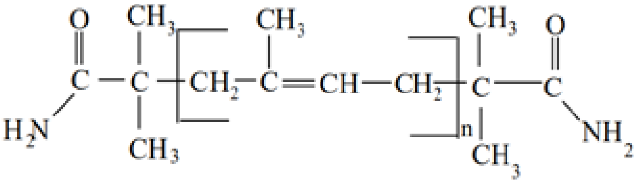
The most well-known methods for obtaining oligomers involve the introduction of -OH, -COOH, $-NH_2$ groups through polycondensation or copolycondensation with various organic monomers, as discussed in the referenced works [1–3].

Modifying the nature of the terminal functional groups in oligomers leads to variations in their physicochemical properties, thereby enabling a wider range of composite materials to be obtained for use in various industrial sectors. Good adhesion, enhanced dielectric characteristics, high moisture resistance, and resistance to chemically aggressive environments can be achieved with nitrogen-containing oligomers as the base [4–7].

In recent years, the synthesis of oligomers using amide groups has made it promising due to the formation of additional physical bonds due to the presence of the polarity of the amide groups themselves. Using monomers such as isoprene and styrene synthesis of oligomers and co-oligomers with amide groups at the end, it is possible to increase the yield of the main product up to 60%, depending on the initiator, the nature of the monomer and, importantly, on the ratio of the initiator.

In the study, 2,2'-azobis-isobutyramide is used as the initiator in a methanol solution at a temperature of 100 °C, with a minimum contact time of 10 hours.

The study demonstrates the synthesis of oligoisoprene and oligostyrene, as well as their copolymers with varying contents of amide groups.



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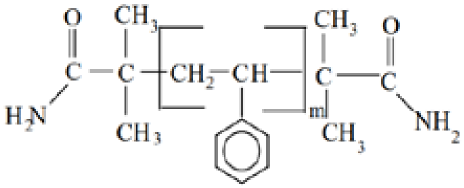

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Where n- 50–60, m- 90–100

The mentioned characteristics of the synthesized oligomers with amide groups indicate that the molecular weight depends on the ratio of monomer and initiator concentrations. The obtained oligomers are predominantly bifunctional. In terms of physical properties, the synthesized oligomers are viscous liquids, soluble in benzene, toluene, acetone, and cyclohexane, but insoluble in water.

The structural features of the starting reagents and the final products are studied using infrared spectroscopy. The specific heat resistance and curing temperature of the obtained samples are determined in the presence of dry nitrogen within the range of 100 to 250 °C. The physicochemical properties are investigated using the differential thermal analysis (DTA) method within the range of 100–600 °C.

The use of bisamidocarboxylic acid as a modifier for the epoxy oligomer is attributed to the presence of functional carboxylic and amide groups in the polyamide acid molecule. Experimental results have shown that solutions of polyamide acid containing 4,4' – diaminodiphenyl oxide and pyromellitic dianhydride readily mix with solutions of epoxy oligomers in dimethylformamide. These mixtures do not separate upon prolonged storage and exhibit minimal viscosity changes over time (within 2–24 hours). Moreover, it was found that films can be successfully formed from these mixtures. The synthesized composite materials exhibit high adhesive strength to various substrates. Interestingly, the film-forming ability of the compositions is maintained even with the addition of the modifier at concentrations up to 5%.

The curing process of epoxy resin-based coatings involves a polycondensation reaction [9]. The degree of conversion into a three-dimensional oligomer is directly related to the curing time and temperature. The curing conditions are of particular importance for coating materials that transform into a oligomer directly on the surface of the substrate. The more complete the conversion, the higher the adhesion and protective properties of the resulting coating film. Studies have been conducted to determine the optimal curing conditions for the developed compositions to achieve the best properties of the coatings widely used in shipbuilding and mechanical engineering. According to the obtained data, the optimal curing temperature is 100 °C, with a duration of 2 hours and 40 minutes. Adhering to these conditions achieves an optimal combination of physicochemical properties for the developed epoxy compositions. The main focus of this study was on the ED-41r epoxy resin, which is the result of the polycondensation of low-molecular-weight ED-40 epoxy resin with diphenylol propane. In a free state in a thermal chamber, the compositions containing a solution of ED-45 polyamide resin in xylene underwent curing for two-time intervals: 1 hour and 1 hour 20 minutes.

Experimental studies have shown that the dependence of the aforementioned parameters on the concentration of polyamide acid exhibits a pronounced extremal character. The optimal mechanical, adhesive, deformation-strength, and protective properties of epoxy compositions are achieved at a concentration of polyamide acid in the range of 1–3%. Even the addition of just 1% of polyamide acid to the ED-41r-ED-45 epoxy system increases the adhesive strength of the coating by 3 times, impact strength by 11 times, and material hardness by 18%.

During the curing of the developed epoxy composition with polyamide acid as a modifier, competing and interdependent reactions take place. On one hand, polyamide acid can interact with the epoxy oligomer, promoting the formation of a three-dimensional structure. The interaction between the epoxy group and the amide group of the polyamide oligomer and polyamide acid leads to the formation of chemical bonds. On the other hand, during curing at elevated temperatures, partial conversion of polyamide acid into polyimide may occur, accompanied by the formation of imide cycles and the release of water. The presence of a small amount of water in the oligomer accelerates the curing process.

Additionally, the polyimide copolymer has a significant influence on the structure and properties of epoxy coatings. The polyimide enriches the epoxy matrix, enhancing its mechanical strength and deformation resistance. This allows for the creation of coatings with increased resistance to mechanical loads, impacts, and abrasion.

Furthermore, the polyimide modifier promotes the formation of dense and strong bonds with the surface of the coating, ensuring high adhesion to various materials. This is particularly important in shipbuilding and mechanical engineering, where coatings need to securely bond to metals, wood, and other substrates. Due to its chemical structure, the polyimide modifier also improves the protective properties of the coatings. It can form barrier layers that prevent the penetration of moisture, aggressive chemicals, and corrosion.

This significantly extends the service life of coatings and enhances their resistance in extreme conditions. Thus, the polyimide copolymer in epoxy coatings is not only a modifier but also a key component that imparts improved mechanical properties, high adhesion, and effective protection to the coatings. Moreover, protective coatings based on oligomer matrices of various compositions are one of the most effective methods for safeguarding the technological equipment of chemical production facilities against corrosive degradation.

To achieve the required characteristics of such oligomer coatings, functional modifiers are introduced into their composition, enhancing their strength, tribotechnical, thermophysical, and other properties. Composite materials based on oligomers, such as epoxy, polyether, and phenol-formaldehyde oligomers, are widely used in industry due to their diverse raw material base, relatively low cost, and ability to provide quality surface protection for equipment. Further improvement of the compositions of composite protective materials with the aim of enhancing their properties is highly relevant.

In the studies mentioned in references [10–11], it has been demonstrated that epoxy binders cured with novolac phenol-formaldehyde oligomers (NFO) exhibit high physico-mechanical properties. Typically, the block copolymer formed by the interaction of epoxy and novolac oligomers is cured at temperatures above 120 °C in the presence of curing agents for a duration of 0.5–6 hours.

Curing of epoxy-phenolic oligomers without the addition of curing agents or catalysts occurs at temperatures of 160–180 °C through the interaction between epoxy and hydroxyl phenolic groups. Interaction between the epoxy group and the secondary hydroxyl group is also possible. At higher temperatures above 200 °C, condensation reactions can occur between the alkyd and phenolic hydroxyl groups of the macromolecules in the epoxy-phenolic oligomer. Epoxy-phenolic polymers exhibit the following characteristics: hardness ranging from 190 to 220 MPa and a glass transition temperature of approximately 95 to 100 °C.

Furthermore, the conducted research has shown that increasing the duration of thermal treatment of epoxy-phenolic oligomers also improves the wear resistance of the coatings. This is attributed to the formation of a denser and stronger oligomer structure through additional thermal processing. However, excessive thermal treatment can lead to the breakdown of the oligomer network and a deterioration of the mechanical properties of the coatings. Therefore, optimal technological thermal treatment conditions need to be carefully determined to achieve the best tribotechnical characteristics and wear resistance of coatings based on epoxy-phenolic oligomers.

Experimental studies [12] also emphasize the importance of considering the interlinking segment Mc when developing coatings based on epoxy-phenolic oligomers. As the interlinking segment Mc decreases, the ability to form a highly elastic layer diminishes. This can result in a reduction of the protective properties of the coatings, as a highly elastic layer is capable of absorbing and dissipating mechanical loads, preventing damage to the substrate. When optimizing the composition of coatings and the processes of their treatment, it is necessary to consider the interrelation between the interlinking segment Mc, mechanical properties, and wear resistance of the coatings. Understanding these relationships helps in developing coatings with the best tribotechnical characteristics and ensuring long-lasting protection against wear and damage to surfaces.

Further research in this area allows for a better understanding of the mechanisms of interaction between copolymers, the interlinking segment, and the formation of a protective layer, which, in turn, contributes to the development of more efficient coatings with increased wear resistance and resistance to mechanical impacts.

The conducted study was dedicated to investigating the influence of the molecular weight of the block copolymer obtained from the interaction of epoxy binder and phenolic oligomer SF-010 on the structural network of the binder, measured by the value of Mc.

It has been found that changing the interaction time of the components within the range of 0.5 to 5 hours leads to an increase in the average molecular weight of the oligomer from 1050 to 2100. This indicates that the duration of the interaction affects the formation of the block copolymer and its molecular structure.

The variation in the molecular weight of the cooligomer can influence the mechanical and chemical properties of the oligomer, including its strength, elasticity, thermal stability, and other characteristics. Further research can provide a deeper understanding of the impact of molecular weight on the properties of the cooligomer and optimize the processes of its synthesis to achieve desired properties and characteristics of oligomer materials. It is possible to use modified coatings with thermoplastic oligomers having a combined matrix as a base for composite protective materials. In this case, it is recommended to use a thermoplastic modifier with high wear resistance comparable to the wear resistance of the structured matrix. The presence of a thermoplastic component in the combined matrix contributes to a reduction in wear intensity. Thermoplastic oligomers exhibit good plasticity and deformation capability under mechanical loads. This allows them to absorb and dissipate friction and wear forces, leading to improved coating durability.

The selection of a thermoplastic modifier with suitable mechanical properties is an important aspect in the creation of composite protective materials. Such a modifier should provide wear resistance comparable to that of the matrix and contribute to the overall durability of the coating.

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