MODIFICATION OF POLYMERS AND THE PROPERTIES AND APPLICATIONS OF ADHESIVE POLYMERS: A REVIEW

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Abstract. This article reviews, in an integrated manner, the principal methods of polymer modification and the nature, properties, and fields of application of adhesive polymers. Polyolefins such as polypropylene and polyethylene, which are among the most widely demanded products of the petrochemical industry, possess low surface energy and poor adhesion to many surfaces, which substantially limits their practical use; modification is therefore the key route to imparting qualitatively new surface properties to industrial grades of polymer. The work distinguishes structural and chemical modification, examines grafting (graft) polymerisation as a means of altering surface properties, and analyses its advantages and limitations. The essence of adhesive polymers is then considered—their dependence on molecular structure, wetting ability, degree of polarity, elastic modulus, and curing mechanism—together with their main types and their fields of application in construction, the automotive industry, electronics, medicine, packaging, and textiles. The ecological and economic advantages of adhesive joining, along with current problems and prospects for development, are also discussed. The results may serve as a scientific and methodological basis for developing modified polymer materials and new, environmentally safe adhesive formulations.

Keywords: polypropylene, polyethylene, polyolefins, polymer modification, graft polymerisation, surface energy, adhesive polymers, epoxy, polyurethane, acrylic, adhesive strength, ecological safety.

1. Introduction

Today, petrochemical products such as polypropylene and polyethylene are among the most widely demanded basic polymer materials. These polymers serve as raw materials for the production of polymer goods at enterprises of this sector, which testifies to the high profitability of the petrochemical industry and to the multiplier effect it exerts on related fields. For this reason, the state regulates and supervises the conditions necessary for the efficient operation of full-cycle petrochemical production enterprises. The sector is concerned chiefly with the principal grades of polyolefins—primarily polyethylene and polypropylene—and, in the longer term, with polyethylene terephthalate, styrene, and certain other products. It is well known that polyolefins possess low surface energy and weak adhesion to various surfaces, which significantly restricts their practical application [1].

At the same time, advanced polymer-production technologies are directed towards modification, which makes it possible to obtain materials with qualitatively new surface properties on the basis of industrial polymer grades. These properties frequently determine the performance characteristics of products in numerous technical fields. The structure of surface layers plays an important role in catalytic processes and also governs the course of adsorption, filtration, and other technical operations. A number of studies have described various methods of modification [3], which allow the production of polymer materials with improved adhesion, ion-exchange materials, selective catalysts, and other materials [2]. In this connection, it has been concluded that the development and industrial introduction of innovative technologies for modifying the principal grades of polymers—technologies that make it possible to alter the surface properties of materials—is both useful and economically advantageous.

Adhesive polymers, in turn, are high-molecular-weight compounds capable of forming a strong bond with the surfaces of various materials. Such polymers are used to bond two or more layers to one another, to reinforce composite structures, to form protective coatings, and to improve the functional properties of surfaces. They are of considerable importance in many branches of industry, including construction, the automotive industry, packaging, electronics, medicine, and textiles. Modern production technologies require not only high strength but also lightweight construction, corrosion resistance, energy efficiency, and ecological safety; in this respect adhesive polymers possess numerous advantages over traditional mechanical fastening methods—they reduce local stresses, make it possible to join dissimilar materials, and extend the service life of finished products [1, 2].

Aim of the study. To carry out an integrated review of the principal methods of polymer modification—structural, chemical, and grafting—and of the nature, properties, and fields of application of adhesive polymers, and on this basis to substantiate the scientific and practical directions for developing modified polymer materials and environmentally safe adhesive formulations.

2. Methods of Polymer Modification

The modification of polymers is the directed alteration of their properties. A distinction is drawn between structural and chemical modification of polymers. Structural modification consists in altering the supramolecular structure of the polymer while preserving its chemical composition and molecular mass; in chemical modification, a change in the chemical composition or molecular mass of the polymer is frequently accompanied by a very appreciable change in the polymer structure. Modification makes it possible to improve a whole complex of consumer properties of polymer materials and articles—resistance to thermal or chemical influences, hydrophilicity (or hydrophobicity), sorption properties, dyeing and structure-forming ability, elasticity, strength, biological activity, adhesion, solubility, crystallinity, and many other functional characteristics; in a number of cases modification also leads to the appearance of anisotropy in the mechanical and physicochemical properties.

Classification of modification methods. Methods of polymer modification are classified according to various criteria [5]. According to the nature of the processes occurring [2], modification is traditionally divided into a physical aspect, which leads to a change in the supramolecular structure, and a chemical aspect, which involves the introduction of various functional groups into the original polymer. According to the number of stages, modification is most often single-stage; however, in a number of cases two-stage modification with intermediate activation in the form of halogenation, sulfochlorination, phosphonation, or oxidation is more appropriate [1]. According to the functional property being influenced, modification may target adhesion, chemical resistance, thermal stability, electrical conductivity, cold resistance, rheology, biodegradation resistance, ultraviolet and radiation resistance, appearance, moisture resistance, fire resistance, anti-corrosion and anti-friction properties, and others [1]. It should be noted, however, that each modification method is directed only at regulating individual properties, taking into account the specific features of the physicochemical nature of the processes with which they are associated [6].

Structural modification. Structural modification of polymers can be carried out by means of external mechanical actions on the solid polymer body; by altering the temperature–time regime of structure formation of the solid polymer body from the melt; by altering the nature of the solvent and the regime of its removal during the formation of coatings, films, and fibres from polymer solutions; and by introducing small quantities of other substances that influence the kinetics of formation and the morphology of the supramolecular structure of the modified polymer. This type of modification is used to improve fibre quality, increase the impact resistance of plastics, and regulate the structure of polymers during the manufacture of articles (for example, in extrusion, pressing, and the formation of polymer coatings).

Chemical modification. Chemical modification of polymers employs the chemical transformations of an already synthesised polymer, which may proceed without changing the degree of polymerisation of the macromolecules (polymer-analogous transformations and intramolecular reactions), with its increase (cross-linking, synthesis of graft and block polymers), or with its decrease (destruction). The reactivity of the functional groups of polymers differs from that of their low-molecular-weight analogues, since the rate and direction of the reaction of a functional group in macromolecules may be influenced by its proximity to the main chain, its interaction with neighbouring initial or already reacted groups, the conformation of the chain and its change with conversion, electrostatic interactions along the chain, and the supramolecular organisation of the macromolecules. Polymer-analogous processes are used to protect reactive groups of the macromolecule, to synthesise comb-like polymers, and to produce ion-exchange materials, while modification through intramolecular reactions is used to obtain heat-resistant polymers (with conjugated double-bond systems and intramolecular cycles).

The presence of multiple bonds and of hydroxyl, carboxyl, carbonyl, and epoxy groups in macromolecules makes it possible to cross-link the macromolecules even at low concentrations of the modifying reagents. Transformations of this type include the irreversible conversion of liquid reactive oligomers into solid, insoluble network polymers (the curing of plastics) and the production of elastic network polymers—rubbers (the vulcanisation of rubber). The density of the cross-links, their chemical composition and distribution, the initial molecular mass of the polymer, and the structure of the polymer chains incorporated into the network determine the properties and applications of the resulting polymers.

Graft and block polymers; destruction. Graft and block polymers are obtained as a result of the interaction of a monomer with a polymer or of the interaction of polymers or oligomers of different types. Owing to the presence of microregions enriched with one component or another, graft and block polymers are characterised by the additivity of their physico-mechanical properties. Such polymers, composed of thermodynamically incompatible components, separate into microlayers (in contrast to mechanical mixtures of homopolymers, which separate into macrolayers); for this reason, graft and block polymers are used where compatible polymer systems are required. Polymer destruction—that is, a decrease in the molecular mass of the polymer—usually occurs under the combined action of several factors: heat, oxygen, mechanical stresses, light, moisture, and others. Destruction is used for a partial

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reduction of molecular mass, which facilitates the processing and practical use of polymers; it is also used to determine the chemical structure of polymers and to obtain low-molecular-weight substances from natural polymers (for example, the hydrolytic destruction of cellulose or starch to glucose).

3. Graft Polymerisation as a Method of Surface Modification

Graft polymerisation methods, which differ in the nature of their initiation [2], are very widely used to alter the properties of polymers. During graft polymerisation, active centres are formed on the surface, and these initiate the growth of the polymer chain. These active centres are free radicals or peroxides generated as a result of irradiation, plasma treatment, or photoinduction.

If grafting is carried out on a moulded polymer, the grafted fragments do not participate in stretching and remain non-oriented in the amorphous phase. For this reason, at a high degree of grafting a decrease in the mechanical properties of the modified polymer is observed [7]. Before moulding, the grafted fragments must be heat-resistant, since the subsequent moulding is carried out from the polymer melt. This indicates that it is technologically advantageous to carry out graft polymerisation after moulding [3].

Among the disadvantages of the graft-polymerisation method is the fact that the grafting process itself, being difficult to control, leads to a mixture of homopolymer and modified polymer that is difficult to separate [8]. The radical mechanism of graft polymerisation reveals its sensitivity to the presence of impurities, which requires a high degree of purity of the initial polymer and the conduct of the grafting process in an inert medium [9]. The presence of stabilisers in the initial polymers hinders grafting, so thorough purification of the polymer is very important; otherwise there is a risk of forming a mixture of degraded polymer. According to specialists [9], in the future most of the polymers currently used in their pure form may be modified in the form of graft polymers; this already applies to polyvinyl chloride and polystyrene, which are actively used as graft polymers.

4. The Nature and Principal Properties of Adhesive Polymers

The effectiveness of adhesive polymers depends mainly on their molecular structure, surface-wetting ability, degree of polarity, elastic modulus, and curing mechanism. They spread over the surface, penetrate into fine pores and irregularities, and form physical, chemical, or diffusion bonds; as a result, a strong interface is created between the layers being bonded.

In practice, adhesive polymers based on epoxy, polyurethane, acrylic, phenol-formaldehyde, silicone, polyamide, and rubber are widely encountered. Each type is selected for particular operating conditions. For example, epoxy polymers provide high strength and chemical resistance, whereas polyurethanes provide elasticity and impact resistance. Important indicators for adhesive polymers include adhesive (bonding) strength, shear resistance, resistance to heat and moisture, the rate of ageing, the level of toxicity, and technological convenience [3].

5. Fields of Application of Adhesive Polymers

Adhesive polymers are distinguished by the breadth of their fields of application. In many cases they do not compete with mechanical fastening devices but rather replace them or, when used in combination, increase the reliability of the structure. The principal directions of industrial application are summarised in Table 1.

Table 1. Principal directions of industrial application of adhesive polymers.

Sector	Object of application	Useful property	Examples
Construction	Panels, slabs, coatings, sealed joints	Moisture resistance, thermal insulation	Facade panels, sandwich panels
Automotive industry	Body elements, interior parts, glazing	Weight reduction, vibration damping	Bonded body panel, windscreen
Packaging	Multilayer film and cardboard	Rapid curing, food compatibility	Lamination, label bonding
Electronics	Microchips, displays, protective coatings	Dielectric properties, precise placement	Touch screen, module assembly
Medicine	Dressing materials, implant coatings	Biocompatibility, resistance to sterile conditions	Medical tape, wound adhesive
Textiles	Laminated fabric, technical fibre composite	Flexibility, lightness	Sportswear, technical fabrics

Significance in construction and the automotive industry. In construction, adhesive polymers are used in tile adhesives, sealants, waterproofing mastics, facade panels, floor coverings, and the bonding of composite materials. They increase the tightness of structural joints, protect against moisture and temperature variation, and help to reduce heat loss. In the automotive industry, these materials are used to join metal, plastic, glass, and composite parts. As a result of adhesive joining, the number of weld seams is reduced, the weight of the vehicle is decreased, the risk of corrosion is lowered, and the maintenance of the aerodynamic shape is facilitated.

Role in electronics, medicine, and packaging. In the electronics industry, adhesive polymers are required for the delicate fixing of microchip and display modules, for protection against heat, and for the formation of a dielectric layer; in this field, low viscosity, precise dosing, and electrical non-conductivity of the material are important. In medicine, adhesive polymers are used in wound dressings, dental materials, transdermal patches, and biocompatible implant coatings; such products must be compatible with human tissue, non-toxic, and resistant to sterilisation. In packaging, adhesive polymers occupy an important place in the manufacture of multilayer films, cardboard boxes, labels, and food packaging [4].

6. Ecological and Economic Advantages

The ecological advantage of adhesive polymers lies in the fact that they extend the service life of products and reduce the need for repair and replacement. Lightweight structures, in turn, reduce fuel consumption in vehicles and machinery. In many modern systems, solvent-free formulations or formulations with a low content of volatile organic compounds are being developed, which helps to reduce atmospheric pollution. From an economic standpoint, adhesive joining simplifies the production process, reduces the additional costs associated with welding or bolted fastening, decreases waste, and creates favourable opportunities for automation.

7. Problems and Prospects for Development

At the same time, a number of limitations exist in the use of adhesive polymers. Insufficient surface preparation, as well as residues of moisture, dust, or grease, lowers the quality of bonding. Some polymers may age rapidly under the influence of high temperature or ultraviolet radiation. Consequently, the selection of the optimal material and the preliminary preparation of the surface are of great importance. In the future, research is expected to expand on adhesive polymers modified with nanoparticles, as well as on self-healing, biodegradable, and easily recyclable adhesive polymers [5]. The successful application of new composite coatings likewise requires the further improvement of the relevant technology.

8. Conclusion

This review has examined, in an integrated manner, the principal methods of polymer modification and the nature, properties, and fields of application of adhesive polymers. The low surface energy and weak adhesion of polyolefins make modification the key route to obtaining materials with qualitatively new surface properties on the basis of industrial polymer grades. Structural and chemical modification, together with graft polymerisation, allow the directed regulation of a wide complex of functional properties—including adhesion, thermal stability, hydrophilicity, sorption capacity, and others—although each method is, as a rule, directed at regulating individual properties in accordance with the physicochemical nature of the corresponding processes.

Adhesive polymers are an indispensable material of modern industry, forming strong and durable bonds between various surfaces. Their role is increasing in many fields, from construction to electronics and medicine. Advantages such as high adhesive capacity, weight reduction, protection against corrosion, and increased production efficiency make these polymers exceptionally relevant in practical terms. Accordingly, the in-depth study of adhesive polymers, the creation of new, environmentally safe formulations, and their broad introduction into local industrial sectors constitute important tasks. The development and industrial introduction of innovative modification technologies on the basis of domestic raw materials may serve as a scientific and practical foundation for the production of import-substituting polymer materials of a new generation

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