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Modification of Secondary Polymers

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Abstract: The article examines the influence of the type and amount of modifiers on the properties of secondary thermoplastics. The classification and sources of waste formation of high molecular weight materials are given. The physical and chemical properties of plastics are analyzed. Particular attention is paid to composite materials. The features of obtaining mixtures for the manufacture of compositions based on crushed and modified waste are noted.

Keywords: Regeneration, polymer compositions, plastics, composite materials.

The steady growth of polymer materials inevitably causes an increase in polymer waste. Among them, a significant share is occupied by thermoplastics that can be repeatedly processed. However , their reuse does not meet the increased technical requirements of mass production due to destructive processes and reduced properties. Modification of secondary polymers can provide an increase in the level of their properties. But the practical implementation of the processes for producing and using modified thermoplastics is difficult due to insufficient knowledge of the phenomena that arise during their processing: there is not enough information about changes in structure, the emergence of new functional groups, the formation of new types of bonds, and the formation of a set of new physical and mechanical properties. That is why the problem of recycling polymer waste has not yet been completely resolved in any country in the world. Therefore, the use of secondary polymers, in particular thermoplastics , is a pressing problem of our time. Its solution will be able to ensure the effective use of secondary thermoplastics and predict specific areas of application of new modified materials - not only with the required level of properties, but also cheaper ones.

As is known, polymers are crushed at low and normal temperatures using various devices. In our opinion, high-speed grinding with simultaneous mixing of the resulting crumbs with modifying agents is most effective.

Regeneration of cross-linked polymer crumbs can be carried out in the presence of destruction activators: naphthenic oils, tall pitch, emulsifiers and petroleum polymer resins, aqueous solutions of alkalis, surfactants, etc. The resulting regenerate is a partial replacement of the original polymer in compositions for various purposes, but it is more advisable to use crushed cross-linked polymers and elastomers directly in polymer compositions.

Improving the quality indicators of composites is achieved by mixing crumbs with waste synthetic rubber, block copolymers of butadiene with styrene and with targeted additives. The most effective way to improve the quality of crushed polymer waste, and therefore the properties of compositions based on them, is the modification of polymer crumbs with oligomers with epoxy groups; derivatives of nitroso aromatic amines; epoxidized polybutadiene, reaction products of a tertiary amine with aliphatic or aromatic hydroxides and other agents.

To improve the physical and mechanical properties of vulcanizates containing regenerate or crumb rubber, cord waste or activated lignin are introduced into them.

Despite the large number of developments to create compositions containing waste polymers, the problem has not been completely solved, and there are no specific recommendations for the practical use of cross-linked polymers.

Plastics have many valuable physical and chemical properties, and plastic-based composites (with a polymer matrix) acquire additional properties that make the material even more useful from the point of view of operation and, accordingly, attractive to the consumer. A way to add additional or improve existing properties is to foam the composite. The main purpose of using fillers is to reduce the cost of polymer materials and products made from them.

Composite materials (composites) (from Latin compositio - composition) are multicomponent materials consisting of two or more components, the quantitative ratio of which must be comparable. The components differ significantly in properties, and their combination should give a certain synergistic effect, which is difficult to foresee in advance.

Typically one component forms a continuous phase called the matrix, the other component is the filler. An adhesive or autohesive interaction is created between them , which ensures the solidity of the material.

The production of composites makes it possible to significantly expand the range of polymer materials and the variety of their properties based on polymers created and produced by industry. Physico-chemical modification of existing polymers, their combination with substances of a different nature and structure is one of the promising ways to create materials with a new necessary set of properties.

The use of various mixtures of polymers, additives, fillers and methods of their processing, their introduction into the polymer both during the synthesis process and during processing makes it possible to obtain polymer composite materials of different structures, with the required set of performance properties.

Depending on the purpose of composite polymer materials, in order to save expensive raw materials, taking into account the operating environment and decorative requirements, it is possible to widely vary the percentage of raw materials and obtain products with different physical and mechanical properties, coloring and other performance properties .

Therefore, when processing plastics, it is necessary to know the properties of the initial polymer raw materials, additives, methods of their preparation before introducing them into the polymer, the influence of processing parameters and different types of plastic processing equipment on the technological and operational properties of materials, and application conditions.

Modern production cannot be imagined without the use of polymer composite materials in the manufacture of containers and packaging used in various industries.

Polyvinyl chloride is a polymerization product of vinyl chloride, the chemical formula of which is CH2-CHCl. During the polymerization process, linear, weakly branched (the branching of macromolecules is 2–5 per 1000 carbon atoms of the main chain) macromolecules with an elementary unit in the form of a flat zigzag are formed.

The nature of the bonds between the elementary links allows for several options for constructing a molecular chain, which in practice, during the industrial production of polyvinyl chloride, leads to low regularity (syndiotacticity) of its macromolecules: in one macromolecule several options for the bonds of elementary links are realized at once, regular sequences of elementary links are not created and industrial the samples have a low degree of crystallinity.

Industrial production of polyvinyl chloride is carried out in three ways:

1) suspension polymerization according to a periodic scheme. A solution containing 0.02–0.05% by weight of an initiator (e.g., acyl peroxides , diazo compounds) is vigorously stirred in an aqueous medium containing 0.02–0.05% by weight of a protective colloid (e.g., methylhydroxypropylcellulose , polyvinyl alcohol). The mixture is heated to 45–65 ° C

(depending on the required molecular weight of polyvinyl chloride) and the set temperature is maintained within narrow limits in order to obtain polyvinyl chloride that is uniform in molecular weight. Polymerization occurs in droplets, during which some aggregation of particles occurs; As a result, porous polyvinyl chloride granules with a size of 100–300 microns are obtained. After the pressure in the reactor drops (the degree of conversion is about 85–90%), the unreacted monomer is removed, the polyvinyl chloride is filtered, dried in a stream of hot air, sifted through sieves and packaged. Polymerization is carried out in large-volume reactors (up to 200 m^3); new production facilities are fully automated. Specific consumption 1.03–1.05 t/t of polyvinyl chloride Advantages of the method: ease of reaction heat removal, high productivity, relative purity of polyvinyl chloride, good compatibility with components during processing, wide possibilities for modifying the properties of polyvinyl chloride by introducing various additives and changing the mode parameters.

2) Polymerization in bulk according to a periodic scheme in two stages. At the first stage, the reaction mixture containing 0.02–0.05% by weight of the initiator is polymerized with vigorous stirring to a conversion degree of about 10%. A thin suspension of particles ("seeds") of polyvinyl chloride in the monomer is obtained, which is transferred to the second stage reactor; additional quantities of monomer and initiator are introduced here and polymerization is continued with slow stirring and a given temperature until the degree of conversion is about 80%. At the second stage, further growth of polyvinyl chloride particles and their partial aggregation occurs (no new particles are formed). Porous polyvinyl chloride granules with sizes of 100–300 microns are obtained, depending on the temperature and mixing speed at the first stage. The unpolymerized monomer is removed, the polyvinyl chloride is purged with nitrogen and sieved. The powder is free-flowing and easily processed. Advantages over the suspension method: the absence of stages of preparation of the aqueous phase, isolation and drying of polyvinyl chloride, as a result, capital investments, energy costs and maintenance costs are reduced. Disadvantages: it is difficult to remove reaction heat and combat crust formation on the walls of the equipment; the resulting polyvinyl chloride is heterogeneous in molecular weight, its heat resistance is lower than that of the polyvinyl chloride obtained by the first method.

3) Emulsion polymerization according to periodic and continuous schemes. Water-soluble initiators (H_2O_2, persulfates) are used, and surfactants (for example, alkyl or aryl sulfates , sulfonates) are used as emulsifiers . Radicals originate in the aqueous phase containing up to 0.5% by weight of an initiator and up to 3% of an emulsifier; polymerization then continues in the emulsifier micelles. With continuous technology, the aqueous phase and monomer enter the reactor. Polymerization occurs at 45–60 ° C and gentle stirring. The resulting 40–50% latex with polyvinyl chloride particle sizes of 0.03–0.5 μm is removed from the lower part of the reactor, where there is no mixing; the conversion rate is 90–95%. In batch technology, the components (aqueous phase, monomer and usually some latex from previous operations, the so- called seed latex, as well as other additives) are loaded into the reactor and mixed throughout the entire volume. The resulting latex, after removing the monomer, is dried in spray chambers and the polyvinyl chloride powder is sifted. Although the continuous process is highly productive, the advantage is often given to the periodic one, because it can produce polyvinyl chloride of the desired granulometric composition (particle sizes in the range of 0.5–2 microns), which is very important when processing it. Emulsion polyvinyl chloride is significantly contaminated with auxiliary substances introduced during polymerization, so only pastes and plastisols are made from it.

Vinylplast is a product of processing polyvinyl chloride containing the following additives: 1) mainly thermal stabilizers - HCl acceptors (Pb , Sn compounds , oxides and salts of alkaline earth metals), as well as sometimes epoxidized oils, organic phosphites; phenolic antioxidants; light stabilizers (derivatives of benzotriazoles , coumarins, benzophenones , salicylic acid, carbon black, TiO_2, etc.); 2) lubricants (paraffins, waxes, etc.; introduced to improve the fluidity of the melt); 3) pigments or dyes; 4) mineral fillers; 5) elastomer (for example, acrylonitrile-butadiene-styrene copolymer or ethylene-vinyl acetate in an amount of 10–15% by weight; to increase impact strength). The composition is thoroughly mixed in mixers and processed in extruders or rollers.

Plastic compound is a product of processing polyvinyl chloride, containing, in addition to the components used in the production of vinyl plastic, 30–90 parts by weight of a plasticizer . (for example, esters of phthalic, phosphoric, sebacic or adipic acids, chlorinated paraffins). The plasticizer significantly reduces the glass transition temperature of polyvinyl chloride, which facilitates the processing of the composition, reduces the fragility of the material and increases its relative elongation. However, at the same time, strength and dielectric properties and chemical resistance decrease. Plastics are processed mainly in the form of pastes and plastisols (dispersions of emulsion polyvinyl chloride into a plasticizer); produced in the form of granules or tapes, sheets, films. It is used mainly for the manufacture of insulation and sheaths for electrical wires and cables, for the production of hoses, linoleum and floor tiles, materials for wall cladding and furniture upholstery, molded profile products, and artificial leather.

Based on polyvinyl chloride (PVC), more than 3,000 types of composite materials and products are produced, used in the electrical, light, food, automotive industries, mechanical engineering, shipbuilding, in the production of building materials, medical equipment, etc., which is due to its unique physical and mechanical properties. dielectric and other operational properties.

However, at present, the use of PVC is gradually being limited, which is primarily due to environmental problems that arise during the operation of products, their disposal and recycling. When aging PVC-based polymers, along with the loss of physical and mechanical properties, there is a negative impact on the environment and humans due to the processes of PVC dehydrochlorination , which intensify at temperatures of 50 - 80 ° C (highly toxic chlorine-containing polyaromatic compounds are formed).

This determines the relevance of the problem of developing safe technologies for the disposal and processing of waste products containing PVC.

The main methods of recycling waste polymer materials include:

- thermal decomposition in an inert atmosphere (pyrolysis);
- burning;
- decomposition to obtain initial low-molecular compounds (depolymerization);
- recycling (injection molding, extrusion, pressing, etc.).

The most difficult issues to solve are the disposal of mixtures of polymer waste containing, along with PVC, polyolefins (polyethylene, polypropylene), polystyrene, polyurethanes, polyamides, etc.

An analysis of existing technologies for neutralizing a mixture of polymer waste allows us to conclude that it is advisable to use thermal processing based on destruction processes in an inert atmosphere.

The pyrolysis of polymers produces gases, some of which can condense to form high-calorie liquid fuel, non-condensable gases containing methane and hydrogen, which have a high calorific value, and carbonate , which can be used in technological processes. The high energy potential of pyrolysis gases allows the recycling process to be carried out in autothermal mode.

The thermal destruction of polyolefins, polystyrenes, and polyamides has been sufficiently well studied, and the temperature range for their processing has been established at 400 - 500 °C.

The tests carried out confirmed the validity of the conclusions drawn on the basis of theoretical thermodynamic calculations of PVC pyrolysis. The developed method ensures the environmental safety of recycling PVC-containing waste.

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