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Physico-Chemical interactions of Polymers with Mineral, Carbon and Fibrous Fillers

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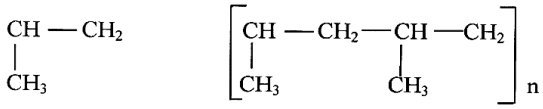
ABSTRACT: In the work of fillers in the polymer noticeably improves its properties. This indicates that after filling we get a new material - a composite polymer material, the interaction mechanism of which is practically not studied. When obtaining composite polymer materials based on a thermoplastic polymer - polypropylene, along with the physical and mechanical influences of the constituent components on each other, to a certain extent, chemical interactions between them also occur. This interaction can manifest itself in the form of the formation of hydrogen bonds, donor-acceptor or ionic bonds between the components, and sometimes with the formation of pronounced complexes.

I. INTRODUCTION

The mechanism of physicochemical interactions of the polymer with mineral fillers. Let us consider as an example the chemical interaction in the system of polypropylene and mineral fillers. Particles of filler in the technological conditions of synthesis of composite polymer materials are wetted with a fused polymer. The formation of adhesive bonds occurs due to weak van der Waals attraction forces with a binding energy E = 0.1-1.0 kcal/mol and due to chemical interaction forces arising between polypropylene macromolecules and structural groups of particles on fillers. Of the hydrogen atoms in the polypropylene macromolecule are the most mobile and positively charged, i.e. activehydrogen atom is located in the α-position to the methyl group CH. Therefore, it is most likely that hydrogen atoms are most involved in the chemical interactions of polypropylene macromolecules. In this regard, we offer the following most probable schemes for the interaction of polypropylene with fillers.

II. METHODS

The structural formulas of the polypropylene monomer and macromolecule, respectively, are:



Where n = 80000÷200000, depending on the quality of the polypropylene. The sizes of macromolecules are, respectively, 20÷50 microns. Linear polypropylene polymers have high spatial regularity and are capable of crystallization. Most of the crystalline modifications that are stable up to the melting point (160÷175°C) have a spiral-like monoclinic structure.

One of the most important methods for quantitatively assessing changes in the structure of polymer in the presence of a filler is the specific surface area and pore volume, which provide valuable information about the packing density of

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macromolecules, the size of supramolecular formations, the nature of the appearance and development of defects, and the stress distribution in the system.

In accordance with the above, it was of interest to study the effect of both non-activated and mechanically activated fillers on the nature of changes in the structure of polyolefins. It was found during mechanical processing of aluminosilicate filler of the kaolin type under the action of shock-splitting - abrasive deformation, they undergo significant structural changes, in particular, an increase in the specific surface area, adsorption capacity and the manifestation of active centers depending on the conditions of mechanical activation (table 1).

Table 1
Adsorption characteristics of kaolin

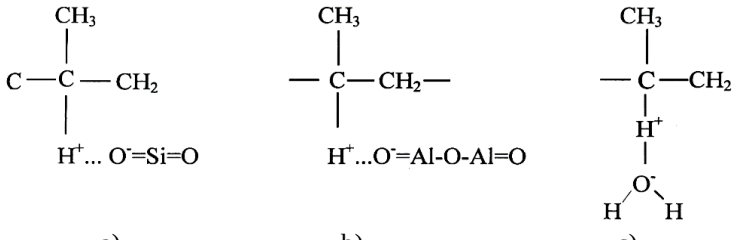
Index	Original kaolin	Activated kaolin
Specific adsorption surface, m^2/g	24	35
Dibutyl phthalate adsorption, $sm^3/100$ g	31	43

As can be seen from the data in table 1, mechanical activation promotes an increase in the specific surface area and an increase in the adsorption characteristics of fillers.

By analyzing the features of the mechanisms interaction and composite polymer materials filled with mineral fillers, it was found that when obtaining composite polymer materials and chemical interaction of fillers with the polymer occurs , which form a strong bond of the filler particles with the polymer, ensures the formation of a dense adsorption layer and adhesive bonds due to chemical interaction forces, arising between polymer macromolecules and structural groups of filler particles. In this case, hydrogen-oxygen or hydrogen-carbon, as well as van der Waals bonds arise, are leading to the strengthening of intermolecular bonds between polymer macromolecules, which improve the properties of composite polymer materials. In addition, it has been established that the structure of the composite polymer material is ahighly crystalline polymer structure with an elastic-rigid integral extended chain of particles of dispersed fillers conjugated with it.

III. RESULTS

In the polypropylene + kaolin system, kaolin is a finely dispersed lamellar rock, consisting mainly of the mineral kaolinite - aluminum hydrosilicate - $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. When using kaolin as a filler, apparently, all constituent components of kaolinite ($A1_2O_3$, SiO_2, H_2O) interact with polypropylene with polypropylene hydrogen atoms located in the α-position to methyl groups, with the formation of hydrogen bonds according to the scheme:



a) b) c)

Cement, in particular Portland cement, has a composition, weight. %: CaO – 62÷76; SiO_2 – 20÷24; $A1_2O_3$ – 4÷7; Fe_2O_3 – 2÷5; MgO – 1,5÷4. Talc is a natural magnesium silicate with a composition $3MgO \cdot 4SiO_2 \cdot H_2O$.

Wollastonite is a natural mineral with a composition$CaO \cdot SiO_2$. As you can see, they all consist of metal oxides and their interaction with polypropylene, mainly, consists in their participation in the formation of hydrogen bonds. The data obtained indicate a radically active nature of mechanically activated fillers. Due to the radical activity of mechanically activated fillers in the processing of composite polymer materials, it is possible that radical processes occur with the formation of chemical bonds with the active centers of polyolefins, leading to structural changes on the

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surface layer of the filler in comparison with traditionally filled polymer materials.

Thus, of the considered mineral fillers, wollastonite imparts greater wear resistance to composite materials, talc and kaolin will increase their hardness, wollastonite and cement will increase impact strength, ultimate bending strength, and, in general, fillers will increase the elastic modulus and strength properties of composite polymer materials.

The mechanism of physico-chemical interactions of polymers with carbon-graphite fillers. Let us consider the physicochemical interaction of graphite-carbon fillers with polypropylene. One of the important methods for quantitatively assessing changes in the structure of a polymer in the presence of a filler is the specific surface area and pore volume, which provide valuable information about the packing density of macromolecules, the size of supramolecular formations, the nature of the appearance and development of defects, and the stress distribution in the system.

In accordance with the above, the effect of non-activated and mechanically activated fillers on the nature of changes in the structure of polyolefins have studied. Itwas found during mechanical treatment of a carbon-graphite filler such as carbon under the action of shock-splitting - abrasive deformation, they undergo significant structural changes, in particular, an increase in the specific surface area, adsorption capacity and the manifestation of active centers depending on the conditions of mechanical activation (table 2).

Table2
Carbon adsorption characteristics

Index	Original carbon	Activated carbon
Specific adsorption surface, m^2/g	24	35
Dibutyl phthalate adsorption, $sm^3/100$ g	31	43

As can be seen from the data in table 2, mechanical activation promotes an increase in the specific surface area and an increase in the adsorption characteristics of carbon.

The obtained data indicates a radically active nature of mechanically activated carbon. Due to the radical activity of mechanically activated carbon under the conditions of processing composite polymer materials, it is possible for radical processes to occur with the formation of chemical bonds with the active centers of polyolefins, leading to structural changes on the surface layer of the filler in comparison with traditionally filled polymer materials. Mechanical activation increases the number of particles, the specific surface area of particles and promotes the activation of the surface arising in the process of grinding particles.

System of polypropylene+carbon, polypropylene+graphite system. It is important to note that the viscoelastic properties of filled polyolefinsare determinedprimarily by the nature of the filler surface chemistry, the filler network structure, the degree of interaction between polymers and fillers, and the molecular mobility of the chains.

In this regard, of particular interest are composite polymer materials consisting of polypropylene+carbon black, which are a micro-heterogeneous system of polyolefin macromolecules adsorbed on the carbon black surface.

It would be reasonable to assume that, due to the specificity of the surface chemistry of dispersed carbon, the presence of polar functional groups: carboxyl, phenolic, hydroxyl, aldehyde, catonic, and others, is of considerable interest in the creation of composite antistatic-heat-conducting polymeric materials with high strength and wear resistance.

In the polypropylene+carbon black system, carbon black particles with polypropylene form an enhanced microheterogeneous structure due to adsorption and orientation of macromolecule sites, as well as due to the effect of carbon black on the structure of the vulcanization network. This significantly increases the strength and wear resistance of polypropylene. The structural formula of carbon can be conventionally represented as (- C ≡ C -) p1 or even (= C = C =) p2, i.e. in both cases, π-bonds are present in the carbon molecules. This bond, due to the mobility of its constituent

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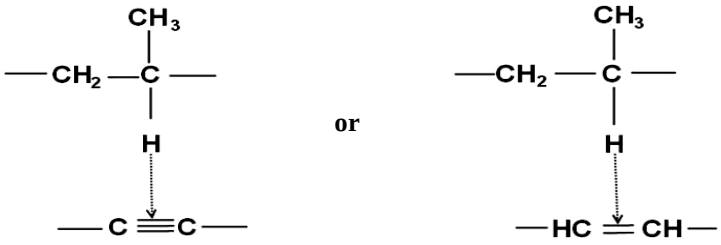
electron pair, easily interacts with the α-hydrogens of polypropylene with the formation of not very strong so-called π-complexes:



In some cases, for example, at elevated temperatures, α-hydrogen can join the carbon. In this case, crosslinking of polypropylene macromolecules occurs.

The crystal lattice of graphite is hexagonal and consists of infinite planar parallel layers are formed by regular hexagons of carbon atoms with a C–C distance of 1.42 Å. The layers are spaced 3.35 Å from each other. Each carbon atom is bonded to adjacent three σ = bonds, and the fourth electron actually remains unpaired. Because of this, the elementary unit of graphite is significantly reactive and very prone to the formation of hydrogen bonds, in particular with the α-hydrogen of polypropylene macromolecules.

In addition, during the formation of composite materials under the action of an elevated temperature, α-hydrogen can be detached from polypropylene macromolecules. As a result, obviously, crosslinking of polypropylene macromolecules occurs through graphite.

IV. DISCUSSIONS

Obviously, in the course of processing, molecular interaction occurs between the active centers of the particles of carbon-graphite fillers and macromolecules of polypropylene. For large particles, these connections are single, and for small ones, they are multiple. In the latter case, the strengthening of intermolecular bonds between polypropylene macromolecules are observed, even if some of these macromolecules have an atactic structure. There is a kind of cross-linking of polypropylene macromolecules. The observed picture can be represented as a point reinforcement of the polymer, as a result, qualitatively new material is formed - a composite polymer material.This material, due to the perfection of the structure, will have improved physical and mechanical characteristics. In this case, carbon and graphite will reduce the coefficient of friction. This bond, due to the mobility of its constituent electron pair, easily interacts with the α-hydrogens of polypropylene to form not very strong, so-called π-complexes.

Under the conditions of processing a carbon-filled polypropylene composition by injection molding at elevated temperatures, it is possible that α-hydrogen interacts with active centers in the carbon structure, leading to crosslinking of polypropylene macromolecules.

Similar patterns in the formation of molecular interactions were observed, when mechanically activated graphite was used as a filler in polymer composite materials. In this case, each carbon atom is bonded to the neighboring three σ - bonds, and the fourth electron actually remains unpaired. Because of this, the elementary unit of graphite is significantly reactive and very prone to the formation of hydrogen bonds, in particular, with the α-hydrogen of polypropylene macromolecules.

In addition, during the formation of composite materials under the action of an elevated temperature, α-hydrogen can be detached from polypropylene macromolecules. As a result, obviously, crosslinking of polypropylene macromolecules can occur by means of graphite.

Summarizing the above, we can come to conclusion that all functional groups on the surface of dispersed carbon are characterized by different degrees of activity and affect the molecular composition of the adsorption layer. It is noted that with an increase in the oxygen content to 5-6% in the functional groups of carbon black, the intensity of its

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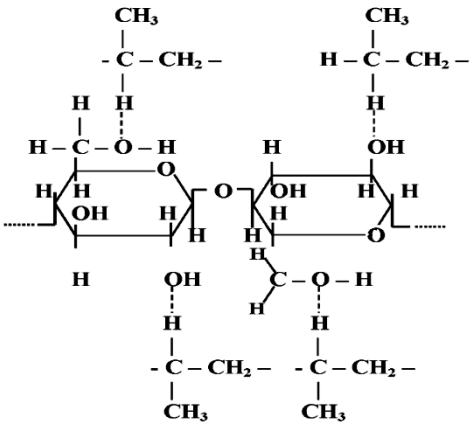
interaction with polymers increases, creating favorable conditions for enhancing interphase interaction, leading to an increase in the physico-mechanical indicators of composite polymer materials.

The mechanism of interaction of polymers with fibrous fillers. In the polypropylene + glass fiber system, glass fiber is an artificial fiber obtained by stretching or dismembering molten glass of the composition, wt. %: SiO_2–56; $A1_2O_3$–5; CaO–22; Na_2O–11; MgO–6. It has high mechanical strength, chemical resistance, and high thermal properties.

All components are oxide components of glass fiber, capable of forming hydrogen bonds between the α-hydrogens of polypropylene and oxygen atoms present in metal oxides.

Cotton lint – is a waste from the processing of cotton cellulose, it is a polysaccharide built from the elementary links of anhydro-D-glucose, which is saturated with hydroxyl groups. The latter interact with the α-hydrogen of polypropylene, creating strong oxygen-hydrogen bonds.

As is known, cellulose, including lint, has a strong interaction between macromolecules due to the presence of numerous hydrogen bonds, mainly between oxygen atoms of hydroxyl groups and hydrogen atoms of elementary units. Moreover, oxygen atoms of lint hydroxyl groups can also interact with other hydrogen-containing reagents, including PP-type polymers due to the presence of more active d-hydrogen atoms in its macromolecules, for example, according to the following scheme:



V. CONCLUSIONS

As a result of the studies, it was found that the structure of the composite polymer material is a highly crystalline polymer structure with an elastic-rigid integral extended chain of particles of a dispersed filler conjugated with it for effective point reinforcement of polypropylene.

Thus, the analysis of the structural features have been carried out and the mechanism of the physicochemical interaction of the components of composite polymer materials filled with fibrous fillers have been revealed. It was revealed that the physicochemical interaction of fillers with the polymer forms strong bonds of the filler particles with the polymer, which ensure the formation of a dense adsorption layer and adhesion bonds between the polymer macromolecules and the structural groups of the filler particles.

In this case, along with hydrogen-oxygen or hydrogen-carbon bonds also arise due to the action of van der Waals forces, there is a strengthening of intermolecular bonds between macromolecules of polymers, which improve the properties of composite polymer materials. In addition, it has been established that the structure of the composite polymer material is a highly crystalline polymer structure with an elastic-rigid integral extended chain of particles of dispersed fillers conjugated. The purposeful use of combinations of organomineral fillers, due to the specific features of the structures, creates favorable conditions for the processing of composite polymer materials with reduced shrinkage, sufficient density and improved mechanical and antifriction characteristics, which are very important in the manufacture of parts

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from composite polymer materials of complex design.

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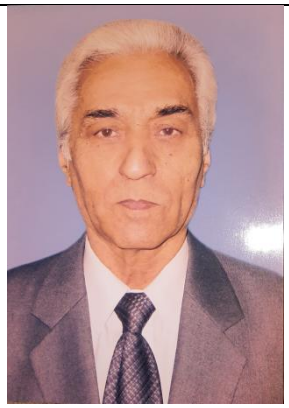 Gulyamov Giyas Gulyamovich	Materials Sciences	Uzbekistan
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