MANUFACTURING TECHNOLOGY FOR BUILDING MATERIALS AND PRODUCTS

Review article
https://doi.org/10.15828/2075-8545-2022-14-4-294-299



# Fillers for polymer composite materials

**Aliya K. Mazitova, Ilnaz I. Zaripov*, Gulia K. Aminova, Maksim V. Ovod, Nina L. Suntsova**
Ufa State Petroleum Technological University, Ufa, Russia
* Corresponding author: e-mail: ilnaz.zaripov1996@mail.ru

**ABSTRACT: Introduction.** For the production of building products made of PVC, compositions are used that, along with the polymer, include additives: plasticizers, stabilizers, modifiers. This leads to a decrease in the chlorine content in the composition and increases the flammability of the productitself. Therefore, nanoparticles of various fillers are added into the compositions. Fillers inPVC compositions (more often inorganic, less often organic substances) are solid additives that differ from the polymer matrix in chemical composition and structure.In most cases, the main function of fillers is to reduce flammability and cut costs of the products obtained, in some cases they serve to impart or improve the following properties: reducing plasticizer absorption, changing in dielectric properties, increasing rigidity and hardness, reducing noise transmission, reducing toxicity of combustion products. **Main part.** Fillers are classified according to various criteria. According to the state of aggregation, they are divided into gaseous, liquid and solid. By their nature, they are divided into organic and inorganic; according to the source of receipt – reinforcing, strengthening, reinforcing, neutral; bythe size, particle shape and structure – into 4 main types: dispersed (powder); fibrous (fibers, threads, bundles, etc.); sheet (film) with a given structure (fabrics, paper, tapes, sheets, films, nets); volumetric (framework) with a continuous three-dimensional structure (bulk fabrics, felt, skeletal and porous frameworks). The most commonly used solid fillers, which are also called dispersed. The introduction of dispersed fillers into polymer composite materials (PCM) is more appropriate for creating mass-produced materials, more technologically advanced, with a low level of strength characteristics. Dispersed fillers are introduced into thermoplastics with high fracture energy to reduce their cost, increase stiffness and compressive strength, and improve their technological characteristics during processing. At the same time, their tensile strength and impact strength decrease due to reduction in the proportion of polymer in the filled composition. The introduction of solid and hard particles leads to an increase in the elastic modulus (E); and soft, elastic or gaseous fillers – to its decrease. According to the mechanism of action, dispersed fillers can be divided into inert ones, which do not affect the properties of the matrix and are introduced into its composition to reduce the cost of the composition, and active ones. Dispersed fillers are divided into mineral, organic and metal. The commonest of those are minerals. **Conclusion.** Thus, at present, there are a large number of substances and materials used as fillers and making it possible to obtain PCM with low shrinkage and shape stability of products, high mechanical properties and the necessary set of special properties. Due to fillers, PCM can compete with other materials such as glass, ceramics and even metal in most areas of human activity.

**KEYWORDS:** fillers, nanoparticles, polymer composite materials, classification.

**FOR CITATION:** Mazitova A.K., Zaripov I.I., Aminova G.K., Ovod M.V., Suntsova N.L. Fillers for polymer composite materials. *Nanotechnologies in Construction.* 2022. Vol. 14, no. 4. p. 294-299. https://doi.org/10.15828/2075-8545-2022-14-4-294-299. – EDN: EKRDWM.

## INTRODUCTION

At present, polyvinyl chloride (PVC) is one of the most common large-tonnage products in the global polymer industry [1]. PVC in its composition contains about 56% chlorine, so it belongs to polymers of low flammability and flammability. For the production of building products from PVC, compositions are used that, along with the polymer, include additives: plasticizers, stabilizers, modifiers [2, 3]. This leads to a decrease in the chlorine content in the composition and increases the combustibility of the product [4]. Therefore, nanoparticles of various fillers are added to the compositions. Fillers of PVC compositions (more often inorganic, less often organic substances) are solid additives that differ from the polymer matrix in chemical composition and structure. In most cases, the main function of fillers is to reduce flammability and reduce the cost of the products obtained; in some cases, they serve to impart or improve the following properties: reduced plasticizer absorption, changes in dielectric properties, increased rigidity and hardness, reduced noise transmission, reduced toxicity of combustion products [5–7].

## MAIN PART

### Classification of fillers

There are a number of approaches to the classification of fillers according to various characteristics (Fig. 1). According to the state of aggregation, all known fillers are divided into gaseous, liquid and solid. By their nature, they are divided into organic and inorganic; according to the source of receipt – reinforcing, strengthening, reinforcing, neutral; by size, particle shape and structure – into 4 main types: dispersed (powder); fibrous (fibers, threads, bundles, etc.); sheet (film) with a given structure (fabrics, paper, tapes, sheets, films, nets); volumetric (framework) with a continuous three-dimensional structure (bulk fabrics, felt, skeletal and porous frameworks) [8].

Gaseous fillers – various gases (nitrogen, hydrogen, ammonia, carbon dioxide, etc.), low-boiling hydrocarbons (pentane, isopentane, etc.), as well as organic and inorganic solids (ammonium carbonates, sodium carbonates, porophores, etc.) that foam the polymers. A porous structure can also be created in the course of physical processes leading to the appearance of a vapor-gas phase in the bulk of the polymer or chemical processes accompanied by the release of gaseous products. The content of blowing agents in the composition is usually 1–10% by weight of the polymer. Gas-filled plastics (foam plastics) are characterized by low density, good heat and sound insulation properties. As a result of filling with gas, light, heat, sound-proof, elastic and rigid foam plastics and foam plastics with specified damping properties are widely used in technology and in everyday life.

Liquid fillers are water and mineral oils [9]. Water is used in the production of rigid materials based on polyester resins. Mineral oils are used to maintain a lubricant layer on the friction surface.

Liquid-filled plastics are obtained by curing (cooling) stable emulsions in which the filler is the dispersed phase and the polymer is the dispersion medium.

As a rule, in filled polymer materials, the dispersed phase is a liquid, and the matrix is a polymer. Water, mineral oils, liquid lubricants, antiseptic and other substances are used as a liquid filler. Liquid-filled polymers are used to make fire-retardant screens, self-lubricating bearings, fragrances, and other materials.

The most commonly used solid fillers, which are also called dispersed.

### Dispersive fillers

The most common type of fillers for polymer composite materials (PCM) are dispersed fillers of various nature. PCM containing dispersed fillers, which are evenly distributed in the material, as a rule, are characterized by an isotropy of properties, the optimum of which is achieved at a degree of filling that ensures the adsorption of the entire volume of the binder by the surface of the filler particles. With an increase in temperature and pressure, part of the binder is desorbed from the surface of the filler, due to which the material can be molded into products of complex shapes with brittle reinforcing elements. The dispersed filler reduces shrinkage during pressing, increases the rigidity and hardness of products made of composite materials (CM), and in some cases products acquire specific properties, such as arc resistance, electrical and thermal conductivity, resistance to electromagnetic and penetrating radiation, etc. Introduction to PCM dispersed fillers is more appropriate for creating mass-produced

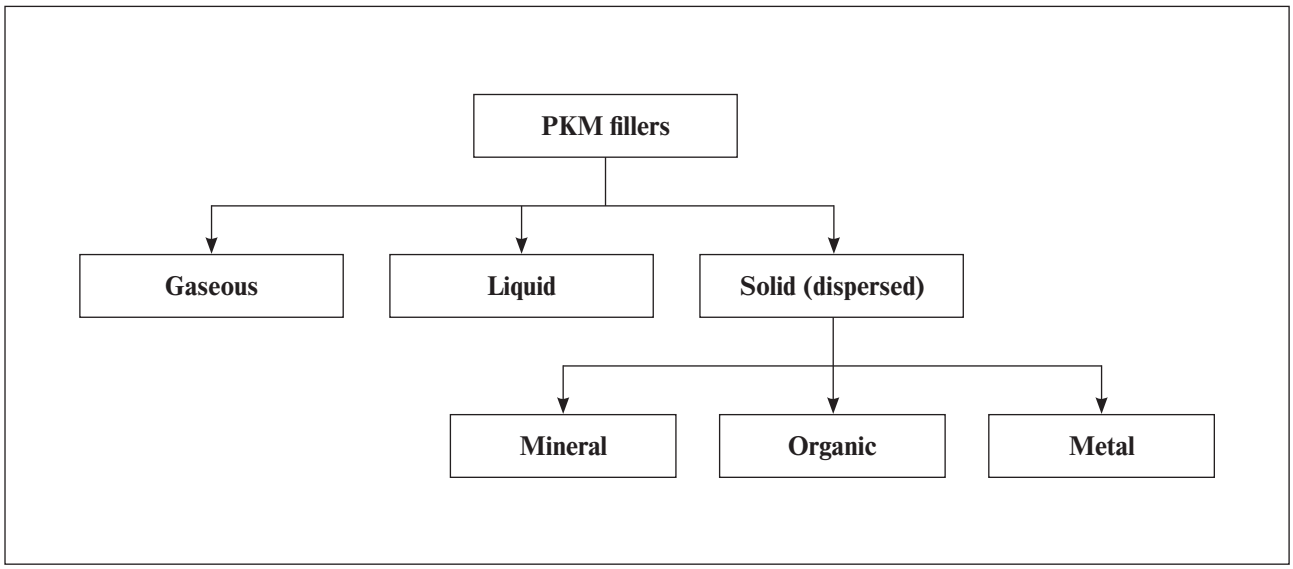


Fig. 1. **Main types of fillers**

materials, more technologically advanced, with a low level of strength characteristics. Dispersed fillers are introduced into thermoplastics with high fracture energy to reduce their cost, increase stiffness and compressive strength, and improve their technological characteristics during processing. At the same time, their tensile strength and impact strength decrease due to a decrease in the proportion of polymer in the filled composition. The introduction of solid and hard particles leads to an increase in the elastic modulus (E), and soft, elastic or gaseous fillers – to its decrease [10].

Among the most important requirements for dispersed fillers are the ability to combine with the polymer or disperse in it, good wettability by the melt or polymer solution, lack of tendency to agglomerate particles, uniformity of their size, and low humidity (as a rule, drying is necessary).

In addition, the type of binder also imposes certain requirements on the filler. Thus, when filling thermoplastics, fillers can have a catalytic effect on the curing process of the binder, and when filling thermoplastics, it is desirable that the filler particles have a rough surface for better adhesion to the matrix.

According to the mechanism of action, dispersed fillers can be divided into inert ones, which do not affect the properties of the matrix and are introduced into its composition to reduce the cost of the composition, and active ones. The activity of the filler is mainly determined by three factors:

– the ratio between the adhesion energy of the polymer to the filler, which can be increased by introducing active compounds into the binder, and the cohesive energy of the polymer;
– the degree of dispersion of the filler particles, which determines the surface area of the contact of the matrix with the filler and can be increased by grinding it;
– the amount of filler introduced, since even fillers that are considered inert in most sources (dolomite, marble, chalk, barite, etc.), at the so-called critical content, begin to affect the mechanical properties of the composite, for example, significantly reducing impact strength [11].

The activity of the filler can be increased by modifying its surface with compounds that give it or the binder additional properties or optimize their characteristics [12]. For example, to improve rheological properties and wetting, the chalk surface is often treated with stearic acid, calcium stearate, or coupling agents, which contributes to a better distribution of chalk particles in the polymer matrix [21]. When obtaining composite materials, inert and active fillers can be used simultaneously.

Active fillers include hydroxides of aluminum and magnesium. Aluminum hydroxide is used in the composition of plastics and many other materials, absorbs heat, suppresses combustion, adsorbs combustible gases, prevents heating and further decomposition of polymers, and reduces the combustibility of materials. Magnesium hydroxide is used as a flame retardant in the production of thermoplastics and polymer compositions. Magnesium hydroxide plays an important role in the production of non-flammable wires and cables (automobile and halogen-free cables), in the production of roofing sheets.

Dispersed fillers are divided into mineral, organic and metal. The most common of them are mineral [13].

**Mineral (light) dispersive fillers**

Mineral disperse fillers include: chalk, aerosil, white soot, aluminosilicates, as well as metal oxides and sulfates [14, 15].

Chalk is a white, odorless powdery substance, characterized by low hygroscopicity, it is an environmentally friendly non-toxic product, non-flammable, explosion-proof. As a filler, it is widely used in materials based on PVC (in rigid and plasticized formulations), polypropylene, polystyrene and its copolymers, in polyester fiberglass (premixes, prepregs). Chalk is also used in rubber compounds based on almost all general purpose rubbers as a cheap inert filler. It is well dispersed in rubbers of various types. Chalk-filled rubber compounds are characterized by high plasticity and good working properties.

Aerosil is a fine white dusting powder, non-flammable, explosion-proof, harmless and does not cause silicosis even at high concentrations. It is an expensive filler, so its use is advisable in rubbers with unique properties: it is mainly used in rubbers based on silicone rubbers. Aerosil-filled rubbers are characterized by high tear resistance, high relative elongation, wear resistance, high resistance to thermal aging, and good dielectric properties.

White soot is an amorphous non-toxic white powder, fire and explosion proof. It is used as a reinforcing filler for synthetic and polymeric materials in the tire, rubber, chemical, light and other industries. White carbon improves mechanical characteristics, increases heat resistance and fire resistance.

Kaolin is a powdered environmentally friendly, non-toxic product, from white to reddish color depending on the iron content, non-flammable, explosion-proof. Kaolin is used in the filling of thermoplastics to impart increased tensile modulus values, as well as to improve electrical properties, in the production of fiber-reinforced plastics based on polyester binders – to increase viscosity, as well as to increase volumetric electrical resistance and water resistance. It is also used as a semi-reinforcing filler for general purpose rubbers. Its introduction into rubber compounds leads to an increase in their viscosity, an increase in carcass and a decrease in shrinkage.

Diatomite is a natural aluminosilicate, is a soft rock, non-toxic, fire and explosion-proof. It is currently most

widely used as an antiblock additive in the production of low density polyethylene films. It is also used as a technological additive (absorbent) in highly oil-filled rubber compounds. The introduction of diatomaceous earth into rubber compounds increases their carcass and reduces shrinkage.

Bentonite is a natural layered aluminosilicate, non-toxic, fire and explosion-proof. Due to the active surface, bentonite is a good object for modification in order to direct changes in properties. It is used in rubber compounds of various hardness for the manufacture of molded products.

Talc is a natural mineral in the form of a soft, greasy to the touch white powder. The product is non-toxic and fireproof. It is most widely used as a filler for thermoplastics, primarily polypropylene (automotive, instrumentation). Talc-filled polymer compositions are characterized by higher rigidity and creep resistance. It is also used in the rubber industry mainly as a powdering material. To a lesser extent, it is used as a filler for rubbers, which are subject to increased requirements for rigidity, hardness, and dielectric properties. The introduction of talc into the elastomer increases the resistance to tear, thermal aging and provides low compression set.

Titanium dioxide is a white, odorless powder. Physiologically, it is safe, belongs to the fourth hazard class, fire and explosion proof. The widespread use of titanium dioxide as a white pigment in the polymer industry is due to the effective scattering of visible light: when the dispersion is introduced into the plastic mass, the effect of whiteness and opacity is created, and the brightness of the color is provided.

Zinc oxide is a white, slightly yellowish or gray odorless powder, belongs to the second hazard class, is fire and explosion safe. It is used as an activator for sulfur vulcanization of all diene rubbers, a vulcanizing agent for chloroprene rubbers. It is limitedly used as a heat-resistant and heat-conducting filler for light and dark rubbers.

Lithopone is a non-toxic and non-flammable white powder. It is used for pigmenting paints and varnishes based on any film-forming agents, it is especially suitable for water-dispersion paints, since it does not cause coagulation. Due to insufficient light and weather resistance of the coating, paints pigmented with lithopone are suitable for indoor use only. Lithopone is also used as a white pigment for the manufacture of colored rubbers and as a filler for acid-alkali-resistant rubbers.

### Organic dispersive fillers

Organic particulate fillers include graphite, wood flour, coke, and soot.

Graphite is practically pure carbon, has high thermal and electrical conductivity, and is a good dry lubricant. It is widely used in polymer composites, alone or in combination with reinforcing fibres, as well as in various inorganic fillers and blends, e.g. mica, talc. Such composite materials with graphite include dry sliding, sealing properties (which are important in automotive and micro-mechanical parts and components).

Wood flour consists mainly of cellulose and lignin. When introduced into CMs, it improves their dimensional stability, tensile strength, and electrical insulating properties. Disadvantages (especially from hardwood) – low heat, moisture and chemical resistance.

Soot is a highly dispersed carbonaceous material formed during the incomplete combustion and thermal decomposition of hydrocarbons contained in natural or industrial gases and liquid products (oils) of petroleum and coal origin. The hardening effect of soot in CM is determined by its fineness, roughness, and specific activity. When introduced into PCM, it increases the dimensional stability, rigidity, heat resistance, thermal and electrical conductivity [16, 17].

### Metal dispersive fillers

Metal powders have little effect on strength, but allow a wide range of changes in thermal and electrical conductivity, heat capacity, magnetic characteristics, electrical properties, as well as to give materials protection from electronic and penetrating radiation, change their density, combustibility, etc. Copper, aluminum, iron, bronze, tin, silver, lead, zinc are most often used as metal dispersed fillers. The surface of metal powders is often finished to increase adhesion and reduce moisture adsorption, and also covered with protective films (for example, in the form of a varnish layer) to exclude their influence on curing and degradation. A special group of metal-containing fillers are magnetic fillers. These fillers include oxide isotropic ferrites of barium and strontium, powders of alloys of rare earth metals with iron and boron ($Nd_2Fe_{11}B$), as well as binary alloys of samarium and cobalt ($CmCo_5$, $CmCo_{17}$) [18–20].

## CONCLUSION

Thus, at present, there are a large number of substances and materials used as fillers and making it possible to obtain PCM with low shrinkage and shape stability of products, high mechanical properties and the necessary set of special properties. Due to fillers, PCM can compete with other materials such as glass, ceramics and even metal in most areas of human activity.

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INFORMATION ABOUT THE AUTHORS

**Aliya K. Mazitova** – Dr. Sci. (Chem.), Prof., Head of Applied and Natural Sciences Department, Ufa State Petroleum Technological University, Ufa, Russia, elenaasf@yandex.ru, https://orcid.org/0000-0003-2304-1692

**Ilnaz I. Zaripov** – Assistant, Applied and Natural Sciences Department, Ufa State Petroleum Technological University, Ufa, Russia, ilnaz.zaripov1996@mail.ru, https://orcid.org/0000-0003-2051-831X

**Gulia K. Aminova** – Dr. Sci. (Eng.), Prof., Head of Applied and Natural Sciences Department, Ufa State Petroleum Technological University, Ufa, Russia, aminovagk@inbox.ru, https://orcid.org/0000-0001-7830-9954

**Maksim V. Ovod** – postgraduate student of Building Constructions Department, Ufa State Petroleum Technological University, Ufa, Russia, Maxov001@ya.ru, https://orcid.org/0000-0003-4008-6294

**Nina L. Suntsova** – Cand. Sci. (Philol.), Assistant Professor of Foreign LanguagesDepartment, Ufa State Petroleum Technological University, Ufa, Russia, sunc-nina@yandex.ru, https://orcid.org/0000-0002-1384-3598

CONTRIBUTION OF THE AUTHORS

**Aliya K.Mazitova** – scientific management; final conclusions.

**Ilnaz I. Zaripov** – research concept; writing the draft; follow-on revision of the text.

**Guliya K. Aminova** – methodology development.

**Maksim V. Ovod** – collection of materials.

**Nina L. Suntsova** – participation in the development of the material.

**The authors declare no conflicts of interests.**

**The article was submitted 02.06.2022; approved after reviewing 21.06.2022; accepted for publication 27.06.2022.**