It is now accepted that the chemical grafting of different compounds to the surface of solids or else chemical surface modification is capable of yielding many new and extremely useful materials for practical purposes. The diversity of chemically modified materials is inexhaustible, since, essentially, any of the chemical compounds described can be fixed on a surface. Surface-modified materials have a number of parameters that can vary within a wide range. These are the chemical nature of the support, the magnitude of its specific surface and the pore size distribution, the chemical nature of the graft molecules or modifier particles, the structure and length of the “foot”, the composition and structure of the “anchor”, the structure of the graft layer, the distribution of molecules in the graft layer, etc.

Thus, it can be stated that, in recent years, at the point where several scientific disciplines (organic and inorganic chemistry, colloid chemistry, and the chemistry of high molecular weight compounds) meet, a new scientific specialisation has emerged – the chemistry of graft surface compounds. This scientific specialisation has its own original subject of investigation – a solid that includes a support with a layer of molecules, their aggregates, or macroscopic particles chemically fixed on its surface. The fundamental problem confronting specialists dealing with the chemistry of graft surface compounds is to establish the laws governing the synthesis of these materials; researchers must learn how to carry out the targeted synthesis of products with specified properties [1–3].

Earlier, we synthesised polypropylene–polystyrene (PP–PSt) fibrous materials using different methods of initiation of grafting of styrene (St) to polypropylene fibre (PPF); sulphonated cation-exchange resins (SCERs) were produced by the sulphonation of graft products [4, 5]. References [6] and [7] were devoted to developing SCERs based on PP–PSt fibrous materials – products of the graft polymerisation of styrene on polypropylene fibre synthesised using ultrasound. In the present work, a study will be made of certain aspects of the production of the given PP–PSt fibrous materials that are important for an understanding of the processes occurring in the reaction system under the action of ultrasound. Modern high technologies, which have developed so explosively recently, among which ultrasound treatment has its own special niche, are quite naturally attracting the interest of researchers, including the present authors.

1. SONOCHEMICAL APPLICATION OF STRONG ULTRASOUND

At present, research in the area of sonochemical application of strong ultrasound is being carried out along such lines as sonochemical catalysis, organic synthesis, nanotechnology, solid-state chemistry, polymer chemistry, etc. [8–29].

The sonochemical production and activation of heterogeneous catalysts are extremely productive methods, although the prolonged action of ultrasound on certain catalytic systems may lead to their deactivation by the adhesion of particles and a reduction in pore size. Thus, as a result of ultra-high-speed collisions of zinc particles, their localised melting or plastic deformation occurs, leading to the formation of a neck between them (Figure 1).
Of great importance is the choice of conditions, upon which surface purification and variation in particle size depend. Owing to the capacity of strong ultrasound to activate metals, dispersing, purifying, and etching them, considerable progress has been possible in the field of organic synthesis.

Ultrasound causes active mixing, both in homogeneous and in heterogeneous systems. In the case of the latter, mixing is an important problem, since, when the reaction occurs on the surface of a solid, effective transport of reagents to this surface is necessary, and also the removal from it of reaction products at the end of the process.

Furthermore, metal complexes produced under the action of ultrasound can be used in organic synthesis. Thus, in the sonolysis of iron pentacarbonyl, products characteristic of a thermal or photochemical reaction are not formed, and dissociation of ligands occurs. In spite of the fact that the formation of particles such as Fe₃(CO)₁₂ has been reliably established, in a sonochemical reaction they were probably obtained from other intermediates.

We will dwell in more detail on questions of polymerisation with the use of ultrasound [8, 9, 16, 17, 23, 24, 27–29].

The formation of radicals, in the same way as the occurrence of polymerisation processes with their participation, is attributed by researchers to the formation of very high temperatures within cavitation bubbles.

Thus, it was observed that, when acrylonitrile in a weak aqueous solution is subjected to ultrasound, the particles initiating the polymerisation process are either H⁺ and OH⁻ radicals (separately or together) or radicals formed by degradation of the polymer.

The free-radical nature of polymerisation processes was confirmed by experiments in the presence of radical traps such as diphenylpicrylhydrazyl (DPPH), as a result of which it was established that the observed induction period is roughly proportional to the DPPH concentration.

Lorimer et al., comparing the action of ultrasound on the polymerisation of N-vinylcarbazole in solution, established that, at a specified rate of irradiation, there is an optimum time of action on the system, the overstepping of which leads to a reduction in the amount of polymer formed. Furthermore, the polymer yield increased with decreasing temperature and ultrasound intensity (Figure 3).

Lorimer and Mason, studying the emulsion polymerisation of styrene in the presence of potassium persulphate, found that the additional action of ultrasound on the initial mixture (under the same conditions) leads to a marked increase in the initial rate of the process (Figure 4).

The absence of an induction period in the sonochemical process was attributed by the authors to the fact that, on exposure of the given system to ultrasound, a greater number of radicals are formed (since decomposition of the initiator is accelerated, and degradation of the polymer occurs), and a more stable suspension is formed. As a result, owing to the greater number of radicals formed, the rate of the process increases.
2. GENERATION OF RADICALS AND PROCESSES WITH THEIR PARTICIPATION

As stated above, the aim of the present work was to examine certain important aspects of the production of PP—PSt fibres with the use of ultrasound [8, 9, 15, 18–22, 25, 26, etc.].

2.1 Homolysis of Water

The primary reaction under the action of ultrasound is normally homolysis of the solvent with subsequent radical attack of the entire system; the presence of oxygen, however, increases the probability of formation of oxidation products [19–22].

The action of ultrasound on water causes cavitation and leads to its homolysis:

\[ \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+ \]

The formation of \( \text{HO}^- \) and \( \text{H}^+ \) radicals was confirmed by EPR spectroscopy using spin traps. Hydroxyl radicals and hydrogen atoms are primary reaction products, and here the former are able then to enter into recombination reactions leading to the formation of hydrogen peroxide:

\[ 2\text{HO}^- \rightarrow \text{H}_2\text{O}_2 \]

The hydrogen peroxide formed on exposure of water to ultrasound promotes the occurrence of oxidation reactions in the system. In the presence of oxygen, subsequent processes can develop by the following scheme:

\[ \text{H}^+ + \text{O}_2 \rightarrow \text{HO}_2^- \]
\[ 2\text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]
\[ \text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]
\[ \text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{HO}^- + \text{H}_2\text{O} \]

2.2 Formation of Macroradicals

The formation of radicals and the occurrence of polymerisation processes with their participation are explained by the emergence of very high temperatures within the cavitation bubbles. At the same time, the high pressures that propagate in the medium in the form of shock waves also cause degradation of the polymers. The Dowlah model, describing the degradation of polymers in an acoustic field, assumes that the shock waves caused by the collapsing of bubbles generate microflows that interact with the macromolecule in solution.

When the macromolecule ruptures, macroradicals are formed, the existence of which was confirmed spectrophotometrically using diphenylpicrylhydracil [25, 26]. Here, the degradation of macromolecules can occur both through ruptures of the main chain and through C–H bond rupture, since the energy of the latter is higher than the energy of C–C bonds by a total of 20% (412 and 350 kJ/mol respectively).

Thus, ultrasound initiates polymerisation processes, and at the same time, as it is formed, the polymer partially degrades. It becomes understandable that, in our case, along with homolysis of the solvent, the fragmentation of polypropylene under the action of ultrasound leads to the additional formation of macroradicals.
2.3 Hydroperoxidation of PPF and Radical Polymerisation on an Activated Solid Surface

A great deal of attention has recently been paid to the features of heterogeneous polymerisation systems in which the conditions of formation of polymer phase on a solid surface are specially created. The possibility of such polymerisation is achieved by fixing active centres of initiation on the surface of the materials selected for this purpose.

The formation of a polymer matrix on solid material (filler, support, etc.) with the use of active centres chemically bound with the surface ensures maximum interaction of the polymer and filler, uniform distribution of the filler in the polymer, and so on. As a result, the production of new materials with special properties becomes possible.

As established earlier, the activity of the initial PPF material selected in the present work is due primarily to the presence on its surface of hydroperoxide (HP) groups formed during preliminary oxidation of the PPF [30]. The number of surface HP groups depends on the selected method and the oxidation conditions of the PPF.

During the oxidation of PP fibrous material, a concentration of hydroperoxide groups that is sufficient for the subsequent graft polymerisation on its surface of different reactive compounds can be achieved under relatively mild conditions, since polypropylene contains tertiary carbon atoms. The scheme of hydroperoxidation of PP can be presented as shown in Scheme A.

The reaction of breakdown of the hydroperoxide groups proceeds by a bimolecular mechanism; in this case it can largely be reduced to the interaction of HP groups with hydrogen atoms primarily at tertiary carbon atoms:

\[ \text{ROOH} + \text{RH} \rightarrow \text{RO}^\cdot + \text{R}^\cdot + \text{H}_2\text{O} \]

The decomposition of the hydroperoxide groups may proceed by a monomolecular mechanism:

\[ \text{ROOH} \rightarrow \text{RO}^\cdot + \text{OH}^\cdot \]

Thus, the oxidation of PPF with the formation of HP groups makes it possible, on the subsequent breakdown of these groups, to use the free radicals formed as initiators of graft chain growth.

On the other hand it is known that one of the ways of modifying solid surfaces in order to increase the effectiveness of grafting is to treat them with peroxides. The surface of solid materials generally has a promoting effect on the decomposition of peroxides, a large role in which is played by their adsorption interaction with the developed surface of materials. Here, new surface radicals are formed, the recombinations of which with free radicals leads to fixing of the latter on the surface.

Earlier (see Section 2.1) we noted that, during the ultrasound-induced homolysis of water, hydrogen peroxide is formed. Consequently, the presence of the latter in the system can be regarded as additional hydrogen peroxide treatment of the oxidised polypropylene fibrous material selected in the present work. This leads to additional hydroperoxidation of the PPF, while promotion by the surface of the PPF of the decomposition of H\(_2\)O\(_2\) promotes the formation and fixing on it of new radicals capable subsequently of acting as initiators of graft chain growth.

Furthermore, it is worth noting that the indicated processes are extremely sensitive to the presence in the system of oxygen, molecules of which react with surface radicals to form new reactive groups. These groups, in turn, interacting with hydrogen peroxide, yield new radicals that are active in macrochain breakage, and so on. Thus, oxygen, ultimately, is capable of promoting the process of graft polymer formation.

When a monomer is present in the reaction system, the reactions occurring in the liquid phase (chain initiation, growth, transfer, and breakage) compete with reactions occurring on the surface (breakage of the primary radicals, breakage of the growing macrochains) [31, 32]. The reactions given below illustrate the course of the process on the surface, which leads to the formation of a graft polymer:

- The formation of a radical on the surface
  \[ \text{R}^\cdot + \text{S} \rightarrow \text{S}^\cdot \]
- Transfer of a polymer chain on to the surface
  \[ \text{Pn}^\cdot + \text{S} \rightarrow \text{S}^\cdot + \text{Pn} \]
- Chain growth on the surface
  \[ \text{S}^\cdot + \text{nM} \rightarrow \text{SMn}^\cdot \]

\[ \text{...} \overset{\text{O}_2}{\text{CH}_3 \overset{\text{CH}}{\text{CH}_2 \overset{\text{CH}}{\text{CH}_2 \overset{\text{O}}{\text{CH}}\cdot \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_3 \overset{\text{Scheme A}}{\text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_3}} \right. \]
Since the intensity of the surface reactions in the given case is extremely high, the process of polymerisation within the bulk of the material is slowed down considerably, or inhibited entirely.

2.4 Graft Polymerisation of Styrene

The present authors do not currently have a strict quantitative evaluation of the composition of PP–PSt fibrous material; furthermore, the pattern of individual stages of formation of its microheterogeneous structure, governed by the action of ultrasound on the initial system, is not entirely clear. The given fibrous material, however, can be presented as a multicomponent heterogeneous material consisting of a solid fibrous polypropylene base, graft polystyrene, and a discrete polystyrene phase, the domains of which are immobilised in inter fibrillar regions of the fibre.

The phenomenological pattern of processes occurring in the system can be presented, it seems, in the following form:

- (a) graft polymerisation of styrene on the surface of the PPF ("grafting to");
- (b) graft polymerisation of styrene from the inter fibrillar space of the PPF ("grafting from");
- (c) homopolymerisation of styrene in the polystyrene phase;
- (d) homopolymerisation of styrene in the polypropylene phase.

On the basis of the above, the structure of PP–PSt fibre can be presented as a polystyrene matrix with a polypropylene core [see (a)] and certain homopolystyrene inclusions within the PP core (so-called occlusions of polystyrene). Occluded polystyrene can be subdivided into occlusions of the first and second kind. Occlusions of the first kind include polystyrene inclusions formed as a result of ultrasound "driving" the homopolymerisation products of styrene into the PP fibre [see (c)]. Occlusions of the second kind include polystyrene inclusions formed in the inter fibrillar space of PP as a result of the "capture", by the growing chains of PSt "grafted from" the fibre [see (b)], of the homopolymerisation products of St within the latter [see (d)].

The scheme of graft polymerisation of styrene, both on the surface and within the PPF, can be represented by the following reactions:

- Formation of primary radicals of monomer (styrene)
  \[ 2M \rightarrow 2R' \]

- Initiation of homopolymerisation of styrene
  \[ R' + M \rightarrow RM' \]

- Chain transfer to polypropylene (PP)
  \[ R' + PP \rightarrow PP' \]

- Initiation of grafting reaction
  \[ PP' + M \rightarrow PPM' \]

- Chain growth reactions
  \[ PPM' + M \rightarrow PPM + M + 1 \]

- Chain breakage reactions
  \[ PPMn' + PPm' \rightarrow PP + mPP + 1 \]

Above (see Section 2.3) we observed an increased intensity of surface reactions (in the present case, grafting) by comparison with the reactions within the bulk of the material (here, homopolymerisation), connected with the high surface activity of the PP fibre, which slows down or inhibits entirely the processes within the bulk of the system. In view of this, it is worth dwelling once more on the question as to which reactive groups on the surface of the PPF give it its activity.

The activity of the initial PP material, as stated above, is due primarily to the presence on its surface of hydroperoxide groups formed both during preliminary oxidation of the PP fibre and during interaction of the PPF with hydrogen peroxide which is the homolysis product of water under the action of ultrasound (see Sections 2.1 and 2.3).

Furthermore, an extremely important role can be played by the presence in the molecules of the initial material of –C=C– groups. Double bonds are formed owing to the thermal degradation of polypropylene under the action of high temperatures, both at the stage of production of fibrous material (in an extruder) [33–36] and under ultrasound. The thermal degradation of PP proceeds by disproportionation with the formation of vinylidene groups and propyl branches at the ends of chain fragments. During the pyrolysis of polypropylene, secondary reactions between the low molecular weight products of degradation lead to the formation of polyene systems. The thermal degradation of PP leads to the polymer chains breaking by the C–C bonds with the formation of free radicals (initiation). Macroradicals can
accept a hydrogen atom from their own or another chain to form an unsaturated group and a new free radical (chain transfer); chain breakage occurs by the recombination of free radicals. With most chain ruptures, the transfer of hydrogen occurs, but the other ruptures lead to the formation of free radicals continuing the decomposition of the chain until the formation of a monomer (however, according to literature sources, the propylene content in the products of thermal degradation of PP remains negligible) [36].

CONCLUSIONS

Thus, the processes occurring in the production of polypropylene–polystyrene fibrous materials with the use of ultrasound bear a radical character. Here, the generation of radicals occurs by the homolysis of water and styrene, the fragmentation of polypropylene (with the formation of macroradicals), and the breakdown of the hydroperoxide groups formed both during preliminary oxidation of the polypropylene fibre and during the interaction of PPF with hydrogen peroxide (the homolysis product of water under the action of ultrasound). As a result, in the bulk of the system, on the surface, and in the interfibrillar space of the PP fibre, reactions occur that lead mainly to the formation of a graft product, since the high surface activity of the PP fibre slows down or inhibits entirely the polymerisation processes in the bulk of the material.

In the present work we have examined certain aspects of the production of graft polypropylene–polystyrene fibrous materials that are important for an understanding of the processes occurring in the selected initial system under the action of ultrasound. The task of further investigations is to continue working on this problem, which holds great promise, since, on the basis of its solution, new ways can be found to control processes of production of new materials with special properties.

REFERENCES


(No date given)