Functional Polystyrene Materials

E Kh Karimov¹, O Kh Karimov¹, R R Daminev¹

¹Department of General Chemical Engineering, Branch of the University in the City of Sterlitamak, Ufa State Petroleum Technological University, Prospekt Oktyabrya, 2, Sterlitamak 453118, Russian Federation

E-mail: karimov.oleg@gmail.com

Abstract. The article presents successful technologies for isolation of functional polystyrene materials. The results of analysis of a material with current and heat-conducting inclusions, of an antibacterial component for medical purpose are given. The material has polymer characteristics and is suitable for obtaining a product with specified functional properties. Ways of copper formation having nanometer dimensions, a brief methodology and possible structure of the resulting filler are shown. Copper nanoparticles have unique anti-bacterial, current and heat-conducting properties. These properties are largely retained in the polymer material. The used carrying agent - polystyrene - is a product of large-capacity production; therefore the resulting materials are based on developed raw materials base all over the world. Isolation of copper ions from nanoparticles depends on the type of stabilizing agent and chemical nature of the environment. Implementation of antimicrobial properties in polymer materials is achieved by the dosage of copper in the amount of 1-2% by weight. Giving to material the conducting properties of copper nanoparticles requires higher concentration of metal. The shown way of synthesis of copper nanoparticles is suitable for implementation in polystyrene. Physical properties of the catalyst, so that an efficient, industrially applicable process.

1. Introduction

Styrene is worldwide produced in large capacities. This monomer was isolated from natural products in 1831 by Bonastre [1], but the build-up of industrial capacities began with the study of unique properties of polystyrene. Today, styrene is mainly produced by means of dehydrogenation of ethylbenzene, which is synthesized via alkylation of benzene by ethylene. Nearly 50% of global produced benzene (benzol) is used for producing styrene. In 2010, 25 million tons of styrene was produced. The approximate market value of styrene is 1,3 thousand U.S. dollars per ton [2].

The study of properties of polystyrene allowed its usage as a carrier of functional groups. As a result, the resulting material has technological and mechanical-and-physical properties of polymer and at the same time has functional properties.

In many cases, the joining of polymeric material and functional fillers is complicated by a sharp deterioration of the properties of one of the components. Either the filler deteriorates the properties of polymer (strength, fluidity, etc.) or the polymer breaks the morphology of filler, and its functional properties become deteriorated.

In the present work, a successful application technology of polystyrene as the carrier of functional groups is shown. The way of obtaining functional polystyrene material - mechanical implementation
of functional copper nanoparticles is considered. As a result, polystyrene retains its original polymeric properties and the material acquires the required functional characteristics.

2. Relevance and scientific significance
Mechanical introduction of metal nanoparticles into the polymer mesh allows creating thermoplastic material having unique properties of nanoparticles. For example, thermoplastic polystyrene with copper nanoparticles is of great interest due to the widespread use of copper as the current and heat-conducting inclusions, antibacterial component for medical purposes [3-6].

The antibacterial effect of copper nanoparticles (as an analogue of silver nanoparticles) is proved [7-9], which expands its practical application. The complex mechanism of antibacterial action is not studied in details. Most researchers adhere to the mechanism of action of copper ions which are released from nanoparticles [10-12]. Copper ions are most efficiently released from the copper nanoparticles. A mechanism for antibacterial action of copper consisting in the violation of plasmatic membrane of bacteria is offered [13, 14]. Therefore, to achieve maximum effect it is necessary to keep the set fractional composition of copper, morphology and crystal structure on the carrier. The joining of the processes of synthesis of copper nanoparticles and synthesis of polymeric material is a challenging technological task considering the features of chemical transformations and mutual influence of components on the properties of final material.

3. Synthesis of functional polystyrene material
As the carrier of the nanoparticles, polystyrene (PS) syndiotactic is used, the crystallization speed of which is much higher than of isotactic PS (refer with: Figure 1). The melting point of syndiotactic PS is 270 °C. At such and higher temperature begins the destruction of the polymer, thus complicating the technological processing of the polymer. Initially, introduction of metal nanoparticles in PS was done for thermal stabilization of the polymer [15-17]. Wide application of PS for packaging the foodstuff has led to the studying of antibacterial effect of copper nanoparticles embedded in PS [18, 19].

Technologically simpler method consists in mixing of 3% wt. copper nanoparticles with melted PS. The process of mixing lasts 3 hours at the temperature 270 °C (30 rpm). The resulting melt is solidified by cooling therefore the resulting polymeric material is to be grinded. In the technologies of mixing, larger copper nanoparticles of up to 150 nm in diameter are used.

Similar concentrations of copper nanoparticles in polypropylene [20] showed the hardening of polymer by 5%. Despite the relatively large size of copper particles, analyses of micrographs [20] show a uniform distribution of copper in the polymer without agglomeration. The used filler concentrations did not show significant hardening of PS.

The presence of copper nanoparticles affects the phase transition temperatures of PS in an ambivalent manner: the melting point remains constant but the crystallization temperature is shifted to higher temperatures.

Figure 1. Formula of isotactic PS (left) with the location of benzene rings on one side and syndiotactic PS (right) with alternating left and right benzene rings.
In the polymerization of styrene, the introduction of copper nanoparticles is held under more difficult conditions. Similar investigations have been conducted in [18]. For this purpose, copper nanoparticles were dispersed in the supercritical carbon dioxide at 70 °C and pressure of 207 bar; the same time the polymerization of the monomer was being carried out. By so doing, a uniform distribution of copper nanoparticles in polymer and high antibacterial properties are observed. The technology requires maintaining high pressure in the reactor but it is characterized by low toxic and inexpensive auxiliary components (supercritical carbon dioxide) [18]. Despite the successful results, implementation of this method is complicated by high pressures during the polymerization.

The most successful way for the synthesis of copper nanoparticles for filling the polystyrene appeared the method of polyol. This method [dissolution of inorganic precursors in alcohols] shows rapid nucleation and slow growth of particles via regulation of temperature [19-20]. Alcohol acts as a chelating agent. It is the formation of chelates that favors rapid nucleation and subsequent slow growth of metal particles. This method allows obtaining metal nanoparticles (or metal oxides) with low size distribution and controlled morphology.

As the inorganic precursors of copper nanoparticles, copper chloride CuCl₂ 2H₂O is used. An important role As a reducing agent of copper salt, an important role for preventing oxidation of copper nanoparticles plays the excess of ascorbic acid (sodium hydroxide [22] or natrium borane [11] can be used too). Antioxygenic properties of ascorbic acid are manifested because of its ability to attach free radicals through electronic donation via donor-acceptor mechanism:

![Figure 2. The donor-acceptor mechanism.](image-url)

The primary indicator of a change in ionic state of copper is the color system (refer with: Table 1).

**Table 1.** Color values of the system depending on the precursor and reducing agent type.

| Recursor         | Initial color | Under the action of sodium hydroxide | Under the action of ascorbic acid |
|------------------|---------------|-------------------------------------|----------------------------------|
| Cupric chloride  | blue          | brown                               | colorless → white → orange → dark brown* |

*Intermediate colors (stabilization of the final color after 12 hours).

Dispersing agent (antibonding substance) is polyvinylpyrrolidone (PVP), which stabilizes copper nanoparticles. The size and shape of the nanoparticles strongly depend on the concentration of this agent. PVP has the structure of polyvinyl skeleton with polar groups of oxygen and nitrogen, which have pairs of free electrons. These electrons participate in the interaction with copper ions, thus creating the chemical bond PVP-Cu2⁺ [23]:
In practice, these transformations are confirmed by the color transitions of solutions from light blue to yellow and the subsequent red (Cu°). Reducing agent and dispersing agent are separately dissolved in ethylene glycol (glycol alcohol). After their mixing and heating, anhydrous cupric acetate is thereto added. After exposure of agents on copper ions, copper separation via centrifugation is carried out, followed by washing with acetone and repeated centrifugation until a reddish copper powder is obtained.

4. Conclusions
The resulting polymeric materials are homogeneous with a uniform distribution of the functional filler throughout the volume and on the surface. Strength features of resulting material are identical to polystyrene. During processing to a product it demands the same mode of processing as well as the original polystyrene. Considering the current trends of development of chemistry and petrochemistry, the derived materials find broad application in these industries [24, 25].

5. References
[1] Maul J, Frushour B G, Kontoff J R, Eichenauer H, Ott K H and Schade C 2007 Polystyrene and Styrene Copolymers Ullmann's Encyclopedia of Industrial Chemistry (Weinheim: Wiley-VCH) chapter 1
[2] Richter F H 2013 Mesoporous Polymers as Catalysts for the Conversion of Biomass (Bochum: Ruhr-University Bochum)
[3] Park B K, Kim D, Jeong S, Moon J and Kim J S 2007 Thin Solid Films 157 706–11
[4] Choi Y, Lee C, Hwang Y, Park M, Lee J and Choi C 2009 Curr. Appl. Phy. 9 124–27
[5] Gurav P, Naik S S, Ansari K, Srinath S, Kishore K A and Setty Y P 2014 Colloids Surf. A 441 589–97
[6] Bogdanovic U, Lazic V, Vodnik V, Budimir M, Markovic M and Dimitrijevic M Mater. Lett. 128 75–78.
[7] Yoon K, Byeon J, Park J and Hwang J 2007 Science of the Total Environment 373 572–75.
[8] Cioffi N, Torsi L, Ditaranto N, Tantillo G, Ghibelli L and Sabbatini L 2005 Chemical Mater 17 5255–62
[9] Ojas M, Bhagat M, Gopalakrishnan C and Arunachalam K D 2008 J. Exp. Nanosci. 3-3 185–93.
[10] Li W R, Xie X B, Shi Q S, Zeng H Y, Ou-Yang Y S and Chen Y B 2010 Appl. Microbiol. Biotechnol. 85 1115–22
[11] Patla H, Gutierrez S and Delgado K 2010 Macromol. Rapid Comm. 31 563–67
[12] Xiu Z M, Ma J and Alvarez P J 2011 Environ. Sci. Technol. 45 9003–08
[13] Gunawan C, Teoh W Y, Marquis C P and Amal R 2011 ACS Nano 5 7214–25
[14] Zinck P, Bonnet F, Morteux A and Vissieux M 2009 Prog. Polym. Sci. 34 369–92
[15] Chrissafis K and Bikiaris D 2011 Thermochimica Acta 523 1–24
[16] Bikiaris D 2011 Thermochimica Acta 523 25–45
[17] Kamrupi I R and Dolui S K 2011 J. Appl. Polym. Sci. 120 1027–33
[18] Chrissafisa K, Pavlidoue A, Gkogkoua D and Bikiaris D 2013 Thermochimica Acta 561 26–35
[19] Park B K, Jeong S, Kim D, Moon J, Lim S and Kim J S 2007 J. of Colloid and Interface Science 311 417–24

Figure 3. The chemical bond PVP-Cu2.
[20] Karimov E K, Karimov O K, Kasyanova L Z, Movsumzade E M and Dmitriev Y K 2016 Key Engineering Materials 685 764-67
[21] Shankar H and Rhim J W 2014 Materials Letters 307 132-33
[22] Guzman A, Arroyoa J, Verdea L and Rengifo J 2015 Procedia Materials Science 9 298-304
[23] Karimov E K, Kasyanova L Z, Movsumzade E M, Karimov O K and Yalalov M R 2016 Theoretical Foundations of Chemical Engineering 50 92-96
[24] Karimov E K, Kasyanova L Z, Movsumzade E M and Karimov O K 2015 Russian Journal of Applied Chemistry 88 289-94
[25] Yashtulov N A, Zenchenko V O, Lebedeva M V, Samoilov V M, Karimov O K and Flid V R 2016 Russian Chemical Bulletin 65-1 133-38