CHARGE-CARRYING SUPERCONDUCTING POLYMER-CERAMIC NANOCOMPOSITES

S. P. DAVTYAN¹, A. O. TONOYAN¹, A. R. MICHAELYAN and STEFAN MÜLLER²*

¹ Armenian National Polytechnic University
105, Teryana Str., Yerevan, 0009, Armenia
E-mail: atonoyan@mail.ru
² Institute of Experimental Physics
Magdeburg University, D-39106 Magdeburg, Germany
E-mail: stefan.mueller@ovgu.de

With the use of yttrium and bismuth ceramics’ powders (Y₁Ba₂Cu₃O₆₋ₓ and Bi₂Sr₂Ca₂Cu₂O₈), on the basis of super-high molecular polyethylene binder, charge-carrying polymer-ceramic nanocomposites are obtained. It is shown that the implementation of the proximity effect between the ceramics’ grains leads to produce superconducting polymer-ceramic nanocomposites with a transport current. Additives of silver and aluminum nano-scale powders cause a significant increase of current density, and the application of acoustic fields during the formation of samples allows to further increase this density up to ~ 4·10⁵ A·cm⁻². Physical and mechanical properties of these charge-carrying nanocomposites have been investigated and it is shown that nano-sized aluminum additives increase the breaking strength and the elasticity modulus of the samples. Furthermore, the morphological features of the interphase layer of charge-carrying polymer-ceramic nano-composites have been studied on the basis of various binders (polymethylmethacrylate, polystyrene, super-high molecular polyethylene and isotactic polypropylene).

Figs. 8, tables 3, references 26.

Introduction

In order to obtain high-temperature superconductive products with a transport current, various metals have been used as binders [1-10], particularly silver [1-3,10] and metals of transitive row, Mo, Zn, Sr [8], and others.

For polymer-ceramic composites there are descriptions in the literature about using as binders both thermoplastics [11,12] and reacto-plastics [12]. In Ref. [11], polymer additives were chosen to protect high-temperature superconductors from moisture, whereas in [13-21], for obtaining polymer-ceramic samples of different
geometries (rods, tubes, rings, etc.), both the method of hot pressing [13,15,16,18,19] and of polymerization filling [14-15,17,20,21] were applied. In the publications [14,15,17,18,20,21] superconducting, physical-mechanical, thermo-chemical, and thermo-physical properties of polymer-ceramic nanocomposites were studied. It was shown [14-21] that for high temperature superconductive (SC) nanocomposites, the critical temperature of transition to the superconducting state is 2-30 times higher than that of the original ceramics.

It becomes obvious that the burning of organic parts of polymer-ceramic nanocomposites, their sintering and recovering at any particular thermal regime in analogy with [11], give rise, as a rule, to a transport current. However, polymer-ceramic nanocomposites with a superconducting (SC) transport current can be obtained without the stages of burning and sintering. This is achievable via the so-called nearing effect, thus effectively shielding dielectrization of near-to-surface layers of the ceramic's grains.

In summary, this study is based on yttrium and bismuth ceramics, fine dispersed powder of super-high molecular polyethylene as a binder and nano-sized additives of aluminum and silver, to obtain polymer-ceramic nanocomposites with a transport current.

**Experimental**

In this work synthesized yttrium and bismuth oxide ceramics \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.97} \) and \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_8 \) were used as a high temperature ceramic powder, with a dispersion (via molecular sieves) of less than 50 µm and a critical transition temperature to the superconducting state of 93 K and 109 K, respectively. As polymer binders in the form of fine dispersed powders served super-high molecular (HMPE) (brand U506-000) and branched (BPE) polyethylene with melting temperature \( T_m = 128-135^\circ\text{C} \) and 105-108°C, respectively, isotactic polypropylene (IPP) with \( T_m = 167-171^\circ\text{C} \), polymethylmethacrylate (PMMA) with temperature of vitrification point \( T_v = 110-115^\circ\text{C} \) and polystyrene (PS) with \( T_v = 98-102^\circ\text{C} \) [22].

For finding out the influence of nano-sized powders of aluminum and silver on the transport current of received composites, experiments were conducted, where in one case the powders of polymers (HMPE, BPE, IPP, PMMA, polyanilin) and superconducting ceramics \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.97}, \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_8 \) were pre-mixed in an agate mill, while in other cases nano-sized powders of aluminum (40 nm) and silver (30 nm) were added to this mix. From the homogeneous mixtures obtained by the method of hot pressing HMPE (~ 150 °C under a pressure of 100 MPa) tablets with a diameter of 10 mm and a thickness of 2 mm were molded. The golden contacts by the thermo compression method were deposited on the tablets. The resistance of the samples was determined by the conventional 4-lead method. In some cases forming the samples was carried out under the influence of acoustic fields, which causes deagglomeration of the agglomerated nano-particles (sonofication at 500W was kept on for the entire process of the samples' formation). The start of the superconducting
transition \( (T_s) \) and its width were determined by measuring the magnetic susceptibility at the frequency 1 kHz (kilohertz) with an amplitude of the magnetic field of 10 Oe. Physical-mechanical properties and the heat of sample fusion of SC polymer-ceramic nanocomposites were measured on the following instruments: Differential scanning analyzer (DSA) and differential scanning calorimeter (DSC) [both from Perkin-Elmer].

**Results and Discussion**

**Regulation of the current density in superconducting polymer-ceramics**

The characteristic change of resistance of the samples with temperature for polymer-ceramic nanocomposites of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.97} : \text{HMPE} : \text{Al} = 80 : 10 : 10 \) (mass) is shown in Fig. 1 (curve 1).

![Fig. 1. Change of resistance of the \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.97} + \) HMPE nanocomposites with the additives of nano-sized aluminium powder as a function of temperature.
Curve 1 – critical temperature of superconducting transition for the initial sample; Curves 2, 3 – critical temperature of superconducting transition for the thermo processed sample (obtained during repeated thermal cycling); Curve 4 – after four thermal cycles.](image)

Up to the critical temperature of superconducting transition, the course of the resistance curve (curve 1) has a semi-conducting character. Further, at the SC transition temperature 96 K, a decrease in resistance is noticed, and at 78 K, the transition ends and the sample resistance turns to zero.

Unexpected results are obtained during repeated thermal cycling of the very samples. The behavior of the samples’ resistance up to the critical transition temperature to the superconducting state again remains semi-conductive (Fig. 1, curves 2, 3). However, the level of residual resistance increases with every following cycle, and after the transition to the superconducting state, no zero resistance is achieved. Here, there is a plateau, up to 8.5 K. Moreover, after four thermo-cycles the SC transition disappears altogether (Fig. 1, curve 4).

These results can be explained either by the accumulation of residual strains on the binder-ceramic phase boundary, as a result of micro-crack formation while thermo-cycling, or by the poor contacting which tends to deteriorate as the cycling progresses. The developing current creates its own magnetic field, which eventually destroys the SC temperature transitions.

Similar results were obtained for the composites consisting of bismuth ceramic-polyaniline-HMPE with addition of nano-sized silver powder. Consequently, it is to
be stated that here, in the temperature range 109-115 K, the "SC-step" is observed, as well (Fig. 2) without reaching the resistive zero.

By contrast, in nano-composites with bismuth ceramics, a repeated thermal cycling (5-6 cycles) does not affect the dependence of resistance on temperature. We note that in this case up to the transition temperature for the superconducting state, the course of the resistance depending on temperature is semi-conductive.

![Fig. 2. The change in resistance of nanocomposites with bismuth ceramics with aniline, with HMPE binder and with the addition of nano-sized silver powder.](image)

It is obvious that the increase in current density can be achieved by the implementation of the proximity effect, i.e., decrease of the binder quantity in the composite SC polymer-ceramic nanocomposites. For this purpose, by the hot pressing method a number of polymer-ceramic nanocomposites were formed, in which nanopowders were not added, and the proportion HMPE ranged from 1 to 5 wt. %. The dependence of current density on the amount of binder is shown in Fig. 3 (curve1).

![Fig. 3. Dependence of current density on the amount of polymer binder.](image)

Indeed, as seen from the figure, the implementation of the proximity effect leads to a substantial increase in current density. In this case, with the increase of the share of binder the current density decreases monotonically and becomes zero at 5% of the content of HMPE. Additives in the same nanocomposite of nano aluminum powder in the proportions HMPE: nano-additives = 1:1 (wt%) increases the current density else more (Fig. 3, curve 2).
As indicated by curve 2 in Fig. 3, increasing the quantity of HMPE also reduces the current density from $-1.5 \cdot 10^3\ A\cdot cm^{-2}$ to $\sim 150\ A\cdot cm^{-2}$ (1% mass content of binder), and already at 10% content of HMPE it becomes equal to $\sim 150\ A\cdot cm^{-2}$.

The critical transition temperature into the superconducting state is 96 K and its width is 6°. A probably relatively low current density in the nanocomposites is determined by the agglomerated state of aluminium nanoparticles.

Therefore, the further shaping of superconducting nanocomposites was carried out under the influence of acoustic fields. Indeed, as recognized from curve 3 in Fig. 3 the application of acoustic fields in the pressing process leads to a rather sharp increase in current density, which is associated with deagglomeration of aggregated particles and their uniform distribution over the volume of the samples. Curve 3 in fig. 3 shows that at 1% binder content of HMPE the current density reaches $4\cdot 10^3\ A\cdot cm^{-2}$.

**Physical-mechanical properties of polymer-ceramic nanocomposites with transport current**

Samples with low content of HMPE are quite fragile. In connection with this difficulties arise when applying contacts by thermo-compressing. For example, superconducting polymer-ceramic nanocomposites with 5% HMPE have the following physical and mechanical properties: ultimate tensile strength of $0.7\ MPa$, modulus of elasticity of $-1.4\ MPa$, and elongation -3%.

Interestingly the addition of nano-sized aluminum powder in superconducting polymer-ceramic nano-composite with nearly constant critical transition temperature into the superconducting state (Meissner effect) and of the current density leads to a significant improvement in the physical-mechanical properties (Table 1).

<table>
<thead>
<tr>
<th>Weight ratio HMPE: nanoadditive ceramics, mass. %</th>
<th>$\sigma$, MPa</th>
<th>E, MPa</th>
<th>$\epsilon$, %</th>
<th>$T_c$, K</th>
<th>$T_k$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 1: 98</td>
<td>0.27</td>
<td>0.4</td>
<td>2.0</td>
<td>95</td>
<td>88</td>
</tr>
<tr>
<td>2: 2: 96</td>
<td>0.33</td>
<td>0.56</td>
<td>3.5</td>
<td>95</td>
<td>88</td>
</tr>
<tr>
<td>3: 3: 94</td>
<td>0.68</td>
<td>1.2</td>
<td>5.0</td>
<td>96</td>
<td>88</td>
</tr>
<tr>
<td>4: 4: 92</td>
<td>1.00</td>
<td>2.0</td>
<td>7.0</td>
<td>96</td>
<td>88</td>
</tr>
<tr>
<td>5: 5: 95</td>
<td>1.50</td>
<td>5.0</td>
<td>9.0</td>
<td>95</td>
<td>88</td>
</tr>
<tr>
<td>10: 10: 80</td>
<td>3.80</td>
<td>9.0</td>
<td>11.0</td>
<td>96</td>
<td>88</td>
</tr>
</tbody>
</table>

The increase of the critical transition temperature into the superconducting state is evidently associated with the processes of intercalation of binder macromolecule fragments into the layered structures of ceramic grains [19-21]. Regarding a noticeable improvement in physical-mechanical properties of SC polymer-ceramic...
nanocomposites, it is possible that such a fact is associated with the introduction of nano aluminum particles into the polymer matrix HMPE, as well as their uniform distribution in the volume of binder and the formation of a rigid amorphous fraction of the polymer on the surface of nano-particles [23-26].

Thus, on the basis of these results we can conclude that the simultaneous implementation of the proximity effect, additives of nano-sized powders of aluminum and their uniform distribution over the sample volume under the influence of acoustic fields provide a charge-carrying SC polymer-ceramic nanocomposite with current density up to ~ 4·10^3 A·cm^-2 with simultaneous improvement of physical and mechanical properties.

Morphologic peculiarities of current-carrying SC polymer-ceramic nanocomposites

To study the morphological features of charge-carrying polymer-ceramic nanocomposites the melting temperature (Tm) and the enthalpy (ΔHm) of nanocomposites containing 5% nano-sized aluminum (mass relative to HMPE) are defined by differential scanning calorimetry. A wide range of the nanocomposites composition (the ratio of HMPE with an oxide ceramic Y$_1$Ba$_2$Cu$_3$O$_{6.97}$) was studied. The results are shown in Table 2.

It is seen that with increasing of the filling degree in nano-composites the enthalpy of melting is increasing.

<table>
<thead>
<tr>
<th>Weight ratio HMPE: Y$_1$Ba$_2$Cu$<em>3$O$</em>{6.97}$</th>
<th>Tm start</th>
<th>ΔHm, per gramm HMPE</th>
<th>Degree of crystallinity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>140</td>
<td>115.0</td>
<td>39.1</td>
</tr>
<tr>
<td>80:15</td>
<td>151</td>
<td>121.5</td>
<td>41.4</td>
</tr>
<tr>
<td>45:50</td>
<td>140</td>
<td>128.5</td>
<td>43.7</td>
</tr>
<tr>
<td>10:85</td>
<td>138</td>
<td>130.0</td>
<td>44.2</td>
</tr>
</tbody>
</table>

The observed increase in enthalpy value is associated either with the degree of crystallization (Table 2 and 3) or with a change in morphology of the binder in the surface layers of the phase.

However, on the basis of the obtained results it is impossible to establish unambiguously the decisive role of any of these factors. For clarification of the mentioned factors we studied by DSC methods in the regime of the scanning temperature the influence of oxide ceramic quantities Y$_1$Ba$_2$Cu$_3$O$_{6.97}$ on the heat of melting and carried out electron-microscopic investigations of samples of polymer-ceramic nanocomposites with transport current properties.
The dependence of the samples melting heats on temperature for the SC polymer-ceramic nanocomposites, obtained by varying the initial temperature of samples’ molding, and its content with a binder of BPE is shown in Fig. 4.

According to Fig. 4 the maximum values of the melting heats (curves 1-4, Fig. 4) SC polymer-ceramic products are practically independent of the initial forming temperature (curve 1,2,3, Fig. 4), whereas they depend quite strongly on the amount of ceramics in the composite (curves 4,5, Fig. 4). Temperature of melting and enthalpy determined from the data in Fig. 4 are presented in Table 3.

<table>
<thead>
<tr>
<th>Weight ratio of BPE: Y$_1$Ba$_2$Cu$<em>3$O$</em>{6.97}$</th>
<th>Tm start</th>
<th>$\Delta$Hm, per gramm BPE</th>
<th>The degree of crystalline, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>90:10</td>
<td>107</td>
<td>84</td>
<td>29</td>
</tr>
<tr>
<td>97:3</td>
<td>107</td>
<td>97</td>
<td>33</td>
</tr>
<tr>
<td>99:1</td>
<td>105</td>
<td>133</td>
<td>45</td>
</tr>
</tbody>
</table>

Thus, in the case of a binder of BPE with the increase of the filler amount the enthalpy and the degree of crystallinity are increasing. Therefore, based on the measured data we can suppose that a fairly strong increase of the value of $\Delta$Hm (calculated per gram HMPE and BPE) could be due to two reasons:

• the increase of the amount of SC ceramics leads to an increase in the degree of crystallinity;

• intercalation of fragments or individual elements of macromolecular binding into the interlayer spaces of the ceramic grains alters the morphology of super-high-molecular or branched polyethylene on the boundary of a phase section of the ceramic binder - which is more likely [18-21].

Indeed, the study of the structural features of the charge-carrying SC polymer-ceramic nanocomposites by scanning electronic microscopy when using both amorphous and crystalline polymers, with complete and uniform enveloping of
ceramic grains by polymer binders (Fig. 5a, b), indicates that there is a quite strong interaction on the boundary of the ceramic-polymer phase.

![Fig. 5. EM microphotography of nanocomposite SC samples with binders of the PMMA (a) and PS (b). Ratio of binder : ceramics = 15 : 85.](image)

The interaction of macromolecular binder of PMMA and PS with the surface of the ceramic grains $Y_1\text{Ba}_2\text{Cu}_3\text{O}_{6.97}$ may contribute to the formation of a rigid amorphous fraction (RAF) of polymer binder.

In charge-carrying SC nanocomposites with binders HMPE, PP, regardless of the amount of SC-ceramics, by analogy with [23-26], there are formations of fiber structures. For example, in Fig. 6 electron a microphotograph of a sample with the HMPE binder is presented. The figure depicts how the formation of fiber structures, not typical for polyethylene, takes place.

![Fig. 6. EM microphotograph of polymer-ceramic nanocomposite with HMPE binder. Ratio of binder : ceramics : nano aluminium = 5 : 90 : 5.](image)

As already noted in [18-21], fiber formations are the result of intercalation of macromolecular fragments of HMPE in the layered structure of ceramic grains. Such a binding of macromolecules affects the mobility of macro-chains of super-high molecular polyethylene and reduces their flexibility. Consequently, the crystallization of macromolecules, associated in this way, takes place via cooperative interaction between them.

It should be specially noted that in case of charge-carrying polymer-ceramic nanocomposites with a binder of IPP, the above mentioned phenomena are more emphasized. Indeed, as it is seen from the change of the dependences of heat
capacity on temperature (Fig. 7), a splitting of peaks into two components is observed.

![Figure 7: Temperature impact on the varying character of melting heats for the SC polymer-ceramic nanocomposites obtained at different initial ratios of PP with ceramics. Y$_1$Ba$_2$Cu$_3$O$_{6.97}$: PP = 85:15 (1) 70:30 (2), 50:50 (3).](image)

Possibly, the splitting is a result of the presence of two various structures in polymer-ceramic nanocomposites with IPP binder.

As a proof of such an assertion can be the electron-microscopic investigations. Indeed, as it is seen from the microphotographs of samples with IPP binder (Fig. 8), here the number of fibers formations is much larger than in HMPE binder.

A large number of formed fibers structures are probably to be the cause of splitting (Fig. 8) peaks of melting temperatures in SC polymer-ceramic nanocomposites with a binder of isotactic propylene.

![Figure 8: EM microphotography of polymer-ceramic nanocomposite with IPP binder. Ratio of binder: ceramics: nano aluminium = 15 : 80 : 5.](image)

**Concluding remarks**

In the presented work we have followed the goal to create polymeric superconducting nanocomposites with transport current properties. For the solution of the given problem superconducting additives of yttrium and bismuth ceramics powders (Y$_1$Ba$_2$Cu$_3$O$_{6.97}$ and Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_8$), as well as nanopowders of aluminum and silver were used. On the basis of super-high molecular polyethylene binder, charge-carrying polymer-ceramic nanocomposites were obtained.

Thus, our results permit to conclude that the introduction of nano-sized aluminum powders allows to produce SC polymer-ceramic nanocomposites, with a transport current having a current density up to \(~ 4 \cdot 10^3 \, A/cm^2\). A natural question arises regarding the possibility of increasing the current density. The answer is
positive: the increase is possible by using other binders and nano-fillers of a different nature with varying average size of nano-particles.

Acknowledgements: The authors would like to thank the State Committee of Science of Armenia for their support in this research. This research was supported by scientific grants 2015-2016 on the topic – Macrokinetics of Polymer Processes and Polymer’s Nanocomposites.

TOKONECUSHCHIE SVERKHPROVODOCHESKIE POLIIMER-KERAMICHESKIE NANOКОМПОЗИТЫ

С. П. ДАВТЯН, А. О. ТОНОЯН, А. Р. МИКАЕЛЯН и СТЕФАН МЮЛЛЕР

С использованием порошков иттриевой и висмутовой керамик (Y₁Ba₂Cu₃O₆.₉₇ и Bi₂Sr₂Ca₂Cu₂O₈) на основе сверхвысокомолекулярного полиэтиленового получены токопроводящие полимер-керамические нанокомпозиты. Показано, что реализация эффекта близости между зернами керамики приводит к получению сверхпроводящих полимер-керамических нанокомпозитов с транспортным током. Добавки порошков наночастиц серебра и алюминия вызывают значительное увеличение плотности тока, а применение акустических полей при формировании образцов позволяет еще больше увеличить плотность до ~4·10³ A·cm⁻². Были исследованы физико-механические свойства токопроводящих полимер-керамических нанокомпозитов, и показано, что напоразмерные добавки алюминия увеличивают прочность на разрыв и модуль упругости образцов. Изучены морфологические особенности межфазного слоя токопроводящих полимер-керамических нанокомпозитов на основе
REFERENCES