

REVIEW

Chemical Mesoscopics Notions in the Explanation of Polymeric Materials Modification Mechanism with Participation of Metal Carbon Mesocomposites

V.I. Kodolov^{1,2*} V.V. Kodolova-Chukhontseva^{1,3} I.N. Shabanova^{1,4} N.S. Terebova^{1,4} Yu.V. Pershin^{1,2} R.V. Mustakimov^{1,2}

1. Basic Research - High Educational Centre of Chemical Physics & Mesoscopics, UD, RAS, Izhevsk, Russia
2. M.T. Kalashnikov Izhevsk State Technical University, Izhevsk, Russia
3. Institute of Macromolecular Compounds, Russian Academy of Sciences, St Petersburg, Russia
4. Udmurt Federal Research Centre, Russian Academy of Sciences, Izhevsk, Russia

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ABSTRACT

The paper is dedicated to the consideration of the chemical mesoscopics notions application for the explanation of polymeric materials modification mechanism by the metal carbon mesoscopic composites. The main peculiarities of these nanosized particles are following: a) the presence of unpaired electrons on the carbon cover; b) the structure of carbon cover consists from poly acetylene and carbene fragments; c) the atomic magnetic moment of inner metal is equaled to more than 1,3 μB . The metal carbon mesocomposites activity depends on the medium and conditions influence because of the possible changes of the phase coherency and quantization of negative charges.

1. Introduction

The article is presented as the review of series of papers, manuscripts and patents on the obtaining, investigations and applications of uncials mag-

netic mesoparticles which are mesoscopic metal carbon composites [1-25]. The mesoscopic composites can be participates in reactions, especially, in radical processes and reduction oxidation processes. This activity may be used in modification processes mesocomposites accompanied

*Corresponding Author:

V.I. Kodolov,

Basic Research - High Educational Centre of Chemical Physics & Mesoscopics, UD, RAS, Izhevsk, Russia; M.T. Kalashnikov Izhevsk State Technical University, Izhevsk, Russia;

Email: vkodol.av@mail.ru

by the magnetic characteristics changes in modified mesoscopic composites. The expansion of metal carbon mesocomposites application chances takes place.

2. Discussion of the Polymeric Materials Modification Mechanism by Mesocomposites (on the Base of Series Experimental Results)

The mesocomposites activity in the different media (materials) is changed in the dependence on polarity or polarization of their media. Therefore the modification conditions for the different materials can be differed from each other. It's noted,^[1,2] that the mechanism of polymer modification by the nanostructures or mesoparticles differs from the correspondent mechanism at the micro particles using. The nanostructures radiate the quants of negative charges which increase polarization of medium and lead to the self organization of medium molecules accompanied the density growth.

According to scheme (Figure 1), the possible polarization leads to the increasing of medium (material) density owing to the regular orientation of material fragments or the macromolecules self organization with the creation of super molecular and crystalline structures. On the scheme the direct motion of electron quants shows by the arrows, and the polar (functional) groups - by the correspondent signs ♀, macromolecular chain of polymer is designated as line, the presence of mesoscopic composite is noted as MC.

The polarization extent depends on the quants electromagnetic radiation phase velocity. This velocity depends on the medium polarity and can be decreased at the polarity fall.

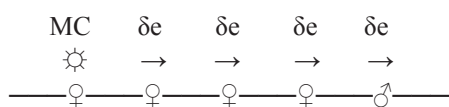


Figure 1. Scheme of polarization at charge quantization with expansion of quant influence on materials polar groups

The polarization increasing of polymer macromolecules at the mesoscopic composite action can be expressed by the following equation:

$$P_{\text{com}} = \sum p_{\text{fg}} + p_{\text{NC}}, \quad (1)$$

where P_{com} - the common (summary) polarization, $\sum p_{\text{fg}}$ - sum of functional groups polarizations, p_{NC} - the polarization (or dipole moment) of mesocomposite

The electromagnetic radiation phase velocity will be decreased in the media with high dielectric constant ac-

ording to following formula:

$$v = c/\sqrt{\epsilon}, \quad (2)$$

where v - the phase velocity of electromagnetic radiation, c - the light velocity, ϵ - dielectric constant.

When the dielectric constant is increased the decrease of mesocomposite influence on the media arises and the self organization process is finished.

Depending on the development of self organization process (single measured - 1D, double measured - 2D, third measured - 3D) the super molecular structures (mesoparticles) of correspondent forms and sizes are organized. The surface energy of embryos increased influences on the mesoparticles formation. This energy can be express as the sum of energetic parts for the realization of different movements:

$$E_s = E_{(\text{tr})} + E_{(\text{r})} + E_{(\text{osc})} + E_{(\text{em})}, \quad (3)$$

where E_s - surface energy of macromolecule (mesoparticle), $E_{(\text{tr})}$ - part of translational motion energy, $E_{(\text{r})}$ - part of rotary motion energy, $E_{(\text{osc})}$ - part of oscillatory motion energy, $E_{(\text{em})}$ - part of electron motion in surface layer.

In accordance with the formation of mesoparticles which have the identical orientation with each other, the parts of translational motion energy and of rotary motion energy will be near to zero. Therefore the main contribution into the mesoparticle surface energy will be bringing the oscillatory motion and transport of electrons in surface layer of macromolecules (mesoparticles). Then the change of character of quants radiation wave propagation from 2D (in the surface plane) to 3D (in the space field at surface).

The composition polarization is possible because of the presence of the charge quantization with the wave expansion on polar functional groups of media (for example, polymer macromolecule, Figure 1). In table 1 the instance of fine dispersed suspension Cu-C mesocomposite (hardener for epoxy resin) is shown. According to data of Table 1, the decreasing of mesocomposite quantity to 0,001% leads to the intensity increasing of some fields in IR spectra.

Table 1. The change of peaks intensity depending on Cu-C mesocomposite concentration

N	cm ⁻¹	I _i /I ₀	I _{0,01} /I ₀	I _{0,001} /I ₀	Atomic groups
1	1050	1,235	1,411	1,686	C-O-C st
2	1450	1,179	1,590	1,744	C-H
3	1776	1,458	1,347	1,691	C=O st as
4	1884	1,463	1,412	1,678	C=O st sy
5	2860-3090	1,182	1,545	1,750	C-H

At the second day of that suspension existence the

floccules are formed and peaks intensity sharply drops. However the suspension activity can be increased with the using of ultrasound treatment (Table 2). The treatment optimal duration determined as 7 minutes (the peak intensity in IR spectra is increased in 2-4 times).

Table 2. The changes of peaks intensity in IR spectrum of Cu-C mesocomposite depending on the duration of ultrasound treatment

$\nu(\text{cm}^{-1})$	I_7/I_0	I_{10}/I_0	Atomic groups
1776,6	3,7932	0,7575	C=O st as
1844,1	2,5065	0,9115	C=O st sy
3039,1	2,3849	0,9589	C-H

The charge (electron) quantization should lead to the macromolecule electron structure change and, as corollary, to change sub molecular structures of polymeric substances. Therefore the special film of nanostructured materials, for example, polyvinyl alcohol, polymethyl metacrylate, polycarbonate, which contain metal carbon mesocomposite in the minute quantities (10^{-1} - 10^{-5} %) are prepared. The films obtained are studied by x-ray PES and by AFM. The investigations by x-ray PES show that the films based on polycarbonate have more changes of electron structure at the minute quantities introduction of Copper Carbon mesocomposite in comparison with other polymeric films because these films are more polarized.

According to the results of C1s spectra for polycarbonate, contained the different minute quantities of Cu-C mesocomposite, can note that after concentration equaled to 10^{-2} % of Cu/C mesocomposite the peaks correspondent to sp^2 and sp^3 peaks are appeared in these spectra. In other words, the “stamp” of mesocomposite which is used during modification is appeared.

That “stamp” is observed also at the mesocomposite containing, equaled to 10^{-5} %, in polycarbonate film. It's noted, that the relation between sp^2 and sp^3 peaks changes. For instance, the intensity of sp^2 hybridization carbon peak is upper the intensity of sp^3 peak in the concentration interval from 0,01 to 0,001% of mesocomposite. The change of concentration to 10^{-4} % bring the proximity of intensities sp^2 and sp^3 peaks.

For the decision of question about the nanostructure influence on sub molecular composition structures the atomic force microscopy method is applied. Below some images of polycarbonate nanostructured films surface are presented. Polycarbonate is modified by Cu-C mesocomposite minute quantities (from 10^{-1} to 10^{-4} %). As follow from AFM images (Figure 2), the surface layers structure strongly changes at the concentration of Cu-C MC equaled to 10^{-4} % the transition from two-dimensional level to three-dimensional

level of sub-molecular structures orientation. This fact is confirmed by the growth of sp^3 in comparison with sp^2 peak from x-ray photoelectron C1s spectra.

The changes of the image surface are also observed for the poly methyl metacrylate films modified by Cu C mesocomposites.

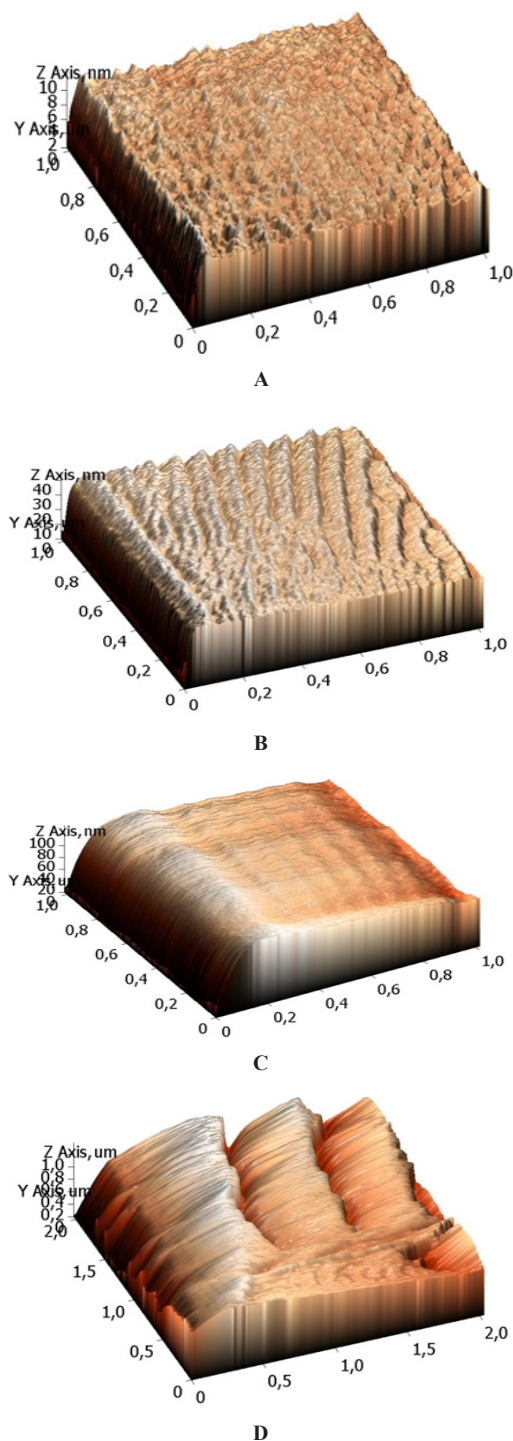


Figure 2. AFM images of polycarbonate nanostructured films surface: A - 0,1% Cu-C MC; B - 0,01% Cu-C MC; C - 0,001% Cu-C MC; D - 0,0001% Cu-C MC

It's necessary to note that the results obtained by AFM conform by the x-ray PES data (on C1s spectra).

Thus, the self organization mechanism for polymeric compositions modified by the metal carbon mesocomposite minute quantities is concluded in the conditions creation for composition polarization, which leads to the great change of electron and sub molecular structures of materials. Certainly, these changes influence on the modified materials properties.

Below in the example, the epoxy compositions with different additives, which include mesoscopic composites, are investigated. As cross-linking agent is used the fine dispersed suspension on based of isomethyl tetra hydro phthalates anhydrate and Copper Carbon mesocomposite.

On the Figure 3 the results of modification epoxy compounds (materials 1 and 2) are given. The process of modification by Copper Carbon mesocomposite in quantity equaled to 0,005% improves the adhesion characteristics for the material 1 (green) on 59,77% and for the material 2 (dark blue) on 47,17%.

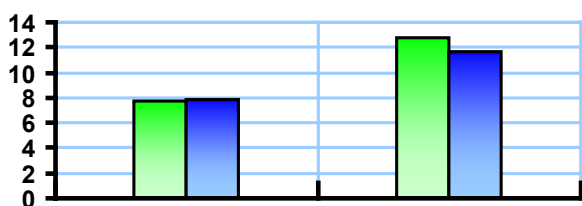


Figure 3. Comparison of adhesion strength for materials 1 (green) and 2 (dark blue) before (A) and after (B) the modification by Copper Carbon mesocomposites

It's possible also other applications that nanostructures owing to its uncial structure and properties.

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