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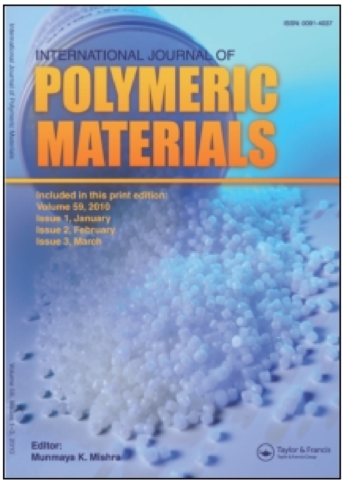

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The Role of Active Carbon-fibrous Filler in Decrease of Combustibility of Semi-penetrating Polymeric Networks

L. M. Sergeeva[a]; V. I. Dubkova[b]; A. A. Fainleib[a]; V. I. Alekseenko[b]; A. A. Brovko[a]; O. I. Maevskaya[b]
[a] Institute of Chemistry of High molecular Compounds of an Academy of Sciences of Ukraine, Kiev [b] Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, Minsk

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The Role of Active Carbon-fibrous Filler in Decrease of Combustibility of Semi-penetrating Polymeric Networks

L. M. SERGEEVA[a],*, V. I. DUBKOVA[b], A. A. FAINLEIB[a],
V. I. ALEKSEENKO[b], A. A. BROVKO[a] and O. I. MAEVSKAYA[b]

[a] *Institute of Chemistry of High molecular Compounds of an Academy of Sciences of Ukraine, 253160 Kiev, Harkov highway, 48;* [b] *Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus,*
220072 Minsk, Surganov str., 9

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The development of semi-interpenetrating polymeric nets having wide capabilities of modification of properties determines great prospects of their application as binder at obtaining of compositions reinforced by fibers [1]. As well as for all polymeric composite materials the question of their combustibility reduction arises. The use of fibrous filler ensuring high adhesion strength with binder [2] is one from ways of solution of this problem.

Keywords: Combustibility; carbon fiber; fillers; networks

INTRODUCTION

In this article the influence of phosphorus-carbon fibrous filler (PCF) on structure and properties of semi-interpenetrating polymeric nets on the basis of copolymers of epoxycyanate and polyurethane has been investigated. For the synthesis of semi-IPN as of cooligomers (CO) the dicyanic ester of bisphenol A and epoxydianic oligomer ED-20 and also

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*Corresponding author.

linear polyurethane (PU) of mark "Vitur" have been used. Formation of semi-IPN were realized in presence of PCF sections in length up to 1 mm. The fibers were introduced in fresh prepared oligomeric mixtures at various ratios of reacting oligopolymeric components. We have also investigated the individual components of semi-IPN-copolymer and PU unfilled and discretely reinforced by PCF and also the composition with the unmodified carbon fibers obtained in identical to PCF conditions.

BACKGROUND

There are various research methods of process of formation and structure of spatially sewed polymers [3]. From undestroying methods the most universal are electrophysical ones as practically all electrical parameters: the loss tangent of a dielectric (tg δ), capacitance (C) and specific volume resistance (ρ_v) – are sensitive to internal changes of a composition and structure of oligomeric units, the structures and way of packing of macrochains, intermolecular interactions having a place at formation spatially sewed polymer [4]. Being based on it, for investigation of influence of fibrous filler on the structure and properties of semi-interpenetrating polymeric nets which synthesis was carried out in presence of solid surface, the electrocapacitive method of the control of the dielectric characteristics of a forming product [5] has been chosen.

Determination of parameters of the indicated properties was conducted with use of the measuring electrode system in which the change of a gap between measuring electrodes with the help of micrometric screw is stipulated. Such system allows to investigate the dielectrics and semiconductors by various ways: both with use of usual Q-meter and on the method of the variable gap. For decreasing of errors of measurement (C, R) the instrument capacitor was fulfilled in form of concentric stainless steel plates. In the system of electrodes the ungrounded electrode having the acute edge and protected ring was introduced that allows to remove errors at the expense of edge effect. The electrophysical parameters were registered by the of immitance E7-14 in frequency band 100 Hz, 1 kHz and 10 kHz.

Determination of piezoelectric parameters have been conducted on the method of static loading in conditions of single-axis compression. The measuring system consisted of laboratory hydraulic press, oscillograph of a universal type C8-13, measuring electrodes and dielectric insulation. Load given on a sample removed instantly at the beginning of sweep on the oscillograph. Potential difference arising at loading of sample was determined on number of points on which the electron beam of the oscillograph deviated taking into account factor of attenuation. The sweep of oscillograph was chosen within the limits of 0, 5 – 1 point per one second. The input of the oscillograph for a signal was engaged in the position of galvanic connection. Cathode-ray tube of the oscillograph worked in the regime "Memory". The method is suitable especially for determination of charges at deformation of piezoelectrices possessing rather large conductivity and is convenient due to a capability of observation and remembering of all dynamics of piezoelectric effect taking into account of remanent polarization.

The thermal analysis of unfilled binder and separate its components and also their fresh prepared mixtures with sections of PCF have conducted with use of derivatograph of the system Paulik-Paulik-Erdey in air medium (the sensitivities of DTA and DTG methods is 1/3 and 1/5 accordingly. Aluminum oxide was used as the standard). Depth of transformation of separate components of binder on the surface of PCF in spatially sewed polymer has been estimated on an yield of a gel-fraction after a warming-up of model bicomponent systems of PCF-oligomer (polymer) in the chosen conditions of possible physical – chemical interaction of components (according to the data of the differential – thermal analysis) and extraction of compositions by an acetone in the Sokslet apparatus during 24 hours.

Hardness of semi-IPN discretely reinforced by CF and PCF (point of fluidity for tempered steel cone having the angle of vertex 53° + 10′) has been determined with use of Heppler consistometer.

RESEARCH RESULTS AND DISCUSSION

The general analysis of the obtained data indicates the introduction of phosphorus-carbon fibers in composite oligomeric systems at stage of synthesis of semi-interpenetrating polymeric nets results in essential changes of all electrophysical parameters (tg δ, C and ρ_v) of formed products. The substantial increase of specific electroresistance (Figs. 1 and 2a) is observed, dielectric relaxation times (Figs. 1b, 2b) connected

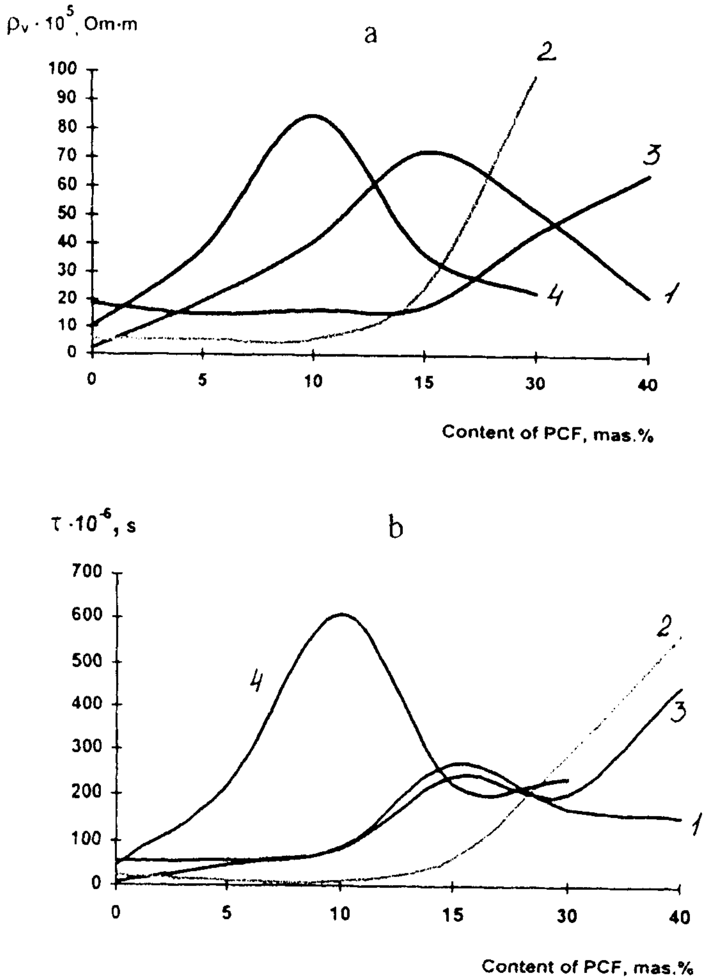

FIGURE 1 Specific volume electrical resistance (a) and dielectric relaxation time (b) of semi-IPN at the ratio of CO/PU: 100/0 (1), 80/20 (2), 50/50 (3) and 0/100 (4) and at various content of PCF in the composition.

as is known with segmental thermal motion macromolecule and formation of transversal sewings sharply increase. The data testify about the redistribution of inside and intermolecular interactions in a semi-IPN forming in presence of solid-phase component having chemically active surface and speak for the benefit of formation of a more rigidly

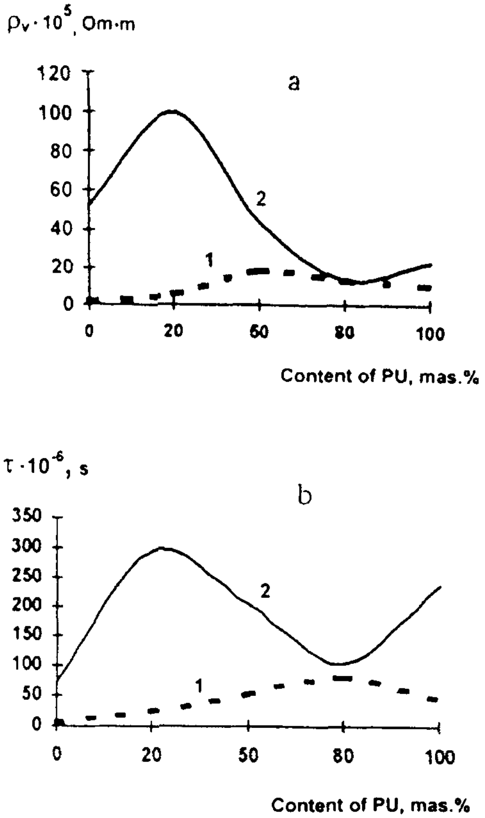

FIGURE 2 Specific volume electrical resistance (a) and dielectric relaxation time (b) of semi-IPN unfilled (1) and discretely reinforced by PCF (2) at various content PU in the composition.

fixed structure of polymeric net preventing transference of the all molecule in whole and the lateral groups of segments.

However at that it is impossible to speak about adequacy of change of electrical properties of a polycomponent system as with increase of the content of discrete PCF and at consecutive change of ratios of linear and net ingredients in binder. As it is visible from Figures 1a, b curves 2, 3 the greatest effect in structurization of semi-IPN discretely reinforced by PCF is observed at filling of their fibers > 15 mas.%. At the same time from Figures 2a, b, the curve 2 follows at gradual increase in binder of portion of linear polyurethane values ρ_v and τ_p

pass through maxima at the content of PU 20–50 mas.% (depending on a degree of filling of composition by sections of PCF).

The reduction of transference of various kinetic units of semi-interpenetrating polymeric net forming in presence of fibers and increase of relaxation times stipulated by it can be explained by effective influence of interfaces to microphase separation of binder in boundary layers and participation of surface groups of the carbon fiber in physical–chemical processes taking place in interface zone. As was shown by us earlier for oligoepoxide ED-20 [7] and was established in the present research for other separate components (dicyanic ester of bisphenol A and polyurethance) the surface-active groups of phosphorus-carbon fibers can react with functional groups of oligomeric and polymeric component of binder. The data of the chemical and differential–thermal analyses testify about it.

On Figure 3 DTA-curves of model two-component of mixtures PCF ingredients of binder which precisely state the changed character of thermochemical transformations of semi-IPN and individual components in the presence of active carbon fiber are shown. On the DTA-curve of the system PCF-dicyanic ester of bisphenol A (Fig. 3, curve 4) in the area of temperatures 100–225°C when the losses of oligomer weight are insignificant (1,0–6,0 mas.%) new exothermal effects having maxima at 145°C and 220°C appear. The chemical analysis of above-stated bicomponent mixture after warming-up at temperatures of revealed maxima and consequent extraction with boiling acetone indicates on the formation of net polymer. The quantity of gel-fraction unextracted from the surface of fibers makes up 25–60 mas.% depending on time and temperature of treatment of mixture while individual oligomer unfilled and filled by the unmodified carbon fibers after warming-up in the same conditions is extracted completely.

At introduction of PCF in cooligomer of dicyanic ester of bisphenol A and epoxide ED-20 the chemical reactions of surface groups of fiber are possible both with one and with other oligoepoxide their exothermal effects being superimposed against each other slightly change a general contour of DTA-curve (Fig. 3, curve 6). Thus this or that process dominants depending on a ratio of cooligomers in a mixture and temperature of heating that is reflected in a total contour of a DTA-curve and yield of a gel-product. The data of the chemical analysis have shown the chemical interaction of PCF with epoxycooligomers results

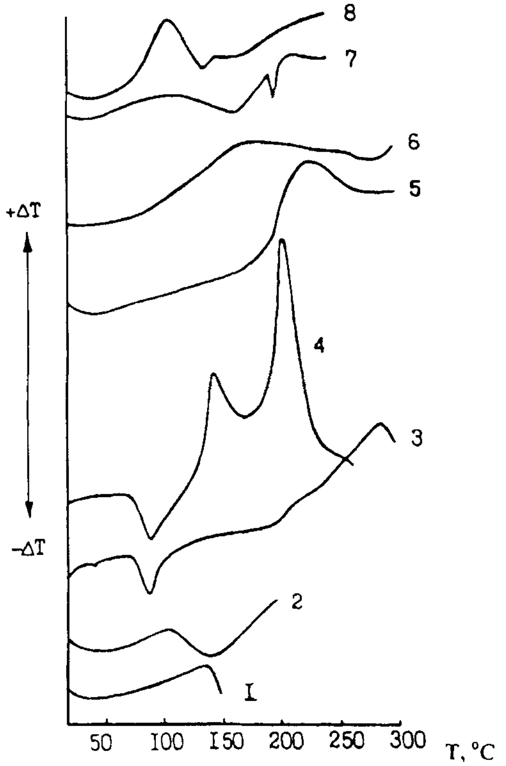

FIGURE 3 DTA-curves of polyurethane (1), dicyanic ester of bisphenol A (3), copolymer of dicyanic ester of bisphenol A with ED-20 (5), semi-IPN at the ratio CO/PU = 60/40 (7) unfilled and discretely reinforced by PCF (2, 4, 6, 8) accordingly.

in formation of gel-fraction of polymer unextracted from the surface of fibers (up to 100 mas.%). The results satisfactorily agree with ones obtained by us earlier for similar systems. The similar picture was observed and at research of the binary mixture PCF-polyurethane. The appearing new exothermal effect on the DTA-curve of the researched mixture with the maximum at 105°C (Fig. 3, curve 2) corresponds to temperature at which the formation of product (in quantity up to 40–65 mas.%) insoluble and unremoved from the surface of fibers is observed. The unfilled polyurethane warmed up in the same conditions is dissolved completely. The grafting of polyurethane to the surface of PCF results in change of character of its further thermal transformations: speed of thermal decay of polymer sharply decreases and at proceeding heating of the composition DTG-curve in contrast to those for the unfilled polyurethane goes on a plateau at temperature 180°C. The losses of weight of polymer in compositions with PCF at temperature 200°C makes up 40, 5 mas.% while for individual polymer losses are equal 60 mas.% already at 150°C. It is necessary also to note as a consequence of chemical structurization of polyurethane at active participation of surface groups of a fiber the polymer compositions with PCF have hardness in 1, 9 – 2, 4 times higher than unfilled polyurethane subjected to treatment in the same conditions (Fig. 4, curves 3, 4).

Not considering in detail in the given article the mechanism of reactions of polyurethane chemical transformations and its interaction with surface-active groups of PCF (it requires more detail research) it is possible to indicate the next. If to take into account that fact the structure polyurethanes are similar to that of polyamides (the amide group is a part of urethane grouping) which as it was shown by us earlier [8] react with phosphorus-acid groups of a carbon fiber and here the same scheme of reactions on the interface is not excluded. Detected thus the increase polyurethane of stability to ignition of

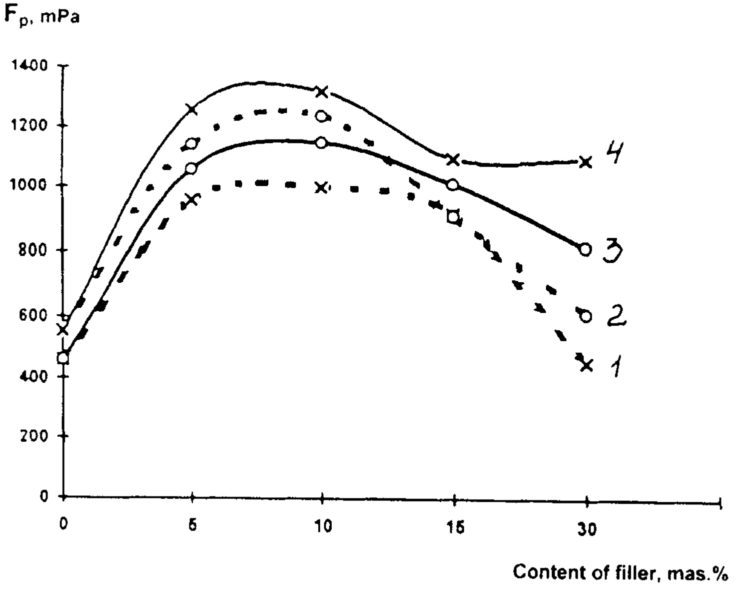

FIGURE 4 Hardness of semi-IPN discretely reinforced by CF (1, 2) and PCF (3, 4) at various degree of filling. The ratio CO/PU: 20/80 (1, 3) and 0/100 (2, 4).

polyurethane discretely reinforced by PCF (the compositions melting in the torch flame in difference from the polyurethane unfilled and filled by unmodified CF are not ignited) can also to testify for the use of above said. In the article [9] is shown the chemical interaction in the surface zone is the dominating factor in increase of stability of composites to inflammation that was confirmed and in the compositions of PCF with polyamides [10]. It is necessary also to note the significant increase of relaxation times (Fig. 1b, curves 1, 4) and specific elecroresistance (Fig. 1a, curves 1, 4) for model systems PCF-copolymer or PU despite of use in compositions of fibers with sufficiently high conductivity (under condition of introduction of their in quantity smaller than critical) is stipulated just chemical interaction of heterophase components on the interface the filler–matrix resulting in formation of a rigidly fixed structure preventing migration of free charges and mobility of lateral groups of the polymeric chain.

As to unmodified CF it is interesting to note the following. Not rendering essential influence on process of thermal-chemical transformations of net component of semi-IPN unmodified CF behave unindifferently in relation to polyurethane. The thermodecay rates of polymer are redistributed and the formation of an insoluble gel-product takes place in their presence. The increase of hardness of polymer is observed as in compositions of polyurethane with PCF (Fig. 4, curves 1, 2) as for ones discretely reinforced by unmodified CF. One can suppose in this case polyurethane (its polymeric chain has also besides urethane groups others reactionable groups) reacts with the unmodified carbon fibers on surface of this ones also there are functional groups in the limited quantity that results in change of the chemical structure, density of a sewing and hydrogenous bonds between macromolecules of polymer and in the interface zone of the composite. However this question requires additional more steep research.

CONCLUSION

Thus the fulfilled researches have shown phosphorus-carbon fibers can react practically with all semi-IPN components used in concrete case. Therefore it is possible to suppose and it is confirmed by results of the differential-thermal analysis the sequence of structurization reactions

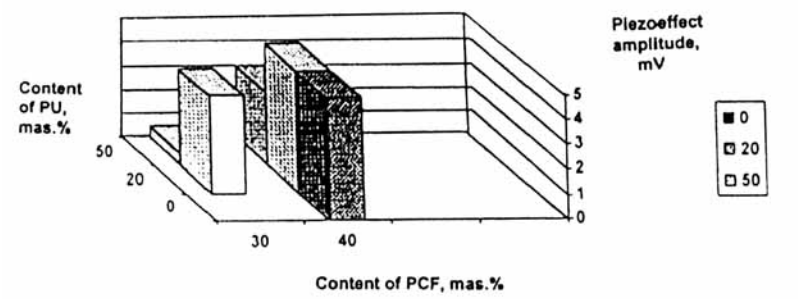

FIGURE 5 The dependence of piezoeffect amplitude from the content of PU and PCF in semi-IPN.

of semi-IPN in presence of PCF differs from one for the unfilled system and depends on concentration of filler, ratio of reacting components of binder, temperature. For example, as follows from a DTA-curve (Fig. 3, the curve 8) process of chemical interaction of PCF and polyurethane prevails at reduced temperature. The maximum appropriate to interaction of PCF and dicyanic ester and epoxy oligomer ED-20 is exhibited in the area of temperatures 140 – 160°C. The contribution of interface grows at increase of a degree of filling of PCF in the composition and at content of fibers above 30 – 40 mas.% when the primary part of binder of semi-IPN is in surface layer the formed composite gains qualitatively new properties. As shown in Figure 5 a semi-IPN discretely reinforced by PCF at enough high degree of their filling have piezoelectric effect.

The formation of a rigidly fixed structure hindering migration of free charges and mobility of lateral groups of polymeric chains results in reduction of material combustibility at improving of complex of other properties. The combustion time of compositions decreases in 5 – 9 times at removal their from the torch of flame. The contribution of interface grows at increase of filling and the composition is not ignited at the definite content of PCF.

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