Rev.Adv.Mater.Sci. 14(2007) 193-196

EFFECT OF THE CARBON C_{60}, C_{70} CONTENTS ON THE DIELECTRIC PROPERTIES OF POLYIMIDE FILMS

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Received: December 30, 2006

Abstract. The paper presents results of dielectric measurements of polyimide films with C_{60} and C_{70} fullerenes added in various ratios. Changes of capacitance and dielectric losses were measured in frequency range 10^2-10^6 Hz, at the temperature of 300K. Relaxation analysis was based on Havriliak-Negami equation. Influence of type and amount of fullerene in samples on dielectric properties was observed. Even its minimal amount (0.05%) increases capacitance from 10 to 20% - depending on type of fullerene. Dielectric losses coefficient is decreasing while C_{60} and C_{70} carbon contents is increasing. Approximation of dielectric spectra with Havriliak-Negami equation allowed to estimate changes of time constants of β-relaxation process. Modification of polyimid with carbon C_{70}-type has no significant influence on time constants, while increasing amount of carbon C_{60}-type leads to shorter β-relaxation times.

1. INTRODUCTION

Polyimides (PI), due to very good physical and chemical properties, stable structure and high thermal resistance are widely used in electrical, electronic, flight and space industry, e.g. at temperatures up to 400 °C [1,2].

Also, their high resistivity (ρ_{ϖ} ~10^{15} Wm), dielectric strength (E_p ~300 MV/m), and low permittivity (ε_r ~3.5) allow to use PI in many applications, even as electret materials [3,4]. These applications and intensive research on Kapton structure (PI) led to profound knowledge of its properties. At present, main tendencies in research on Kapton are set to its modifications and special applications, e.g. PI is modified with additive and structural nanostructures admixtures (carbon nanotubes) to achieve compound characterized with non-linear optical properties [3].

This paper describes influence of C_{60} and C_{70} carbon admixtures on dielectric properties of polyimide composites and on relaxation phenomena.

2. MATERIALS

Material used for this research was polyimide foil with admixtures of C_{60} and C_{70}-type fullerenes. Mixture of 72 parts by weight of C_{60}-type carbon and 15 parts by weight of C_{70}-type carbon was added to first series of polyimide samples. This admixture was completed with 13 parts by weight of amorphous soot in form of carbon nanoparticles. Concentrations of this admixture were 0.05, 0.1,

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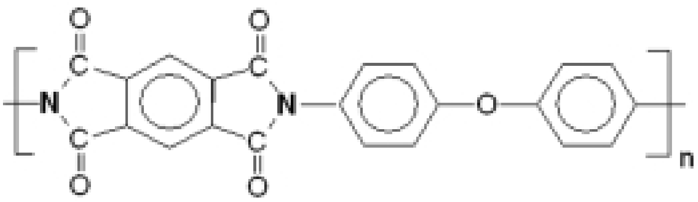

Fig. 1. Structure of the Kapton.

0.2, and 0.5 parts by weight. Second series of samples was PI modified with C_{60} fullerene. Samples were prepared with concentrations of admixture: 0.05, 0.1, 0.2, and 0.5 parts of C_{60} by weight. Third series of samples included the same concentrations of C_{70}-type carbon. Thirteen various composites were obtained for research, all of them based on polyimide Kapton (Fig. 1) [1].

3. RESEARCH METHODICS

Measurements of frequency dependence of permittivity real part – ε' and imaginary part – ε" were conducted at temperature 300K for frequencies in range 100 Hz ÷1 MHz. Measuring device was RLC bridge HP 4284A. Material samples were formed in 20 μm thick foil with silver electrodes sputtered in vacuum conditions (diameter Φ = 50mm). Data analysis was conducted with help of ORIGIN v.7.5 and WinFit v.2.9 computer programs from Novocontrol.

For modeling electrical phenomena and determining the influence of material modifications on relaxation parameters Havriliak-Negami model (H–N) was used, which allows to describe most of relaxation phenomena in polymeric materials [5].

Obtained values of ε'(ω), ε"(ω) were approximated with equation [5]:

$$\varepsilon^*(\omega) = \sum_{K=1}^{2} \left(\frac{\Delta\varepsilon_K}{\left(1 + \left(j\omega\tau_K\right)^{\alpha_K}\right)^{\beta_K}} + \varepsilon_{\infty K} \right), \qquad (1)$$

where ε*(ω), ε_∞ – complex and optical dielectric permittivity, Δε – polarizability, ε_0 – vacuum permittivity, τ – relaxation time constant, α and β – relaxation coefficients.

It was assumed that there are two dielectric structures in considered frequency range and that electric conductivity has no effect on values of dielectric losses.

4. RESULTS OF RESEARCH

Influence of modification on frequency spectrum of dielectric properties was presented in Fig. 2, on example of C_{60} fullerene admixture.

Cole-Cole characteristics (Fig. 2a) confirmed preliminary assumptions that, at temperature 300K, there are two relaxation structures. Similar effect was also observed in the rest of composites. Obtained values of relaxation parameters showed, that one of them is β-relaxation which describes mechanism of molecular interactions based on dipole groups rotation.

Influence of temperature on dominant frequency of rotation of these groups can be given as Arrhenius equation:

$$f_{\max} = f_\infty e^{-\frac{E}{RT}}, \qquad (2)$$

where: f_{max} – dominant frequency of β-relaxation phenomena, f_∞ – pre-exponential factor, E – activation energy, R – gaseous constant, T – temperature (K).

Second type of relaxation is probably connected with unbalanced Maxwell-Wagner space charge occurring in electrode surroundings.

Results of approximation dielectric spectra with Eq. (1) show that values of time constants of space charge relaxation were independent from their contents in composites that contained C_{70} and mixture of C_{60}+C_{70}.

It was observed that value of τ_1 time constant increases unexpectedly in case of adding C_{60}

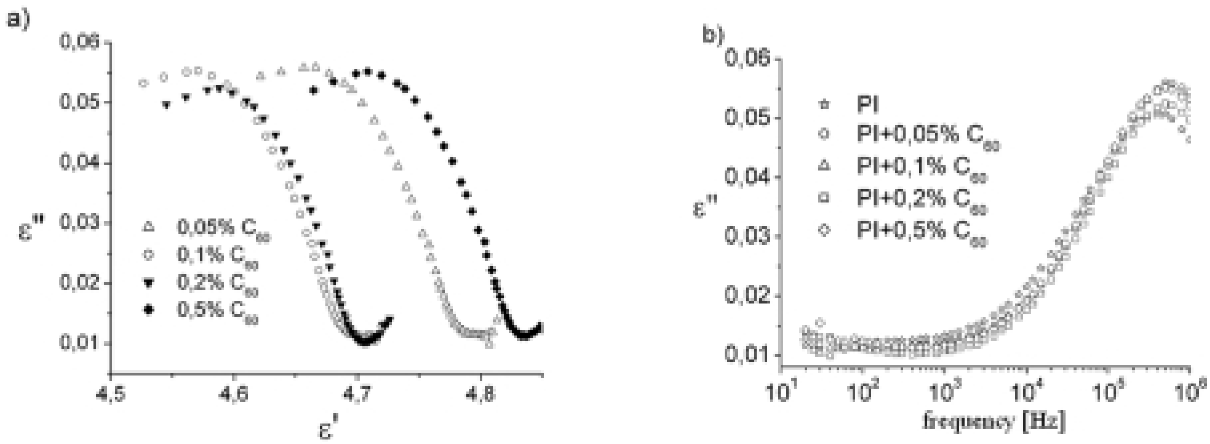

Fig. 2. Characteristics of the Kapton with various fullerene contents: Cole-Cole relationships (a), imaginary part of permittivity vs. frequency (b).

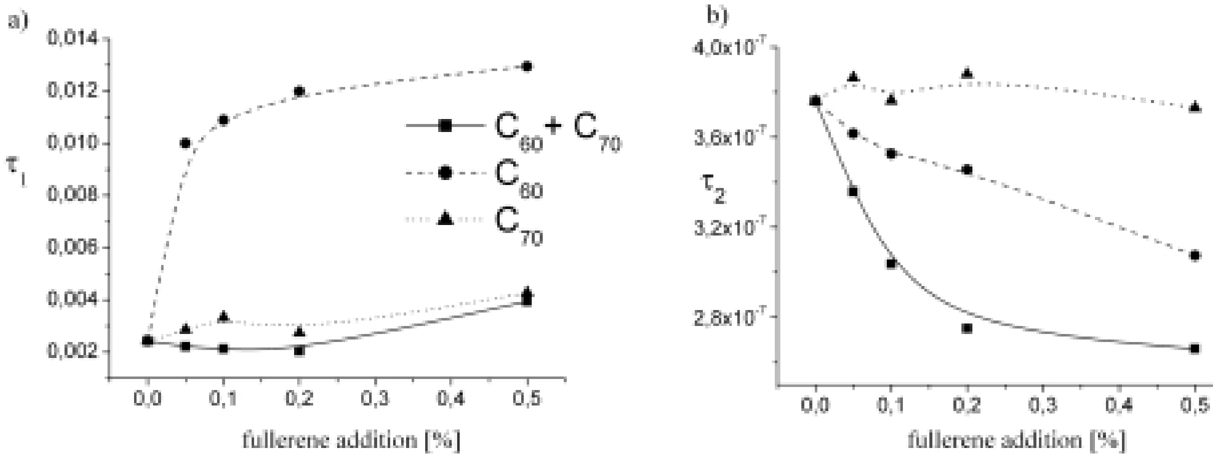

Fig. 3. Dependence of time constants on amount and type of fullerene addition: a) τ_1, b) τ_2.

fullerene to samples. It is probably connected with specific structure of this particle, which can become an additional group of the main polyimide chain, having properties of carboxylic bonds. In this way the new space charge distribution appears. This new phenomena, observed for carbon C_{60}, confirms need for further research on space charge distribution in structures with admixtures (Fig.3a). It was observed that C_{70} fullerene presence has no effect on value of β-relaxation time, while carbon C_{60} and especially mixture of C_{60}+C_{70} have influence on shortening β-relaxation time constant. This influence depends on fullerene concentration. Values of τ_2 are much lower for the mixture of two types of fullerenes than for each of them. This effect can results from presence of carbon in the form of soot nanostructures which appear as contaminants in C_{60}+C_{70} admixture (Fig. 3b).

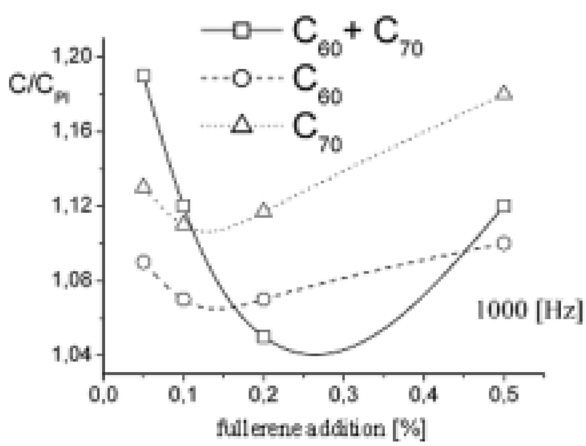

Fig. 4. Dependence of capacitance changes on fullerene amount.

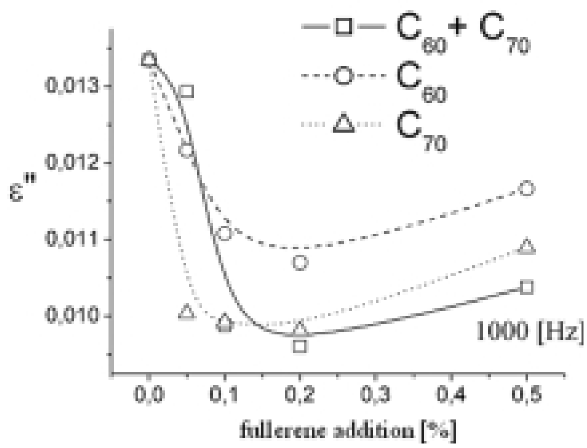

Fig. 5. Dependence of changes of imaginary part onelectrical permittivity on fullerene amount.

Quite unexpected result of fullerenes presence in polyimide is high increase of samples capacitance value; just 0.05% of admixture in samples increases capacitance in some of them even by 20%, if compared to pure polyimide. Subsequent increase of admixtures concentration generates local minimum of capacitance value (Fig. 4). Simultaneously, a tendency for decrease of dielectric losses with increase of concentrations is observed, with local minimum at the same values of admixture concentration as well. This effect was observed for 1000 Hz frequency (Fig. 5).

5. CONCLUSIONS

– Results of measurements showed, that even small content of fullerenes in polyimide can significantly change some of its dielectric properties. It applies especially for carbon C_{60}, as its 0.05% content by weight in polyimide increases capacitance of sample by 20% and increases multiple times relaxation time of space charge in electrodes surroundings.
– In PI composites containing admixtures, decrease of dielectric losses coefficient was observed. It didn't depend on type of the fullerene admixture.
– Nature of described phenomena hasn't been completely identified so there is need for further research on dependence on temperature in wide range and on space charge distribution in polyimide containing admixtures.

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