View metadata, citation and similar papers at core.ac.uk brought to you by CORE
provided by French-Ukrainian Journal of Chemistry

Dielectric conductivity of cross-linked polyurethanes modified with heteropolynuclear Cu_3Mn complexes

Gagolkina Z. O.[a], Lobko Eu.V. [a], Fomenko A.O. [a], Kozak N. V. [a], Klepko V.V.[a], Kokozay V.M.[b], Petrusenko S.R. [b], Stetsyuk O.M. [b]

[a] *Institute of Macromolecular Chemistry of National Academy of Science of Ukraine, Kyiv, Ukraine*

[b] *Taras Shevchenko National University of Kyiv, Kyiv, Ukraine*

GagolkZoya@i.ua

The dielectric and relaxation properties of cross-linked polyurethane, modified with heteropolynuclear $Cu_3Mn(L_4)$ complexes with various ligands in outer coordination sphere were analyzed by dielectric relaxation spectroscopy. It was shown, that the modifier introduction in polyurethane leads to conductivity level increasing due to: i) complex formation between functional groups of polyurethane and heteropolynuclear compounds and ii) increase in the macrochain mobility.

Introduction

The polymer modification with small amount of coordination metal compounds considerably influenced structure and properties of modified systems, including the conductivity levels [1-4]. By the introduction of transition metal complexes in polyurethanes (PUs) the materials with electronic [1-2] and ionic [3-4] charge transfer were obtained. The range of specific conductivity for the metal component with urethane polymers (0.1-5 %wt. $CuCl_2$, $FeCl_3$) is quite broad - 10^{-8} $Ohm^{-1}\cdot cm^{-1}$ to 10^{-3} $Ohm^{-1}\cdot cm^{-1}$, which corresponds to conductivity level of semiconductors [1]. It was shown [3-4], that the ionic conductivity of polyurethanes with immobilized 1 %wt. of transition metal heteropolynuclear complexes increases up to three orders. In the last case, the question remains open concerned influence of the outer coordination sphere ligands on the conductivity and relaxation properties of PU.

Experimental part

PUs were synthesized in two stages according to standard procedure described in detail elsewhere [5-6] using polypropylene glycol (PPG) with molar mass 1000 and 2,4-/2,6-toluene diisocyanate (80/20) based pre-polymer. 1,1,1-Tris(hydroxymethyl)-propane was used as cross-linking agent to obtain cross-linked polyurethane (CPU). Heteropolynuclear compounds were added into reaction mixture as solution in DMF to obtain the metal containing PUs with homogeneous distribution of the modifier (1 %wt.) in polymer matrix.

The following heteropolynuclear metal compounds were used as PU modifiers:

$[Cu_3Mn(L)_4(CH_3OH)_3]I_3$,
$[Cu_3Mn(L)_4(CH_3OH)(H_2O)_3]Br \cdot 3H_2O$,
$[Cu_3Mn(L)_4(CH_3OH)_3(H_2O)]NCS$ H_2O,
$[Cu_3Mn(L)_4(H_2O)_4]BF_4$,
where L is the product of condensation of salicylaldehyde with ethanolamine.

Dielectric relaxation analysis was performed using dielectric spectrometer based on the alternating current bridge R5083. The complex dielectric permittivity, ε* = ε' – iε'', of disc-like specimens (with diameter of 20 mm) sandwiched between gold-coated brass electrodes was measured over the frequency window from 10^2 to 10^5 Hz in the temperature interval from -40 to 140 °C.

$$\varepsilon' = C_1/C_o,\ \mathrm{tg}\ \delta = \omega R C_1 \text{ and } \varepsilon'' = \varepsilon' \cdot \mathrm{tg}\ \delta$$

Here ε' and ε" are the ….., C_o and C_1 are the instrument and standard capacitor capacities, ω is the cyclic frequency.

These parameters were analyzed from the traditional point of view [7-8]. Additional formalisms such as the complex conductivity (σ*), the complex electrical module (M*) and the complex impedance (Z* contained real, Z', and imaginary, Z", parts) were used according to formulas:

$$\sigma^* = \sigma' + \sigma'',\ \sigma' = \omega\varepsilon'',\ \sigma'' = \omega\varepsilon';$$

$$M^* = M' + M'',\ M' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2),$$

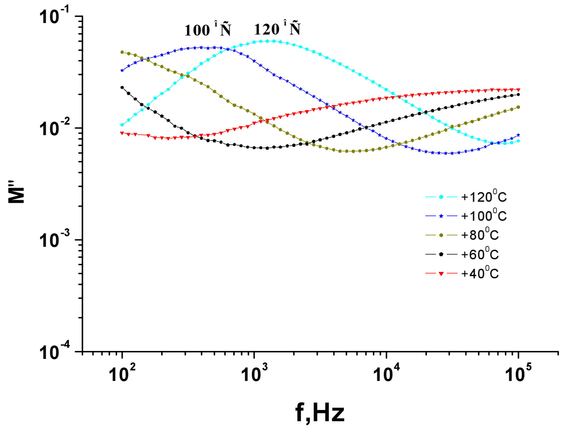
$$M'' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2)$$

$$Z' = M''/(\omega C_o),\ Z'' = M'/(\omega C_o).$$

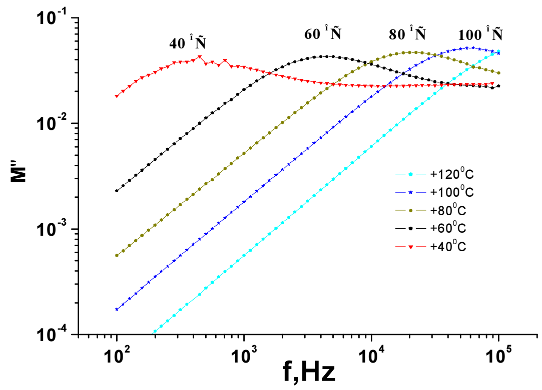
Results and discussion

In this paper, the dielectric and relaxation properties of CPU modified with heteropolynuclear $Cu_3Mn(L_4)$ complexes were analyzed.

To avoid the interference of surface polarization effects, that makes ε*(f) analysis not informative in the used frequency region, the formalism of the complex dielectric modules M* was used.



a



b

Fig. 1. The frequency dependence of M" for CPU - 0 (a) and CPU – 1% $[Cu_3Mn(L)_4(CH_3OH)_3]I_3$ (b)

The temperature-frequency dependence of the imaginary part of the electrical module (M'') for metal-free CPU - 0 and CPU-1%$[Cu_3Mn(L)_4(CH_3OH)_3]I_3$ are presented in Fig. 1.

On the frequency dependences (Fig. 1), the maxima are observed in the temperature range 40 – 120 °C. These maxima are associated with relaxation processes in the CPU. When the temperature increases, the relaxation maxima shift to the high-frequency region. The introduction of modifiers in all the cases also leads to a significant maximum shifting at corresponding temperatures to the high frequency region. This effect can be attributed to increase in a segmental mobility of the CPU soft blocks (i.e. glycol component). Indeed, according to the electron spectroscopy and electron paramagnetic resonance data $Cu_3Mn(L_4)$ modifiers form complexes mainly with the urethane component of CPU. The M"(f) maximum shifts for the modified CPU increase in the series:

$[Cu_3Mn(L)_4(H_2O)_4]BF_4$ <
$[Cu_3Mn(L)_4(CH_3OH)_3(H_2O)]NCS{\cdot}H_2O$ <
$[Cu_3Mn(L)_4(CH_3OH)(H_2O)_3]Br{\cdot}3H_2O$ <
< $[Cu_3Mn(L)_4(CH_3OH)_3]I_3$.

According to the data, the higher shift was observed for CPU modified by complexes with halogen atoms (I-, Br-) in the outer coordination sphere. These atoms can form additional coordination bonds with urethane groups. Thereby, the hydrogen bonding of CPU hard and soft components weakens and the mobility of soft component of CPU increases.

On the frequency dependence of the real part of the complex conductivity (σ'), the presence of a conductivity plateau at the direct current in the temperature region 40 – 100 °C was observed (Fig. 2). It is seen that the frequency at which the maximum is observed on the M"(f) curve corresponds to the inflection on the σ '(f) curve. This correlation is evidence that the above-described maxima (Fig. 1) are also associated with the effects of the conduction relaxation .

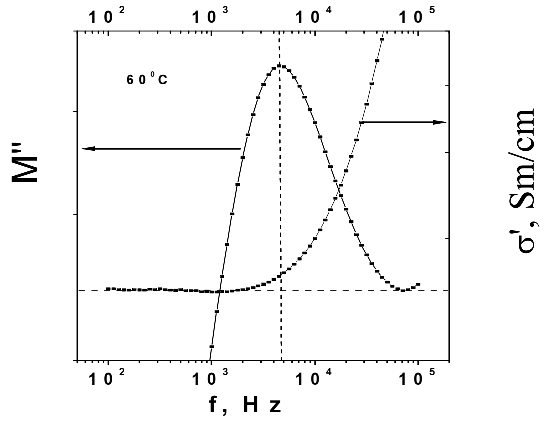


Fig 2. The typical frequency dependence of the real part of the complex conductivity and the imaginary part of the electrical module for CPU.

The spectra of relaxation times for CPUs were calculated using the equation: $\tau_{max} = \frac{1}{2\pi f_{max}}$

and the values of f_{max}, which were determined from the M"(f) curves. A temperature dependence of the relaxation time (τ) in the Arrhenius coordinates is shown in Fig. 3.

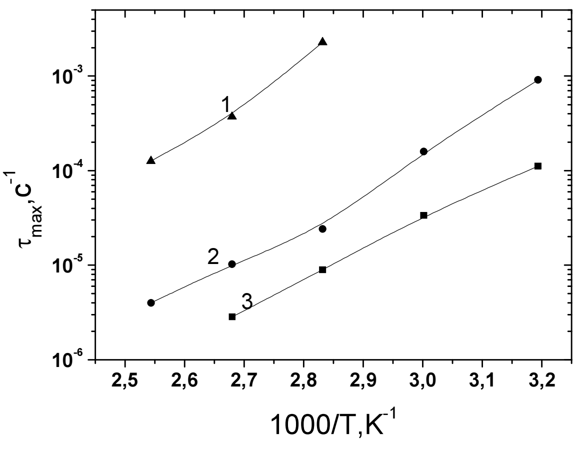


Fig. 3. The plot of τ vs. 1000/T for CPU: (1)

CPU - 0; (2) CPU – 1% [$Cu_3Mn(L)_4(CH_3OH)(H_2O)_3$]Br (2); CPU – 1% [$Cu_3Mn(L)_4(H_2O)_3$]$BF_4 \cdot H_2O$.

Analysis of the results shows that the introduction of heteropolynuclear coordination complexes $Cu_3Mn(L_4)$ in CPU leads in all the cases to decrease in τ over the temperature range 40-120 ^{0}C. This corresponds to increase in molecular mobility of polymer matrix with the introduction of heteropolynuclear complexes $Cu_3Mn(L_4)$. As it was pointed above, this can be explained by the enhance of segmental mobility of the CPU soft blocks (i.e. glycol component).

The impedance Z"(Z') formalism was used to separate the electric charges transfer processes in the systems from the polarization effects at the interface between CPU and electrode. Analysis of Z"(Z') isotherms for the studied CPU allows calculating the values of conductivity at the direct current σ_{dc}. Temperature dependences of σ_{dc} for CPU are shown in Fig. 4.

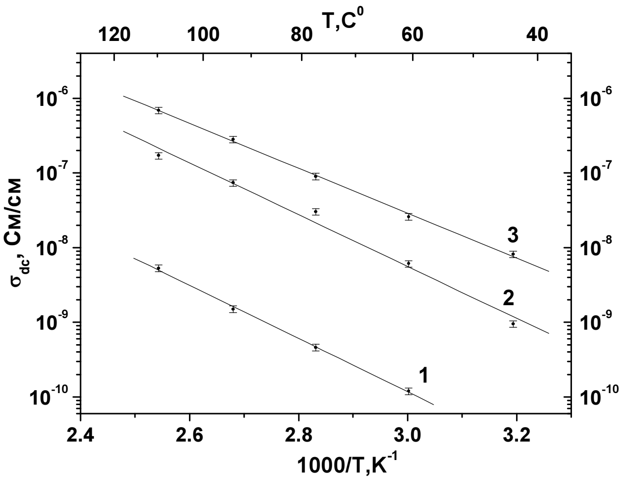


Fig. 4. The σ_{dc} vs. 1000/T for CPU: (1) CPU - 0; (2) CPU – 1% [$Cu_3Mn(L)_4(CH_3OH)(H_2O)_3$]Br (2); CPU – 1% [$Cu_3Mn(L)_4(H_2O)_3$]$BF_4 \cdot H_2O$.

As it is seen (Fig. 4), the CPU direct current conductivity (σ_{dc}) grows with the temperature increasing that is characteristic for the ionic conductivity. The σ_{dc} value for the metal containing CPU matrix increases up to two orders as compared to the metal-free CPU. The metal ion participation as current carrier is unlikely by several reasons: very small amounts of Cu and Mn ions (~ 0.14-0.175 % wt.) introduced into CPUs with heteropolynuclear complex $Cu_3Mn(L_4)$; covalent bonding of metal ions with the complex organic ligands; immobilization of the complex in CPU due to metal compound coordination with macrochains. Ionic mechanism of conductivity and adequate amount of protons presented in PU matrix allows supposing proton participation in the process of charge transport via mechanism of proton migration in flexible CPU component (PPG). This supposition agrees with literature data that the proton conductivity nature is characteristic to PPG [9].

The temperature dependence of σ_{dc} is close to linear for the investigated CPUs. Therefore, to approximate the experimental data, the Arrhenius equation was used:

$$\sigma_{dc} = \sigma_0 \exp(-\frac{E_a}{kT}).$$

The activation energy for the charge transfer process for CPU - 0, CPU – 1% [$Cu_3Mn(L)_4(CH_3OH)(H_2O)_3$]Br and CPU – 1% [$Cu_3Mn(L)_4(H_2O)_3$]$BF_4 \cdot H_2O$ are equal to 0,71, 0,64 and 0,60 eV, respectively. The values of E_{akt} confirm previously results.

Conclusions

Thus, the introduction of heteropolynuclear $Cu_3Mn(L_4)$ complexes in polyurethane leads to the conductivity level increasing due to complex formation between functional groups of polyurethane and heteropolynuclear compounds as well as to enhance of macrochain mobility.

The presence of halogen atoms (I-, Br-) in the outer coordination sphere of the $Cu_3Mn(L)_4$ complexes grows mobility of soft component of modified CPUs.

.

References

[1] I.M. Davletbaeva, A.R. Khairutdinov, R.A. Bylinkin, V.V. Parfenov *J. Appl. chemistry* **2001**, *74*, 805 - 808.

[2]] A.M. Gumerov, I.M. Davletbaeva, V.F. Shkodich *Times of Polymers-TOP and Composites*, Ischia, Italy, **2006**., 19.

[3] N. Kozak, Y. Nizelskii, N. Mnikh et al. *Macromolecular Symposia* **2006**, *243*, 243-262.

[4] N. Kozak, Eu. Lobko *Polyurethanes* **2012**, *4*, 51-78.

[5] J.H. Saunders, K.C.Frish *Polyurethanes. Chemistry and Technology.* New York-London, Part 1, **1962**.

[6] Z. Wirpsza *Polyurethanes: chemistry, technology and applications.* London, **1993**.

[7] K. Pathmanatham, G.P. Johari *Journal of Polymer Science*: B, **1990**, *28*, Issue 6, 675-689.

[8] P. Pissis, A.Kanapitsas *Journal of the Serbian Chemical Society*, **1996**, *61*, № 9, 703-715.

[9] R.E. Baker Pure and Appl. Chem. - **1976**. – 46.- 157-170.