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Electrical Properties of Thermoplastic Elastomers Copoly (Amide-Block-Amide)s

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The paper presents the results of tests aimed at checking suitability and applicability of materials in the group of multiblock thermoplastic elastomers for electrotechnical purposes. The modifications in chemical composition of the materials concerned allow to influence their mechanical and electric properties, and thus better material suitability for particular uses. Special structure of the polymers considered provides more advantageous improvements in properties than the addition of fillers to polymers. There were main electric parameters tested for the series of copoly(amide-block-amide)s - (PA12-b-PA6.36)-n, i.e. volume resistivity, dielectric loss coefficient, electric arc and comparative tracking index (CTI), as well as the changes in the above parameters due to one day water absorption. The results obtained show the influence of hard and soft copolymer blocks shares on electrical parameters.

Keywords: multiblock thermoplastic elastomers, soft and hard blocks, electric properties.

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Introduction

Thermoplastic elastomers (TPE) have emerged relatively recently as a novel group of the constructional polymers, and their characteristics are a subject of intensive studies undertaken by numerous research teams throughout the world.

The properties of thermoplastic elastomers are influenced by an appropriate phase structure and its thermal reproducibility in the heating-cooling cycles, functional mechanical features (e.g. a large reversible deformation) as well as the processability (the possibility of multiple melting and solidification).

A macromolecule of the block elastomers consists of soft and hard blocks distributed alternately. These blocks differ considerably in the physical and chemical properties. The soft blocks are capable of the formation of matrix (soft phase). As a result of aggregation, the hard blocks form the domains of these blocks, constituting the hard phase [1-5].

The development of electronic technology and electrotechnical equipment imposes particular requirements on constructional material properties, which should have low specific weight, should be chemically and thermally resistant, show good mechanical, insulating and electro-insulating properties and could be easily, economically and „ecologically” produced and processed. Such characteristics is offered by multiblock thermoplastic elastomers (TPE).

I. Testing material

In present work, a series of multiblock thermoplastic elastomers poly(amide-block-amide)s (PAA), – [PA12-b-PA6.36]_n– was examined.

Copolymers were obtained in the process of melt polycondensation. Syntheses of oligoamide soft block (PA6.36), oligoamide hard block (PA12) and PAA copolymers were previously described in details [5-7].

Characterisation of copolymers is summarised in Table 1.

Polymers of this series are characterized by a wide range of hardness depending on weight share of soft and hard block, so construction polymers through elastomers to plastomers were prepared. Obtained polymers have a satisfying value of limiting viscosity number, which decreases with the increasing weight share of oligoamide soft block.

They also have very good strength parameters. Some of the obtained polymers (M12, M13) could be included in thermoplastic elastomers group with excellent elastic properties.

II. Testing methods

The samples were placed in a climatic chamber at temperature 40°C and humidity 95% for one day. After that the samples were removed from the chamber and relevant measurements were taken, i.e. resistance to

Table 1

Principal properties of $-(PA12\text{-block-}PA6,36)_n-$ copolymers

Polymer sample	Molar Composition				$[\eta]$ dl/g	H ShD	σ_r MPa	ϵ_r %	T_m °C
	molecular weight of	molecular weight of	hard segment content	soft segment content					
	PA12	PA6,36	W_h [%]	W_s [%]					
M9	2000	1224	80	20	1,2	67	24,8	179,5	152-168
M11	2000	1224	60	40	1,1	54	22,5	183,5	134-152
M12	2000	1224	50	50	1,2	48	11,7	423	128-149
M13	2000	1224	40	60	0,8	47	11,4	363,2	125-144

Table 2

Electrical parameters

Polymer sample	Water absorption %	$\Delta\epsilon$	ϵ_∞	ϵ_0	τ [s]	ρ_v [$\Omega \cdot \text{cm}$]	$\text{tg}\delta$	ϵ	Arc resistance [s]	CTI [V]	
M-9	0,77	dry	3,7	3,1	6,8	1,1E-02	1,6E+14	0,11	4,1	>120	500
		wet	6,6	3,2	9,8	8,7E-04	6,6E+12	0,18	5,8	>120	500
M-11	0,63	dry	6,4	3,3	9,7	1,1E-03	3,4E+13	0,21	5,0	>180	500
		wet	7,5	3,3	10,9	2,0E-04	4,0E+12	0,21	6,9	>180	500
M-12	0,63	dry	5	3,2	8,1	2,7E-04	2,3E+13	0,18	5,3	>180	500
		wet	5,6	3,2	8,8	8,4E-05	3,8E+12	0,16	6,6	>180	500
M-13	0,66	dry	4,5	2,9	7,3	2,7E-04	6,6E+12	0,20	5,0	>180	500
		wet	4,7	3	7,7	7,9E-05	1,4E+12	0,15	6,4	>180	500

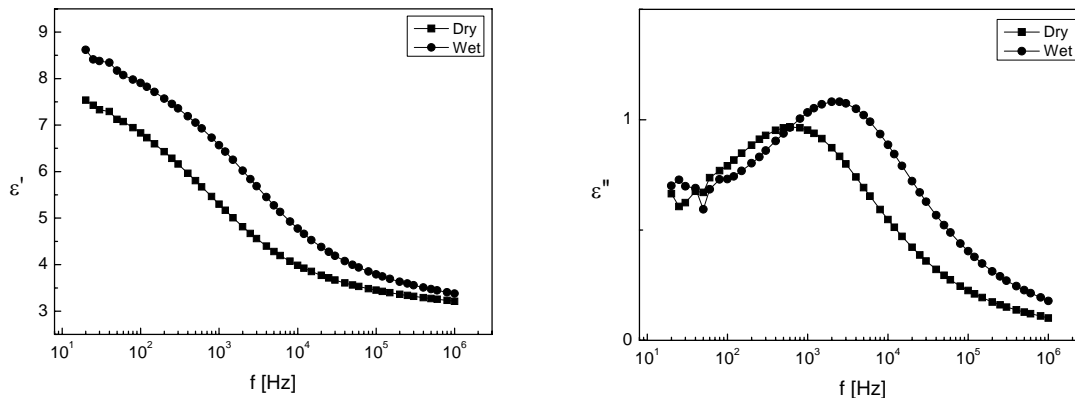


Fig. 1. Real and imaginary components of complex dielectric constant against frequency for dry and wet polymer sample M-12.

electric arc, resistance to creeping currents and resistivity. In order to determine the influence of moist content and copolymer composition on polarization effects, the dielectric constant and dielectric loss coefficient were measured for frequency range 20 Hz – 1 MHz. The results obtained were approximated with Havriliak-Negami's equation, as follows:

$$\epsilon(\omega) = \frac{\Delta\epsilon}{(1+(j\omega\tau)^\alpha)^\beta} + \epsilon_\infty \quad (1)$$

where: ϵ_∞ – optic dielectric permittivity; $\Delta\epsilon$ –

polarizability (difference between ϵ_0 DC permittivity and ϵ_∞) τ – generalized relaxation time constant of certain distribution dependent on α and β ; α, β – constants, ω – frequency.

III. Results

In Table 2 gathered electrical parameters for dry and wet polymer samples are shown. Water absorption for all samples was almost the same. Good electric arc

resistance and excellent comparative tracking index can be seen despite water content. The biggest differences were observed in all parameters related to electrical relaxation phenomena. As it can be seen in Fig. 1, there were considerable differences in both real and imaginary components of complex dielectric constant characteristics due to water content. Mainly time constant and polarizability were affected. Parameters of dielectric relaxation ($\Delta\varepsilon$, ε_∞ , ε_0 , τ , Table 2) obtained by fitting complex dielectric constant characteristics with equation (1) and volume resistivity show bigger influence of water content in polymers with smaller hard block share. Optical permittivity ε_∞ is almost the same for all polymers tested. $\Delta\varepsilon$ and ε generally decrease with dropping hard segment share and the same concerns water content influence. Similar patterns can be observed when the volume resistivity and time constant are concerned. Relative permittivity ε and dissipation factor $\tan\delta$ measured at 1 kHz are affected mainly by the shape of their frequency characteristics and change of loss peak placement, which depends on water content.

Conclusions

The measurement performed confirmed the influence of soft and hard block content on main electrical parameters. Water absorption tests showed that despite its similar value for all examined polymers its influence on dielectric relaxation parameters is totally different. For instance, time constant decreases about twelve times for sample M9 and three times for sample M13.

A change of components share in copolymers is an effective way to obtain materials with required parameters. Examination of dielectric relaxation parameters can easily show differences between materials and influence of ageing factors like moisture on its behaviour.

The materials examined are not suitable for high voltage electrical insulation, but can be used as the construction and coating materials especially for low temperature use because of its sub zero glass transition point.

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Електричні властивості термопластичних еластомерів сополі (Амид блока-амид)ів

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В даній статті представлено результати досліджень, націлених на перевірку придатності і застосовності матеріалів з групи еластомерів термопласта мультиблока в електротехнічних цілях. Модифікації в хімічному складі досліджуваних матеріалів дозволяють впливати на їх механічні і електричні властивості, таким чином покращуючи їх придатність як матеріалів для специфічних застосувань. Спеціальна структура полімерів, котрі розглядаються забезпечують більш вигідні удосконалення властивостей ніж додавання наповнювачів до полімерів. Були перевірені основні електричні параметри, на ряд сополі(амид блока-амид)ів - (РА12-в-РА6.36)-п, тобто питомий опір об'єму, діелектричний коефіцієнт втрат, електрична дуга і індекс порівняння, як і зміни у вище згаданих параметрах після одноденної абсорбції води. Результати демонструють вплив твердих і м'яких сополімерних долів блоків на електричні параметри.