COMPARISON OF RESULTS FROM THE MORE INFORMATIVE VERSION OF TMA WITH OTHER METHODS OF POLYMER TESTING

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Several characteristics of the topological regions determined by the more informative version of TMA for cured rubbers based on NR/CPE and NR/ENR blends as well as PA6/cured rubber blends correlate with static and dynamic mechanical properties. These rubbers differ substantially in the structure of their network and the related topological structure because CPE does not participate in cross-links when ENR can do it. The physical interactions caused by these additives also vary, due to the different polarity that influences the formation of physical networking junctions. In blends of PA6 and cured rubber the networking junctions are assumed as being physical nature only. From these facts and the above-mentioned results it could be preliminarily concluded that the correlation depends on the formulation and related structure of the composite, and on which of the characteristics have been compared. To understand the reasons for the existence, or lack of, correlation observed, further investigations are needed.

Keywords: molecular structure, MMD between junctions, regions, topological structure

Introduction

More and more new versions of thermal analysis were developed during recent years i.e. [1, 2] and using them numerous studies of new phenomena were curried out [3, 4]. Optimizing the formulation of multi-ingredient composites and their compounding technology is a time-consuming and labor-intensive process. It is caused by the fact that a composite usually contains many constituents interacting with each other at compounding and processing according to a multi-stage mechanism. Because of this, branching junctions creating a network or pseudo-network are present there. These junctions are characterized by a spectrum of interaction energies. This determines differences in usage properties, even in the case of a composite of the same formulation, but different homogeneity. From this fact it can be concluded that to make the optimization process more efficient some new ideas are needed on how to select only several characteristics of a complex composite structure. However, to solve this problem a simplified model of a polymer structure needs to be designed in a way, which would ensure correlation of their characteristics with the most important usage properties. One of such ideas relates to the topological structure with numerous characteristics evaluated from a single thermomechanical curve (TMC) using thermomechanical analysis (TMA).

The TMA is based on measurements of the specimen's deformation under very low load at scanned temperature giving the TMC [5–8]. It allows the evaluation of the glass transition temperature that in many cases suit well to those found by other techniques [9]. In addition, the thermal expansion coefficient [10–13], the softening temperature [14], the cross-linking degree (based on the equilibrium elastic modulus) [15, 16], and the average number of degrees of freedom of polymer segments between cross-links [17] could be evaluated.

The more informative version of TMA [18, 19] offers some additional possibilities for the study of complex structures of oligomers, unfilled and filled linear and cross-linked polymers, also with interpenetrating networks of different continuity. This method is based on studies of thermomechanical properties of a bulk polymer and the concept of a simplified polymer network with physical junctions (creating a pseudo-network or temporary network) and/or cross-links (creating a chemical network).

The introduced idea of a topological region is understood to have a complex structure and is manifested on the TMC as a zone that differs from other zones in the thermal expansion properties. A structure with two or three amorphous regions, most likely interpenetrating, and crystalline portion has been found for the polymers under investigation. These regions are assumed to be not divided in space; they represent the average interactions that coexist in polymers. They differ in transition temperatures up to 200°C and related compactness, which influences the distribution of additives within the polymer matrix. Most likely, they are related to some

higher-level arrangement than the molecular one. A similar idea was advanced by Chen and Wunderlich [20], who determined, by using thermally modulated DSC, a rigid amorphous fraction in polymers. Simultaneously, it is assumed that the relaxation of chain segments between the branching junctions follows the same rules for networks with physical junctions and crosslinks. However, despite long-running experimental studies, including the swelling method and nuclear magnetic resonance [21], this idea until now has not yet been sufficiently proved. Especially, one may ask a fundamental question: do the results obtained from TMA have magnitudes comparable with those determined by using standard methods while it is possible to measure the same properties? To answer this question partly, numerous experiments have been performed. In this article the characteristics of the molecular and topological structures evaluated according to the above-mentioned idea are compared with the results obtained by using other methods to support our preliminary conclusion [18, 19] about the usability of TMA while a surface layer (up to 0.5 mm thick) is tested to render a description of a polymer structure in a bulk material. The answer to this question is necessary for easier optimization of both formulation and the compounding process of the polymeric material.

Experimental

Test methods

A UIP-70M apparatus made by the Central Design Bureau of the Russian Academy of Sciences (Moscow) has been used following the procedure: the specimen was put into the measuring cell of the thermostatic chamber. These cubic or cylindrical specimens measuring 1.2–5 mm in height and 1–5 mm in width (preferably 1.5 and 2 mm, respectively) are molded or cut from the plates of the polymeric material. The surfaces of specimen contacting the base of the cell and the measuring probe with the hemispherical tip (its radius usually equals to 1 mm) should be parallel (Fig. 1). The specimen has been frozen without pressing under a scanning rate of about 4 K min^{-1}, starting from room temperature usually up to about –120°C; next, the specimen has been stored for 10–15 min to equalize a thermal field within it. To obtain the TMC, the probe with a stable, but small load is moved down to contact the surface of the specimen, the material of which is heated under a scanning rate of about 4 K min^{-1}. For linear polymers it is loaded with 0.1–0.5 g. Its minimal (critical) magnitude (0.1 g) depends on the sensitivity of the TMA device used. For cross-linked polymers, the applied load depending on the stiffness of the specimen varies between 0.2 and even 200 g for both
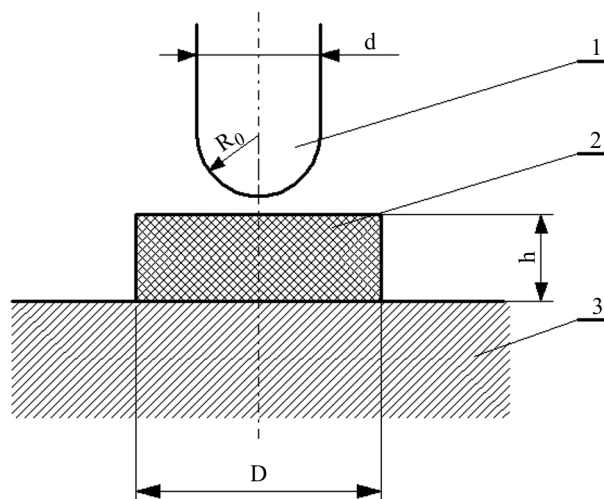

Fig. 1 Scheme of deformation measurements at compression mode of TMA; 1 – a hemispherical tip of the probe, 2 – a specimen, 3 – a base

highly cross-linked and filled rigid composites. This method evaluates mainly [22] the properties of polymeric materials in a layer up to 0.5 mm thick and over a surface area of up to 0.17 mm^2. The measurement accuracy of temperature in the instrument's thermostatic chamber is ±0.05°C and that of deformation is 5 nm. Taking into account some non-uniformity of the specimens and deviations caused by recording of measured values, the characteristic temperatures are evaluated with accuracy higher than ±3–5°C. Simultaneously, the fluctuation of evaluated values of molecular mass (M_m) usually does not exceed ±10%.

In order to determine mechanical properties, tests according to standard procedures have been performed. The Instron tensile testing machine (Instron Ltd. Corp., High Wycombe Bucks, UK) has been used to measure according to ISO 37 the elastic modulus at 100, 200 and 300% elongation, denoted as M100, M200 and M300, respectively. Simultaneously, the tensile strength and elongation at break have also been determined. The tests have been performed with specimens of dumbbell type 1.

The energy loss under static conditions has been measured at deformation rate of 5 mm min^{-1} on the Instron tensile testing machine at compression mode up to 1000 N using cylindrical specimens 18 mm in height and 35 mm in diameter.

Schob elasticity has been measured according to ISO 4662 on cylindrical specimens using a rebound resilience tester (Zwick, Germany, model 5109).

Heat generation has been tested [ASTM D 623] by a Goodrich-type flexometer (model FR-2, Metallist, Leningrad, Russia) in which the specimen as cylinders 25 mm in height and 18 mm in diameter was compressed at a frequency of 30 Hz. As an indirect mea-

sure of energy loss, the temperature of the specimen after 25 min of testing at 40°C has been recorded.

The hardness has been measured according to Shore (A) method according to DIN 53505 on the Zwick 3140 instrument using the same type of specimens as those for resilience.

For dynamic mechanical thermal analysis (DMTA) Analyzer MK III (Polymer Laboratory, Poole, UK) and procedure elaborated at Gdansk Technical University (PL) have been used. During testing $\tan\delta$ and loss modulus $E''=\tan\delta E'$ have been evaluated. The measurements at bending mode at the frequencies of 1 and 10 Hz in a range of temperature from –90 to 240°C at heating rate of 2 K min^{-1} have been performed using specimens in the form of a plate 2 mm thick, from which strips have been cut. DMTA software has been used for data acquisition by a computer.

Test results

Material characteristics from TMA

The standard TMA allows several relaxation transitions to be determined, i.e., the temperatures of the glass transition T_g, the beginning of both melting T_m and flow T_f of polymers, as it had been known for years. The version of TMA used [18, 19] additionally makes it possible to identify several regions in a surface layer of polymers characterized by three states each and differing in linear thermal expansion coefficients in glassy and rubbery states as well as in the zone of melting of a crystalline portion. It also makes possible the evaluation of the molecular mass characteristic in individual regions for the chain segments between junctions. It concerns the pseudo-network in linear and networked polymers as well as for the chain segments belonging to the crystalline portion of polymers. Consequently, it allows the MMD curves for each region to be obtained. Simultaneously, evaluation of the compaction factor could be done from the equation $V_c^{TMA} = 3(\alpha_2 - \alpha_1)T_g$ where α_1 is coefficient of linear thermal expansion in a glassy state$=(\Delta H/H_0)/\Delta T$, where $\Delta H/H_0$ is a relative change in the initial height H_0 (specimen thickness) within the temperature interval, ΔT, α_2 – as α_1 but in rubbery state, T_g is the glass transition temperature. However, only limited information is known about the usability of these characteristics for optimizing the composite formulation and processing parameters. It is due to several factors. Firstly, at TMA tests the evaluated properties are averaged in a surface layer up to 0.5 mm thick when in mechanical measurements a specimen is usually much thicker depending on which test is considered. This fact influences the gradient of cross-link density and both a gradient of crystallinity degree and crystals' sizes distribution while the material is crystallizable. Second are the testing conditions, and third is the material state

when testing (bulk material or a dissolved one). Because of these factors, in the current work, information about several comparisons between generally used mechanical characteristics and those from the TMA are collected.

Molecular mass distribution

The MMD constructed for raw *cis*-1,4-polybutadiene SKD type (from Russia) using gel-permeation chromatography GPC (dissolved material) and by the TMA methods (bulk material) gave similar results [23] to those shown earlier for other linear polymers [24]. However, molecular mass determined by the TMA for a particular topological region often is different from the global value determined by other methods when testing of the dissolved material. Most likely, it is caused by the changes in intermolecular interactions due to different testing temperatures and the penetration of solvent molecules between neighboring segments of polymer chains that increases the distance between them. In addition, one should expect that entanglements would act differently in the molten polymer than in its low-viscous solution.

In order to verify the correctness of our assumptions and the procedure described previously [18], some model linear macrodiisocyanates and respective cross-linked polytriisocyanurates have been analyzed. Synthesis of these macrodiisocyanates was based on oligotetramethylenediol (1) and oligobutadienediol (2) with 2,4-tolylenediisocyanate taken in an amount twice larger than that needed from stoichiometry. These macrodiisocyanates according to GPC measurements had: the first $\overline{M}_n$=1.1 kg mol^{-1}, $\overline{M}_m$=1.65 kg mol^{-1} and polydispersity index K=1.50, and the second $\overline{M}_n$= 9.5 kg mol^{-1}, $\overline{M}_m$=12.3 kg mol^{-1}, and K=1.30. They were cross-linked by end-groups according to the triisocyanurate mechanism. After cross-linking, the two obtained networked polymers had the following molecular properties determined by the TMA; for the first one, $\overline{M}_{n(n)}$=1.25 kg mol^{-1}, $\overline{M}_{n(m)}$=1.66 kg mol^{-1}, and K=1.33, and for the second one, $\overline{M}_{n(n)}$=10.1 kg mol^{-1}, $\overline{M}_{n(m)}$=13.0 kg mol^{-1}, and K=1.29. The results from the two methods compared are close to each other. In addition, the MMD for these macrodiisocyanates and chain segments between junctions of cross-linked polymers (Fig. 2) almost coincide, which support the conclusion about the usability of the TMA for MMD investigation.

Correlation $\overline{M}_{n(n)}$ and T_g

A correlation chart for T_g and $\overline{M}_{n(n)}$ of chain segments between branching junctions in each topological region of rubbers in a cured state has been constructed. For this purpose rubber compounds containing 70 phr (phr=parts per hundred parts of rubber or resin) of NR type SMR 5CV, 30 phr of *cis*-1,4-polybutadiene type
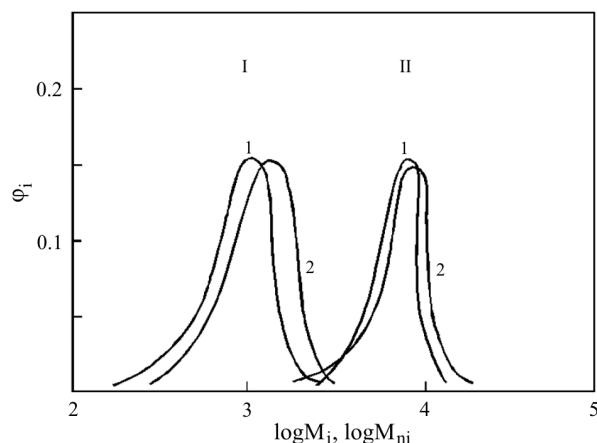
Fig. 2 Molecular mass distributions for macrodiisocyanates I and II determined by GPC method – curves 1 and for chain segments between branching junctions in respective cross-linked polytriisocyanurates determined by TMA method [18] – curves 2

Fig. 3 Correlation chart of devitrification temperature of segmental mobility *vs.* $\overline{M}_{n(n)}$; a – a low-temperature region, b – a high-temperature region for cured rubber containing 70 phr of NR, 30 phr of *cis*-1,4-polybutadiene type SKD

SKD (from Russia), and 50 phr of carbon black grade N220 (ISAF with DBPA=117 cm^3·100 g^{-1}) was used. The other ingredients of compound (phr) were as follows: aromatic oil, 1.5; ZnO, 5.0; stearic acid, 2.6; Santoflex 13, 2.0; Flectol H, 2.6; sulfur, 2.1; and N-cyclohexyl-2-benzothiazol sulfenamide (CBS), 1.2. This compound was cured at 150°C for 20, 25, 30, 40 or 60 min in order to obtain some differences in the structure of the rubber network, because shares of particular cross-links of different sulfidity change during curing. Figure 3a shows that the $\overline{M}_{n(n)}$ in the range of 2–5 kg mol^{-1} of chain segments between junctions in the low-temperature region of cured rubber influences T_g in the same manner as it has been found for low-molecular mass linear polymer [25, 26]. The coefficient of correlation r=0.99 and Snedecor–Fisher test F=114 show that the correlation is significant. For a high-temperature region (Fig. 3b) where $\overline{M}_{n(n)}$=20–80 kg mol^{-1}, such correlation is disputable, because both the coefficient of correlation r=0.49 and F=0.96 are low. In this case, $\overline{M}_{n(n)}$ is much higher than that in the low-temperature region and rubber behaves like a high-molecular mass linear polymer where T_g is usually not related to M_m [26, 27].

The average cross-link density

The average cross-link density of the cured rubber calculated by using the equilibrium swelling method, ν_e^Q, [25] is

$$\nu_e^Q = 35 \cdot 10^{-4} Q_\infty^{-2} \text{ [mol cm}^{-3}\text{]} \qquad (1)$$

where Q_∞ is the volumetric equilibrium of rubber swelling in a 'good' solvent. It is possible to compare its magnitude with that calculated by using the TMA
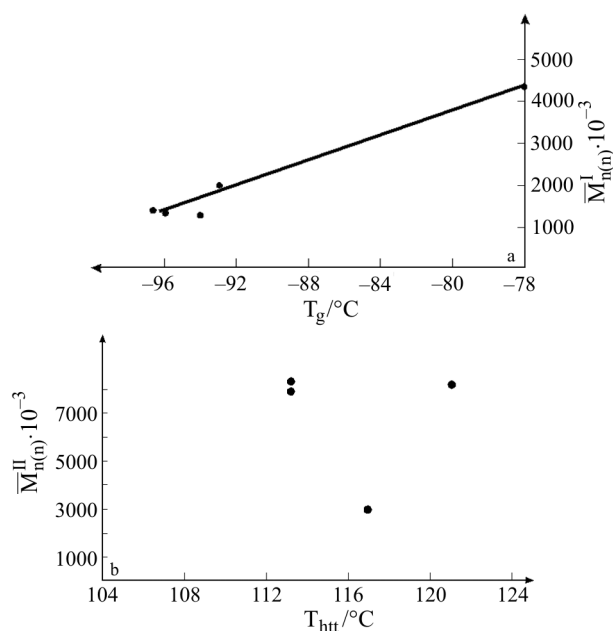
method, ν^{TMA}. The coefficient of correlation between the cross-link densities for the methods being compared is r=0.83 and the value of the Snedecor–Fisher test F=6.6; in calculations an additive influence of each topological region on the total cross-link density evaluated by the TMA [18] is accepted. This provides evidence of an essential correlation between them, despite a high difference in the magnitudes.

The next stage of analysis has been performed on the above-mentioned results of equilibrium swelling compared with those from the TMA, but only for a low-temperature region. Now a much better agreement has been found. Here r=0.98 and the Snedecor–Fisher test F=85. This can be explained by the structure of the tested rubber consisting of interpenetrating networks of two topological regions. As a result, the network restricts the equilibrium of the swelling factor of the rubber differently for each topological region, depending on its cross-link density. In the rubber analyzed, the low-temperature region is more cross-linked, which influences the equilibrium swelling more.

NMR investigations

Nuclear magnetic resonance gives some information about a fine structure of materials. Because of this, some comparative investigations of BR BUNA *cis*-132 made by BSL/DOW Chemical Schkopau, Germany and an anionic polymerized BR made by Bayer Leverkusen/Dormagen, Germany have been

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Table 1 Correlation coefficients between structural and physical characteristics for cured rubber based on a blend of NR and ENR* [28] as well as NR and CPE** [29]. Taking into account 5/4 levels of the second polymer content, respectively***

Correlated value	$φ'$	$\overline{M}'_{n(n)}$	K'	$φ''$	$\overline{M}''_{n(n)}$	K''	$\overline{M}_{n(n)}$	$φ'/\overline{M}'_{n(n)}$	$φ''/\overline{M}'_{n(n)}$	$φ'/\overline{M}'_{n(n)} + φ''/\overline{M}'_{n(n)}$
elastic modulus										
M100	−0.74*/0**	−0.48/0.74	0/0.74	0.74/0	0.65/0.46	−0.70/0	0.73/0.53	0/−0.82	0/−0.43	0/−0.73
M200	−0.80/0.49	−0.72/0.86	0/0.60	0.80/−0.49	0/0.64	−0.87/0	0/0.71	0.58/−0.92	0/−0.62	0.56/−0.86
M300	−0.81/0	−0.64/−0.79	0/−0.69	0.81/0	0.49/−0.53	−0.82/0	0.59/−0.60	0/0.86	0/0.50	0/0.78
M200−M100	0.43/0	0/−86/−0.86	0.41/−0.56	−0.43/0	−0.88/−0.63	0/0	−0.87/−0.70	0/0.93	0.56/0.60	0/0.86
M200/M100	−0.84/0	−0.81/−0.65	0.48/−0.80	0.84/0	0/0	−0.91/0	0/−0.42	0.72/0.75	0/0	0.69/0.63
E'' at 1 Hz for β₁	0.74/−	0.76/−	−0.48/−	−0.74/−	0/−	0.85/−	0/−	−0.79/−	−0.42/−	−0.77/−
E'' at 10 Hz for β₁	0.73/−	0.75/−	−0.47/−	−0.73/−	0/−	0.85/−	0/−	−0.79/−	−0.41/−	−0.76/−
E'' at 1 Hz for β₂	−0.49/−	−0.82/−	0.95/−	0.49/−	−0.96/−	−0.73/−	−0.84/−	0.99/−	1.0/−	1.0/−
E'' at 10 Hz for β₂	−0.49/−	−0.81/−	0.95/−	0.49/−	−0.96/−	−0.73/−	−0.84/−	1.0/−	1.0/−	1.0/−
tensile strength	−0.44/−0.58	0/−0.42	0/−0.57	0.44/0.58	0.78/0	0/0	0.89/0	−0.55/0.41	−0.60/0	−0.56/0
elongation at break	0.74/0	0.62/0.83	0/0	−0.74/0	0/0.66	0.79/0	−0.43/0.72	−0.53/−0.90	0/−0.64	−0.50/−0.85
hardness	−0.74/0	−0.53/0	0/0.58	0.74/0	0.55/0	−0.73/0	0.61/0	0/0	0/0	0/0
tanδ at 1 Hz for β₁	0.74/0	0.75/−0.59	−0.46/−0.86	−0.74/0	0/0	0.85/0	0/0	−0.77/0.67	0/0	−0.75/0.58
tanδ at 10 Hz for β₁	0.73/0	0.74/−0.58	−0.45/−0.87	−0.73/0	0/0	0.84/0	0/0	−0.77/0.66	0/0	−0.74/0.57
tanδ at 1 Hz for β₂	−0.47/0	−0.80/−	0.94/−	0.47/−	−0.97/−	−0.71/−	−0.85/−	1.0/−	1.0/−	1.0/−
tanδ at 10 Hz for β₂	−0.47/0	−0.80/−	0.94/−	0.47/−	−0.97/−	−0.71/−	−0.85/−	1.0/−	1.0/−	1.0/−
Goodrich test at room temperature	−/0		−/0	−/0	−/0	−/−0.56	−/0.42	−/−0.67	−/0	−/59
Goodrich test at 40°C	−0.81/0.79	−0.84/0.98	0.56/0	0.81/−0.79	0/0.91	−0.92/0	0/0.94	0.80/−0.96	0.47/−0.90	0.78/−0.98
energy loss during static compression test	−0.95/−	−0.82/−	0.42/−	0.95/−	0/−	−0.94/−	0.45/−	0.49/−	0/−	0.47/−
Schob elasticity	0.79/−	0.84/−	−0.59/−	−0.79/−	0/−	0.90/−	0/−	−0.83/−	−0.51/−	−0.81/−

***φ' and φ'' are shares of low- and high-temperature regions, $\overline{M}'_{n(n)}$ and $\overline{M}''_{n(n)}$ are number-average molecular masses between the junctions in low- and high-temperature regions, $\overline{M}_{n(n)} = φ'\overline{M}'_{n(n)} + φ''\overline{M}''_{n(n)}$, K is the polydispersity index all from the TMA; M100, M200, M300 are elastic moduli at 100, 200 and 300% elongation, respectively, all from tensile test; tanδ is the ratio of energy loss to energy returned during dynamic deformation, loss modulus $E''=tanδ·E'$ all from DMTA test at 1 Hz, β₁ and β₂ successive relaxation processes

performed [21]. Their characteristics were as follows: BUNA *cis*-132: the number-average molecular mass $\overline{M}_n$ =120 kg mol⁻¹, the mass-average molecular mass $\overline{M}_m$ =450 kg mol⁻¹, the polydispersity index $K = \overline{M}_m / \overline{M}_n$ =3.75 and a 97% of 1,4-*cis* microstructure. Bayer-BR: $\overline{M}_n$ =61 kg mol⁻¹, $\overline{M}_m$ =64 kg mol⁻¹, K=1.05 and the following microstructure: 40% of 1,4-*cis*/50% of 1,4-*trans*/10% of 1,2-*vinyl*. In addition, two partially CD₂-deuterated BR(d₄) with varying microstructure, different molecular mass of the precursor chains and its MMD were used. Their characteristics are similar to those mentioned above for protonated BR: *cis*-BR-A: $\overline{M}_n$ (d₄)= 190 kg mol⁻¹, $\overline{M}_m$ (d₄)=700 kg mol⁻¹, K(d₄)=3.68 and a 98% of 1,4-*cis* microstructure. BR-E: $\overline{M}_n$ (d₄)= 50 kg mol⁻¹, $\overline{M}_m$ (d₄)=52 kg mol⁻¹, K(d₄)=1.04 and the following microstructure: 40% of 1,4-*cis*/50% of 1,4-*trans*/10% of 1,2-*vinyl*.

Dicumyl peroxide has been used as the curing agent in different quantity between 0.8 and 2.5 phr. There are no other ingredients used in the rubber compounds. Specimen curing was performed at a temperature of 145°C for 60 min.

Studies of these specimens show that conclusions from the TMA are not contradictory with the NMR findings concerning butadiene rubbers [21].

Comparison of selected mechanical properties and characteristics from TMA

Mechanical properties are usually taken in engineering practice to be critical for the acceptance of materials to be used. Because of this, optimization of rubber formulation and the technology of its compounding and processing is based on static and dynamic measurements of mechanical properties. It is well known that properties of the tested material depend on its structure. This means that mechanical properties have to correlate with the characteristics of the material structure if it is be properly characterized. Because of this, two sets of cured rubbers differing substantially in formulations

were used to check the validity of the results from TMA investigations.

In the first case, the rubber compounds containing 100 phr of NR (grade SMR 5CV, Malaysia) and 50 phr of carbon black grade N330 (Carbex N330, Carbochem Factory, Gliwice, Poland) was used. Chlorinated polyethylene [CPE-TYRIN 6000, Dow Deutschland Inc., with elastic modulus at 100% strain 1.0 MPa (based on a formulated resin: 100 phr TYRIN 6000, 0.5 phr stearic acid, 3 phr ESBO); Average particle size: 300 μm, Chlorine content (TGA method): 35.3 mass%] in varying amounts (0, 5, 10, 15 and 20 phr) was added. The amounts of sulfur and N-cyclohexyl-2-benzothiazol sulfenamide (CBS) were not varied with the change of CPE amount, so all rubber compounds had the same concentration of curatives *vs*. the summarized NR and CPE content in phr.

In the second case, cured specimens were made of the rubber compounds containing a blend of natural rubber (SMR 5CV, Malaysia) and epoxidized natural rubber (ENR-25, Malaysia) at different ratios between 100/0 and 80/20, filled with 50 phr of carbon black grade N330 (Carbex 330, Carbochem Factory, Gliwice, Poland). The other ingredients of the compound (in phr) were: a softener (aromatic oil) (Plastyfikator P3, Silesian Refinery, Poland) – 7.3, zinc oxide (Bedzin Metallurgic Plant, Poland) – 5, stearic acid (Kedzierzyn Nitrogen Plant, Poland) – 2.6, Santoflex 13 (Dusantox 6PPD, Duslo-Sala, Slovakia) – 2.0, Polnox R (equivalent Flectol H, Chemical Plant Organika, Zarow, Poland) – 2.6, mineral sulfur (Siarkopol, Tarnobrzeg, Poland) – 2.0, CBS (Vulkasil CBS, Chemical Plant Organika, Zarow, Poland) – 1.2, and Santogard PVI (Duslin P, Duslo-Sala, Slovakia) – 0.2.

Several characteristics of topological regions determined by TMA (Tables 1 and 2) correlate satisfactory with the static and dynamic mechanical properties of the above-mentioned cured rubbers and PA/cured rubber blend – the coefficients of correlation >0.7 are given in bold letters. The specimens tested differ substantially in the structure of their network, because CPE does not participate in cross-links when ENR can

Table 2 Correlation coefficients between structural and physical characteristics of PA6-based composite differing in a content of cured rubber

Property	V_c^{TMA},	φ'_1	$\overline{M}'_n$	$\overline{M}'_m$	K'	V_c^{TMA},	$\overline{M}''_n$	$\overline{M}''_m$	K''	φ_2	φ_{cr}
tensile strength	−0.55	**−0.72**	0	0	**0.89**	−0.60	0	0.41	0.40	**−0.75**	**0.85**
elastic modulus	−0.43	**−0.90**	0	0	**0.91**	**−0.72**	0.65	0.68	0.48	**−0.70**	**0.94**
elongation at break	−0.69	0	−0.66	−0.66	0	0	0	0	0	0	0
impact tensile strength	0	**0.74**	0	0	**−0.98**	0.47	−0.49	−0.52	−0.51	0.63	**−0.80**
log damping decrement	0	**0.97**	0	0	**−0.82**	**0.80**	**−0.88**	**−0.90**	0	0.44	**−0.85**
Schob elasticity	−0.55	**−0.90**	0	0	**0.88**	**−0.77**	0.63	0.67	0.41	−0.69	**0.94**

*description as in Table 1, the compaction factor $V_c^{TMA}=3(\alpha_2-\alpha_1)T_g$, φ_{cr} – the share of crystalline portion

do it. Simultaneously, their physical interactions with NR, due to the different polarity, also vary, what influences the formation of physical networking junctions. In blends of PA6/cured rubber, the networking junctions are assumed to have a physical nature only.

Conclusions

Several characteristics of the topological regions determined by the TMA for cured rubbers based on NR/CPE and NR/ENR blends as well as PA6-based composites filled with cured rubber correlate with their static and dynamic mechanical properties. These rubbers differ substantially in a structure of their networks, because CPE does not participate in cross-links when ENR can do it. Physical interactions caused by these additives also vary, due to the different polarity, which influences the formation of physical junctions. Because of this, the strength of correlation depends on rubber formulation and which of the characteristics have been compared. However, further studies of other rubbers and methods of testing the usage properties are needed, for instance, to find factors giving differences in the cross-link density evaluated by this and by swelling methods.

The results discussed above show that the characteristics of molecular and topological structures evaluated by the TMA give additional information, which could explain some causes for the changes in polymer properties resulted from their formulation and processing conditions. These investigations could be helpful for further improvement of polymeric materials by compounding with additives and in reprocessing. However, further discussion about the reasons for the existence, or lack of, correlations is needed before more general conclusions can be made in the future.

Any model approach involves an idealization of certain properties of a system, while some other properties are not taken into account at all. Only judging from its application in order to solve relevant problems can one assess the validity of this approach. It would be very important to outline the limits of applicability of the TMA for multi-aspect description of polymeric systems.

Acknowledgements

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