

On Some Changes in Polymer Blend Topological and Molecular Structures Resulted from Processing

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ABSTRACT : A general scheme of a rubber structure is proposed. Using the thermomechanical method(TMA), some changes in the molecular and topological structures for uncured and cured, and unfilled and filled rubbers during processing are shown. In our investigations as region it is understood a complex structure, which is expressed at the thermomechanical curve(TMC) as a zone differed from others in thermal expansion properties. This zone is between the noticed temperatures of relaxation transitions, usually on the level like those determined by DMTA at 1Hz. These regions, which shares, are not stable, and differ in molecular-weight distribution(MWD) of chain fragments between the junctions. Differences in dynamics of the formation of the molecular and topological structures of a vulcanizate are dependent on the rubber formulation, mixing technology and curing time. Some of characteristics of these regions correlate with mechanical properties of vulcanizates what is shown for NR rubbers containing ENR or CPE as a polymeric additive. It is well known that the state of order influences diffusivity of low-molecular substances into the polymer matrix. Because of this, the two topological amorphous regions should influence the distribution of the ingredients and resulting in rubber compounds' heterogeneity, and related properties of cured rubber. Investigation of this problem is expected to be, in the future, one of the essential factors in determining further improvement of polymeric materials properties by compounding with additives and in reprocessing of rubber scrap.

Keywords : mastication, mixing, reprocessing, vulcanization, curing, molecular structure, topological structure, correlation, rubber, MWD, compactness, NR, ENR, CPE

I . Introduction

One of the trends in the plastics and rubber industry is to blend two or more polymers in order to achieve a set of properties for specific application. Quite often, this type of blending leads to a new set of properties of polymeric materials, which have specific property advantages over those of the individual

blend constituents.

Optimization of formulation of multi-ingredient composite and its compounding are time consuming processes. To make them more efficient it is needed to use some new ideas about how to select characteristics of composite structure to ensure their correlation with the most important usage properties. One of such ideas could be a topological structure evaluated by thermomechanical method(TMA) according to Y. A. Olkhov et al methodology, which

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make possible to evaluate numerous molecular and topological characteristics from a thermomechanical curve(TMC).¹ This idea is based on a simplified model network with physical and/or chemical junctions and testing of a bulk polymer.

II. Idea of Topological Structure

As a region or topological block it is understood a complex structure, which is expressed at the TMC as a zone different from others in thermal expansion properties. A structure with two or three amorphous regions, probably interpenetrating, and a more ordered portion was found for the studied neat polymers and polymeric materials.

These regions are accepted² as not divided in space; they represent several types of interactions, which coexists in a polymer. At least high-temperature and low-temperature regions have been observed by means of the thermomechanical analysis for uncured and cured as well as unfilled and filled rubbers. They differ in the transition temperatures up to 200°C and related compactness, what should influence distribution of additives within the polymer matrix. They, most likely, describe some higher-level arrangement than molecular one.

It was confirmed experimentally that in raw rubbers, rubber compounds and vulcanizates present a complex topological structure, which changes in a way dependent on rubber formulation and compounding, processing and curing technologies. This structure is not steady (as it was also observed by atomic force microscopy(AFM) investigations³) and depends on numerous factors, which are not investigated yet in full.

In rubber compounds, the following morphological regions could be possible; (1) A pseudo-networked low-temperature amorphous region consisting mainly of the mobile rubber chain fragments. Physical networking junctions there are formed by chain fragments, which do not interact strongly with a surface of active filler or by unstable micro-crystallites in a size about critical as well as a high-

temperature amorphous region because they reduce mobility of polymeric chains. (2) A pseudo-networked high-temperature amorphous region consisting of rubber chain fragments, which interact strongly with a surface of active filler as it reduces essentially its mobility. In addition, could be formed zones of interaction with more polar structures in the polymer creating carbon-black-free cluster type physical junctions between fragments of the chains and by crystalline structures. (3) There could also exist a crystalline portion, which contains the most ordered part of the polymer matrix, especially on the surface of carbon black, including fragments of chains interacting with active sites of a carbon black surface.

In unfilled vulcanizates, a spatial structure is arranged mainly due to both the chemical reactions of the curing system and different structure of the cluster type junctions, being degraded at a temperature lower than that for chemical bonds. Addition of carbon black into the rubber could destroy the energetic balance of intermolecular interactions existing there before mixing. However, new junctions are created. Now conditions to create the cluster type junctions having degradation energy on the level as those for a case without active filler are disturbed. As the concentration of carbon black increases, stronger rubber/carbon black branching junctions having higher such temperature supplement the cluster type junctions with the degradation temperature $\geq 105^\circ\text{C}$. They enhance the concentration of junctions in the high-temperature region and its transition temperature.

Mixing technology and curing time affect both kinetics of formation and properties of the regions. Increased compaction of the structure of a high-temperature region during vulcanization was noticed.

It is known that the state of order influences the diffusivity of low-molecular substances into the polymer matrix. Based on this, it was formulated an idea² about influence of these amorphous regions on the distribution of low-molecular substances and

other composition components within polymer matrix resulted in compounds' heterogeneity, and related properties of cured rubber. Kilian⁴ made similar conclusion when this amorphous portion is located in the boundary between the grains observed by AFM. Investigation of this problem is expected to be one of the factors determining further improvement of properties of polymeric materials by compounding with additives. It was found that molecular and topological structures of cured rubber are formed in a way dependent on the successive stages of processing when usual mixing occurs. This transformation process depends on many factors including order of loading of ingredients and a way of homogenization. Because of this, simultaneous measurements of the average crosslink density (what is generally accepted) also the topological and molecular structures including molecular weight distribution(MWD) of chain fragments between the junctions of the rubber network should give additional information to find the optimal structures for each particular case. Shape of the MWD of the chain fragments between the junctions in both amorphous rubber regions depends on curing time.

In spite of our joint long lasting experimental studies^{1,2,5,6} using different techniques including swelling method and nuclear magnetic resonance (NMR),⁷ the idea of mentioned topological structure is not proved sufficiently till now to be sure about usability of the TMA for a deeper study of a complex structure of rubber. This idea could be useful for practical applications only in a case if parameters of molecular and topological structures of rubber evaluated by the TMA correlate with mechanical properties determined at static and dynamic conditions.

Chlorinated polyethylene(CPE)^{6,8-12} or epoxidized natural rubber(ENR)⁵, taken as polymeric additive, introduced into rubber compounds changes properties of cured rubbers and, most likely, their structure. However, one could expect their different action during rubber network formation and later during transformation under stress and thermal

energy delivered during processing, because polar chlorinated polyethylene is incompatible with non-polar natural rubber(NR) and does not react with typical curatives containing sulfur compounds in contrast to polar ENR being compatible with NR what changes polarity of the polymer blend and also participate in the curing process. Because of this, in the present study, we investigated mechanical properties and characteristics of molecular and topological structures of some rubbers in order to solve preliminarily a problem of usability of the mentioned TMA methodology. The results of testing for rubbers containing CPE or ENR make possible to compare these characteristics and to make some general conclusions. A part of such a study is described in this paper.

III. Experimental

1. Materials

The rubber compound containing 100 phr of NR(grade SMR 5CV) and 50 phr of carbon black grade N 339(Carbex N330 from Gliwice Carbochem Factory, Poland) was used. Polymeric additives (Table 1) were added in amount of 0 ~ 20 phr of CPE or 0 ~ 30 phr of ENR. The amounts of sulfur and N-cyclohexyl-2-benzothiazol sulfenamide(CBS) were not varied with change in amount of additive, so that all rubber compounds have the same con-

Table 1. Elastomers Employed in This Study

Materials	Description
NR (SMR 5CV)	Plastic Retention Index PRI (min.,%): 60, ML ₁₊₄ 100°C: 55
CPE	TYRIN 6000 (Manufacturer: Dow Deutschland Inc.) Elasticity 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: 300µm Chlorine content (TGA method): 35.3 %
ENR	ENR-25, Malaysia, content of epoxy groups: 25 mol.%

centration in phr of curatives against NR content.

The other ingredients of compound (in phr) were: a softener (aromatic oil: Plastyfikator P3, Silesian Refinery, Poland), 7.3; ZnO (Bedzin Metallurgic Plant, Poland), 5.0; stearic acid (Kedzierzyn Nitrogen Plant, Poland), 2.6; N-isopropyl-N'-phenyl-p-phenylenediamine, Santoflex 13 (Dusantox 6PPD, Duslo-Sala, Slovakia), 2.0; Flectol H, 2.6; mineral sulfur (Siarkopol, Tarnobrzeg, Poland), 2.0; CBS (Vulkasil CBS, Chemical Plant Organika, Zarow, Poland), 1.2; Santogard PVI (Duslo-Sala, Slovakia), 0.2.

2. Preparation of Rubber Compounds and Vulcanizates

Mixing was carried out in a laboratory Banbury type internal mixer (2 L volume) at 40 rpm. The fill factor was 0.85, and the chamber temperature at start of mixing was 150°C.

The compounding procedure: loading into the internal mixer a raw rubber, additives and CPE except curatives, and next, carbon black and softener. In a case of compound with ENR and NR these polymers were loaded together. The batch was dumped at 160°C when mixed with CPE and 155°C when mixed with ENR. In the finishing stage of mixing, the curatives were added on the open mill (laboratory type with a friction ratio of 1:1.04) at a temperature not exceeding 80°C. This mixing time was 4.5 min. The mixing torque, which characterizes the blending intensity in the internal mixer, is increased by the addition of 5 phr of CPE, but it is not changed significantly by the further increase in its amount.

The rubber compounds were cured in respective molds in electrically heated press with a table of 400×400 mm at 150°C for optimum cure time (t_{90}), which was determined from an oscillating disk rheometer (Monsanto R100). CPE slightly influences curing process giving some changes in M_{90} being also a preliminary measure of crosslink density.

3. Test Methods

For TMA investigations a UIP-70M apparatus made by the Central Design Bureau of the Russian Academy of Sciences, Moscow was used. The testing sample was put into the measuring cell of the thermostatic chamber. It was frozen without pressing under a scanning rate of 1 ~ 40°C/min starting from room temperature until -120 or -130°C and, next, was stored for 10 ~ 15 min to equalize a thermal field within a sample. To obtain the TMC curve, the rod with a stable load, was moved down to contact the surface of a sample.

Dynamical Mechanical Thermal Analysis (DMTA) was done on Polymer Laboratory Analyzer MK III with frequency of bending 1 Hz and 10 Hz in a range of temperature from -90°C to +240°C and a heating rate of 2°C/min.

Static hysteresis was measured at room temperature using Instron tensile testing machine. Loading was performed in ten cycles running from zero to maximum loading equal 1.8 kN (what equals to 1.2 MPa) and back to zero at compression rate of 10 mm/min. Goodrich flexometer was performed to measure the heat generation and fatigue where sample was compressed with frequency of 30 Hz at both room temperature and 40°C.

IV. Results and Discussion

1. Mechanical Properties

The adding of CPE or ENR changes differently mechanical properties of cured rubber (Table 2 and Table 3). The elastic modulus at elongation does not increase depending upon adding of 5 phr of CPE as can be expected from the values of maximum torque in the Monsanto rheograph. Decrease in elastic modulus and tensile strength is observed with increase in CPE content. However, adding even 5 phr of CPE gives an increase in the resistance of cured rubber to heat ageing (lower change in tensile strength and elongation at break). The influence of

Table 2. Influence of CPE on Properties of Cured Rubber

Mechanical properties*	Content of CPE (phr)				
	0	5	10	15	20
Hardness (Shore A)	57	60	61	58	58
Tensile strength (MPa)	22.1	21.4	19.2	20.9	19.9
M100 (MPa)	4.2	4.0	4.2	3.9	3.5
M200 (MPa)	7.2	6.6	6.8	6.2	5.6
M300 (MPa)	15.5	13.5	13.9	12.3	10.9
Elongation at break (%)	540	590	530	630	650
Oven ageing for 7 days at 100°C					
Tensile strength change (%)	25	20	20	15	15
Elongation at break change (%)	30	25	24	23	23
Tear resistance (Nm)	51	53	58	52	52
Schob elasticity (%)	45	39	36	37	31
ΔT_{25} (°C)	15.1	14.7	16.0	17.2	21.2
Energy loss during static compression test (%)	14.4	18.8	18.5	18.1	20.7

*M100, M200, and M300 represent the tensile moduli at 100, 200, and 300% elongation, respectively, and ΔT_{25} represents the heat generation by the Goodrich flexometer at 40°C.

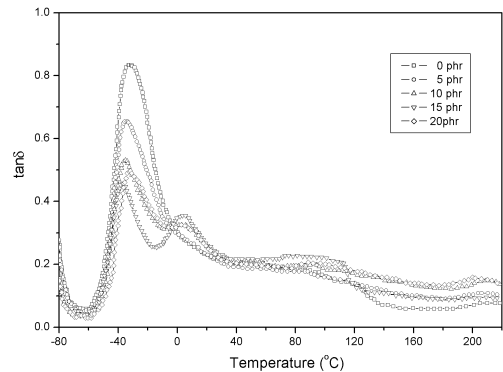
Table 3. Influence of ENR on Properties of Cured Rubber

Mechanical properties	Content of ENR (phr)			
	0	10	15	30
M100 (MPa)	1.65	2.07	2.35	2.26
M200 (MPa)	3.58	4.35	5.04	4.99
M300 (MPa)	9.30	10.67	11.91	11.20
M200 - M100 (MPa)	1.93	2.29	2.68	2.73
M200 / M100	2.17	2.11	2.14	2.21
Elongation at break (%)	743	685	662	661
Tensile strength (MPa)	21.70	21.80	22.40	21.40
Schob elasticity (%)	44.5	40.8	36.75	33.1
Energy loss during static compression test (%)	25.55	26.16	27.66	27.14
$\tan\delta$ at 1 Hz β_1	0.576	0.385	0.284	0.164
$\tan\delta$ at 10 Hz β_1	0.587	0.383	0.283	0.161
T_g for 1 Hz β_1 (°C)	-29.4	-31.4	-32.9	-33.6
T_g for 10 Hz β_1 (°C)	-19.2	-22.8	-24.7	-27.3
$\tan\delta$ at 1 Hz β_2	-	0.355	0.376	0.432
$\tan\delta$ at 10 Hz β_2	-	0.391	0.414	0.474
T_g for 1 Hz β_2 (°C)	-	2.8	1.3	-1.4
T_g for 10 Hz β_2 (°C)	-	6.5	5.1	4.8
ΔT_{25} (°C)	13.6	15	16.5	17.5
Hardness (Shore A)	56	58	59	59

CPE on tear resistance is not observed. Changes in the mechanical properties of the cured rubber upon addition of CPE are rather not supposed to arise in full from variation in crosslink density, but it is possible to expect that they are also resulted from some reorganization in topological structure and/or from changes in concentration of the most thermally stable rubber/carbon black chemisorptive structures.

Additives investigated influence dynamic mechanical properties of the tested vulcanizates. Increase in CPE content gives a small increase in E' value visible in the range of temperatures between -20°C and +5°C. Simultaneously, a small decrease in a value of $\tan\delta$ (Figure 1) and some shift in T_g to lower temperature are observed. When content of CPE is 10 phr and higher, the second relaxation process is observed. In the discussed experiment two relaxation processes are visible when CPE adding in a quantity of 10 phr and more, what confirms a limited compatibility of the tested polymers. When samples are tested at frequency of 10 Hz, the value of T_g is a little higher than that for 1Hz. This confirms a well-known fact that testing frequency influences the value of T_g . The influence of CPE added in amount of 5 phr on heat generation in Goodrich test (Figure 2) and hysteresis losses are visible.

When ENR is added the changes in mechanical properties of cured rubbers (Table 3) go in a little

**Figure 1.** The dependence of $\tan\delta$ from DTMA test at 1 Hz frequency on CPE concentration.

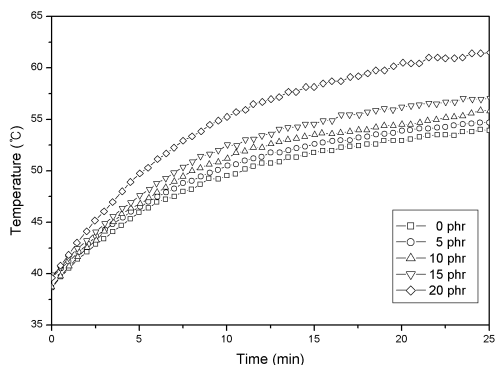


Figure 2. The dependence of heat generation in Goodrich test on CPE concentration.

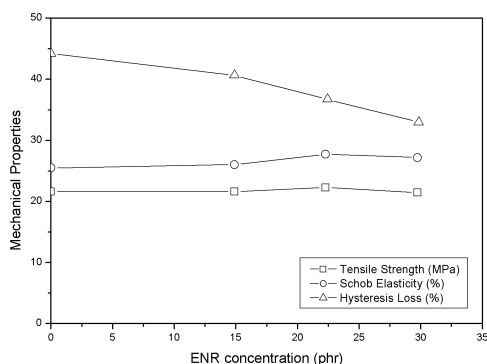


Figure 3. The dependence of tensile strength (MPa), Schob elasticity (%) and hysteresis loss (%).

another way than in a case of CPE adding discussed above. Now is observed a growth of elasticity modulus as the content of ENR increases. Simultaneously, it influences the hysteresis of vulcanizates. Decrease of Schob elasticity (Figure 3) and increase of energy losses during static compression test and ΔT_{25} at Goodrich Test at 40°C were noticed.

2. Topological and Molecular Characteristics

It is known that 1,4-*trans* isomer of the NR have much higher interaction energy than that for 1,4-*cis* isomer. Based on this fact, it is reasonable to accept that 1,4-*trans* fraction of the rubber strongly influences the formation of thermally stable cluster

type associates. It means that such cured rubber have to be characterized by at least two topological regions resulting from differences in interaction energies and differences in a structure of chemical network, what is shown on the TMC, Figure 4. This rubber has two topological regions, as expected.

If presumptions formulated above are true, the rubber network in a low-temperature region could be arranged in such a manner that its branching junctions are resulted from low-energy physical interactions of different nature and relatively labile polysulfidic chemical bonds. The latter could be rearranged in time into lower level sulfidity ones under influence of both thermal energy and stress, what are well known facts from kinetics of the

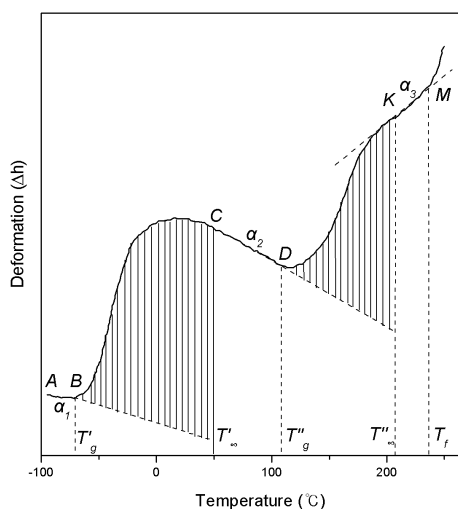


Figure 4. Thermomechanical curve for natural rubber filled with carbon black cured rubber; α_1 : the thermal expansion coefficient of the low-temperature region in a glassy state; α_2 : the thermal expansion coefficient of the low-temperature region in a high-elastic state; α_3 : the effective thermal expansion coefficient of high-temperature region in a high-elastic state; T'_g : the glass transition temperature of a low-temperature amorphous region; T'_∞ : temperature of the beginning of the plateau of high elasticity in a low-temperature amorphous region; T''_g : the glass transition temperature of a high-temperature amorphous region; T''_∞ : temperature of the beginning of the plateau of high elasticity in a high-temperature amorphous region; and T_f : temperature of the beginning of molecular flow.

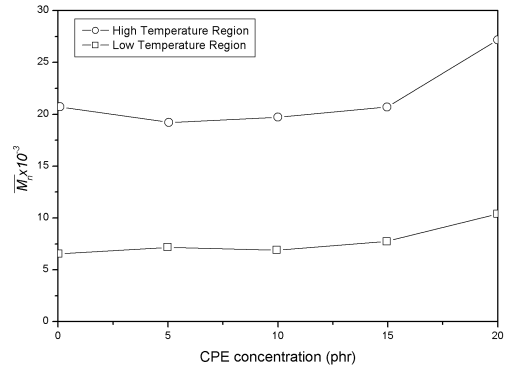
Table 4. Influence of CPE on Molecular and Topological Characteristics of NR/CPE/Carbon Black Vulcanizates

Analyzed parameters*	CPE concentration (phr)				
	0	5	10	15	20
Low-temperature region					
T_g (°C)	-69	-64	-67	-65	-64
$\alpha_1 \times 10^5$ (deg ⁻¹)	5.75	7.40	4.65	6.37	3.74
$\alpha_2 \times 10^5$ (deg ⁻¹)	27.40	27.78	27.40	28.57	22.22
V_f	0.132	0.128	0.139	0.139	0.116
$\overline{M}_n \times 10^{-3}$	6.42	7.09	6.85	7.72	10.24
$\overline{M}_w \times 10^{-3}$	10.34	11.82	11.64	13.24	16.99
K'	1.61	1.67	1.70	1.72	1.66
T_∞ (°C)	54	86	82	87	71
$v_c \times 10^4$ (mole/cm ³)	1.43	1.30	1.34	1.19	0.90
High-temperature region					
T_g (°C)	122	137	131	133	129
$\alpha_3 \times 10^5$ (deg ⁻¹)	-35.7	-32.2	-37.0	-35.7	-33.3
$\overline{M}_n \times 10^{-3}$	20.81	19.25	19.70	20.63	27.14
$\overline{M}_w \times 10^{-3}$	42.83	37.70	40.09	42.08	54.49
K''	2.06	1.96	2.04	2.04	2.01
T_f (°C)	232	234	232	241	237
Ψ''_{top}	0.598	0.604	0.596	0.600	0.590
T_∞ (°C)	219	215	217	217	218
$v_c \times 10^4$ (mole/cm ³)	0.44	0.48	0.47	0.45	0.34
Swelling in TGF-Toluene					
Q_∞	7.2	8.5	16.6	14.7	13.4
$v_Q \times 10^4$ (mole/cm ³)	0.68	0.48	0.13	0.16	0.19

* K' : coefficient of polydispersity, \overline{M}_n : number-average molecular weight between the junctions, \overline{M}_w : weight-average molecular weight between the junctions, T_f : temperature of the beginning of molecular flow, T_g : glass transition temperature, T_∞ : temperature of the beginning of the plateau of high-elasticity, V_f : free volume, α_1 : coefficient of linear thermal expansion in a glassy state, α_2 : coefficient of linear thermal expansion in a high-elastic state, low-temperature region, α_3 : coefficient of linear thermal expansion in high-elastic state, high-temperature region, Ψ''_{top} : a share of topological junctions, v_c : crosslink density calculated from TMA, v_Q : crosslink density calculated from swelling, Q_∞ : volumetric equilibrium swelling.

curing and aging processes, and kinetics of stress relaxation process.

It was found that CPE influences the dynamics of forming of cured rubber molecular and topological structures (Table 4). It is clear that a tendency of transformation of initial topological structure having three regions to a structure with two regions

**Figure 5.** The number-average molecular weight of a chain segments between the junctions in a cured rubber versus CPE concentration.**Table 5. Influence of ENR on Molecular and Topological Characteristics of NR/ENR/Carbon Black Vulcanizates**

Characteristics	Content of ENR (phr)			
	0	10	15	30
Ψ'	0.42	0.43	0.75	0.43
Ψ''	0.58	0.57	0.25	0.57
Ψ'/\overline{M}_n	28.0	21.8	159.8	202.8
Ψ''/\overline{M}_n	14.7	8.6	3.8	15.5
$\Psi'/\overline{M}_n + \Psi''/\overline{M}_n$	42.7	30.4	163.6	218.3
$\overline{M}_n \times 10^{-3}$	15.0	20.0	4.7	2.1
$\overline{M}_w \times 10^{-3}$	39.4	66.3	66.4	36.7
$\Psi'\overline{M}_n + \Psi''\overline{M}_n$	29.1	46.3	20.1	21.8
$\overline{M}_w \times 10^{-3}$	57.1	95.9	95.5	53.9
K'	1.67	1.59	1.67	1.73
K''	1.45	1.45	1.44	1.47

as a concentration of the modifier grows. Adding > 10 phr CPE rapidly reduces a weight share of an intermediate topological amorphous region and gives a growth of a share of a low-temperature topological region. The number-average molecular weight of the chain segments between the junctions in a pseudo-network of a low-temperature and intermediate-temperature topological regions have the minimum at 10 and 15 phr of CPE, respectively (Figure 5). Introduction of ENR also changes a dynamic of forming the molecular and topological structures of vulcanizates, Table 5. However, this influence is not so visible as for master batch.

Since macromolecules of CPE are not included

Table 6. Correlation Coefficients Between Structural and Physical Characteristics of Cured Rubber Based on a Blend of Natural and Epoxidized Natural Rubber*

Correlated value	ψ'	\overline{M}_n	K'	ψ''	\overline{M}_n	K''	ψ'/\overline{M}_n	ψ''/\overline{M}_n	$\psi'/\overline{M}_n + \psi''/\overline{M}_n$	
Elasticity modulus										
M100	<i>-0.741</i>	-0.482	-0.018	<i>0.741</i>	0.653	<i>-0.695</i>	<i>0.727</i>	0.203	-0.206	0.169
M200	<i>-0.804</i>	<i>-0.720</i>	0.324	<i>0.804</i>	0.296	<i>-0.866</i>	0.383	0.575	0.186	0.556
M300	<i>-0.809</i>	-0.641	0.179	<i>0.809</i>	0.489	<i>-0.820</i>	0.587	0.371	-0.006	0.352
M200 - M100	0.429	0.093	0.414	-0.429	<i>-0.875</i>	0.351	<i>-0.872</i>	0.126	0.558	0.166
M200 / M100	<i>-0.836</i>	<i>-0.808</i>	0.477	<i>0.836</i>	0.122	<i>-0.913</i>	0.221	<i>0.716</i>	0.360	<i>0.692</i>
E" at 1Hz for β_1	<i>0.736</i>	<i>0.762</i>	-0.483	<i>-0.736</i>	-0.030	<i>0.854</i>	-0.097	<i>-0.789</i>	-0.419	<i>-0.765</i>
E" at 10Hz for β_1	<i>0.730</i>	<i>0.754</i>	-0.472	<i>-0.730</i>	-0.038	<i>0.848</i>	-0.103	<i>-0.785</i>	-0.410	<i>-0.759</i>
E" at 1Hz for β_2	-0.492	<i>-0.815</i>	<i>0.951</i>	0.492	<i>-0.957</i>	<i>-0.728</i>	<i>-0.836</i>	<i>0.994</i>	<i>1.000</i>	<i>0.995</i>
E" at 10Hz for β_2	-0.489	<i>-0.813</i>	<i>0.950</i>	0.489	<i>-0.958</i>	<i>-0.726</i>	<i>-0.838</i>	<i>0.995</i>	<i>1.000</i>	<i>0.996</i>
Tensile strength	-0.442	-0.054	-0.325	0.442	<i>0.777</i>	-0.207	<i>0.892</i>	-0.546	-0.598	-0.557
Elongation at break	<i>0.737</i>	0.620	-0.209	<i>-0.737</i>	-0.369	<i>0.788</i>	-0.425	-0.532	-0.096	-0.499
Hardness	<i>-0.735</i>	-0.532	0.061	<i>0.735</i>	0.550	<i>-0.733</i>	0.611	0.344	-0.092	0.309
tan δ at 1Hz for β_1	<i>0.735</i>	<i>0.752</i>	-0.462	<i>-0.735</i>	-0.054	<i>0.849</i>	-0.119	<i>-0.774</i>	-0.397	<i>-0.749</i>
tan δ at 10Hz for β_1	<i>0.728</i>	<i>0.741</i>	-0.448	<i>-0.728</i>	-0.066	<i>0.842</i>	-0.128	<i>-0.767</i>	-0.384	<i>-0.741</i>
tan δ at 1Hz for β_2	-0.467	<i>-0.798</i>	<i>0.942</i>	0.467	<i>-0.965</i>	<i>-0.709</i>	<i>-0.851</i>	<i>0.997</i>	<i>0.999</i>	<i>0.998</i>
tan δ at 10Hz for β_2	-0.467	<i>-0.798</i>	<i>0.942</i>	0.467	<i>-0.965</i>	<i>-0.708</i>	<i>-0.852</i>	<i>0.997</i>	<i>0.999</i>	<i>0.998</i>
Goodrich test at 40°C	<i>-0.812</i>	<i>-0.839</i>	0.563	<i>0.812</i>	-0.005	<i>-0.915</i>	0.092	<i>0.801</i>	0.471	<i>0.780</i>
Energy loss during static compression test	<i>-0.954</i>	<i>-0.817</i>	0.416	<i>0.954</i>	0.299	<i>-0.939</i>	0.452	0.492	0.202	0.472
Resilience	<i>0.788</i>	<i>0.840</i>	-0.590	<i>-0.788</i>	0.058	<i>0.904</i>	-0.034	<i>-0.834</i>	-0.513	<i>-0.814</i>

* ψ' and ψ'' are shares of low and high-temperature regions, \overline{M}_n and \overline{M}_n are number-average molecular weights between the junctions in low- and high-temperature regions, $\overline{M}_{n(n)} = \psi'/\overline{M}_n + \psi''/\overline{M}_n$, and K is coefficient of polydispersity.

into the created network of cured rubber as chemical branching junctions, we suppose that their role is limited to changes in concentration of the most thermally stable rubber/carbon black chemisorptive structures and/or polymer/polymer ordered domains and as a result, in changes in cluster type associates both structure and content.

3. Correlation Between Investigated Parameters

In spite of different nature of changes in rubber structure due to introduction of investigated two polymeric additives (CPE or ENR), for cured rubbers with different ratios of NR to such additives, characteristics of topological and molecular structures evaluated by using TMA correlate satisfactory with mechanical properties measured at static and

dynamic conditions (Table 6 and 7). It was also noticed that strength of correlation (in italic are given values ≥ 0.7) depends on which characteristics have been compared. This supports our previous conclusion about usability of the TMA for studies on some of the reasons for changes in rubber properties. However, due to the limited number of experimental points, some dispersion in coefficients of correlation against their real values should be considered.

V. Conclusions

1. Variation in the mechanical properties of the blend upon addition of polymeric additive (CPE or ENR) are not supposed to arise only from some reorganization in its topological structure.

Table 7. Correlation Coefficients Between Structural and Physical Characteristics of Cured Rubber Based on a Blend of Natural and Epoxidized Natural Rubber*

Correlated value	ψ'	\overline{M}_n	K'	ψ''	\overline{M}_n	K''	ψ'/\overline{M}_n	ψ''/\overline{M}_n	$\psi'/\overline{M}_n + \psi''/\overline{M}_n$	
Elasticity modulus										
M100	-0.741	-0.482	-0.018	0.741	0.653	-0.695	0.727	0.203	-0.206	0.169
M200	-0.804	-0.720	0.324	0.804	0.296	-0.866	0.383	0.575	0.186	0.556
M300	-0.809	-0.641	0.179	0.809	0.489	-0.820	0.587	0.371	-0.006	0.352
M200 - M100	0.429	0.093	0.414	-0.429	-0.875	0.351	-0.872	0.126	0.558	0.166
M200 / M100	-0.836	-0.808	0.477	0.836	0.122	-0.913	0.221	0.716	0.360	0.692
E" at 1Hz for β_1	0.736	0.762	-0.483	-0.736	-0.030	0.854	-0.097	-0.789	-0.419	-0.765
E" at 10Hz for β_1	0.730	0.754	-0.472	-0.730	-0.038	0.848	-0.103	-0.785	-0.410	-0.759
E" at 1Hz for β_2	-0.492	-0.815	0.951	0.492	-0.957	-0.728	-0.836	0.994	1.000	0.995
E" at 10Hz for β_2	-0.489	-0.813	0.950	0.489	-0.958	-0.726	-0.838	0.995	1.000	0.996
Tensile strength	-0.442	-0.054	-0.325	0.442	0.777	-0.207	0.892	-0.546	-0.598	-0.557
Elongation at break	0.737	0.620	-0.209	-0.737	-0.369	0.788	-0.425	-0.532	-0.096	-0.499
Hardness	-0.735	-0.532	0.061	0.735	0.550	-0.733	0.611	0.344	-0.092	0.309
tan δ at 1Hz for β_1	0.735	0.752	-0.462	-0.735	-0.054	0.849	-0.119	-0.774	-0.397	-0.749
tan δ at 10Hz for β_1	0.728	0.741	-0.448	-0.728	-0.066	0.842	-0.128	-0.767	-0.384	-0.741
tan δ at 1Hz for β_2	-0.467	-0.798	0.942	0.467	-0.965	-0.709	-0.851	0.997	0.999	0.998
tan δ at 10Hz for β_2	-0.467	-0.798	0.942	0.467	-0.965	-0.708	-0.852	0.997	0.999	0.998
Goodrich test at 40°C	-0.812	-0.839	0.563	0.812	-0.005	-0.915	0.092	0.801	0.471	0.780
Energy loss during static compression test	-0.954	-0.817	0.416	0.954	0.299	-0.939	0.452	0.492	0.202	0.472
Resilience	0.788	0.840	-0.590	-0.788	0.058	0.904	-0.034	-0.834	-0.513	-0.814

* ψ' and ψ'' are shares of low and high-temperature regions, \overline{M}_n and \overline{M}_n are number-average molecular weights between the junctions in low- and high-temperature regions, $\overline{M}_{n(w)} = \psi'/\overline{M}_n + \psi''/\overline{M}_n$, and K is coefficient of polydispersity.

2. Since macromolecules of CPE are not included into the created network of cured rubber as the chemical branching junctions, we suppose that their role is related to changes in concentration of the most thermally stable rubber/carbon black chemisorptive structures and/or polymer/polymer ordered domains-cluster type associates.

3. For cured rubbers with different ratios of investigated polymeric additives (CPE or ENR) to NR, characteristics of a structure obtained by using TMA correlates with mechanical properties measured at static and dynamic conditions. However, it was noticed that strength of correlation depends on rubber formulation and a fact which characteristics have been compared. These correlation coefficients support our previous preliminary conclu-

sion about usability of the TMA for studies some of the reasons for changes in rubber properties.

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