On the Correlation Between Characteristics of Topological and Molecular Structures and Mechanical Properties of NR/Chlorinated Polyethylene Rubbers

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ABSTRACT: Chlorinated polyethylene (CPE) taken as a modifier for NR rubber compound changes the mechanical properties of their vulcanizates. With the help of a novel thermomechanical methodology it was found that it also influences the structures of both the tested master batches and the vulcanizates. Some characteristics of the structure of NR/CPE rubbers obtained by using thermomechanical analysis (TMA) correlate satisfactorily with their mechanical properties measured at static and dynamic conditions. This supports our previous conclusion about the suitability of TMA to study some of the underlying reasons for changes in rubber properties resulting from rubber formulation, compounding, and processing. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2583–2591, 2003

Key words: rubber; NR/carbon black/CPE blends; structure; mechanical properties; structure–property relations

INTRODUCTION

One of the trends in the polymer industry is to blend two or more polymers, mainly in conventional equipment for rubbers and thermoplastics processing, to achieve a set of properties for specific applications. Quite often, this type of blending leads to new set of properties of polymeric materials, which have specific property advantages over those of the individual blend constituents.

To optimize the formulation of multi-ingredient polymer composites and their compounding technology is a time-consuming and labor-intensive process. To make them more efficient new ideas are needed on how to select characteristics of composite structure that are correlated with the most important usage properties of that composite. One such idea relates to the topological structure with numerous molecular and topological characteristics evaluated from a single thermomechanical curve using thermomechanical analysis (TMA). This concept is based on a simplified model network with physical junctions (creating a pseudo-network or temporary network) and/or chemical junctions (creating a chemical network) and testing of a bulk polymer. The idea of a topological region is introduced. A topological region is understood to be a very complex structure, which is manifested on the thermomechanical curve as a zone that differs from other zones in thermal expansion properties. A structure with two or three amorphous regions, probably interpenetrating, and more ordered segments were found for the polymers under investigation. These regions are assumed to be not divided in space; they represent several types of interactions, all of which coexist in polymers. They differ in transition temperatures up to 200°C and related compactness, which should influence distribution of additives within the polymer matrix. Most likely, they describe some higher-level arrangement than a molecular one. However, despite long-running experimental studies using different techniques, including the swelling method and NMR, this idea until now has yet to be sufficiently proved. Because of this, further investigations are needed to compare the characteristics of molecular and topological structures evaluated according to the mentioned methodology with results obtained by using other methods. Part of such an evaluation is presented in this study.

Polyethylene or chlorinated polyethylene (CPE) introduced into rubber compounds influences mechanical properties of cured rubbers.[1-8] In this study, a structure of NR/CPE rubbers was investigated with the help of TMA according to the procedure described elsewhere.[9] Mechanical properties in both static and

TABLE I
Elastomers Used in This Study

Material	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: 300 μm, chlorine content (TGA method): 35.3 wt %

dynamic conditions of such cured compounds were tested to correlate tests results with parameters of topological and molecular structures of rubber described by means of TMA.

EXPERIMENTAL

Materials

For this study, the compound containing 100 phr of NR (grade SMR 5CV) and 50 phr of carbon black grade N330 (Carbex N330 Carbochem Factory, Gliwice, Poland) was used. CPE was added in varying amounts (0, 5, 10, 15, and 20 phr). The amounts of sulfur and N-cyclohexyl-2-benzothiazol sulfenamide (CBS) were not varied with changes of CPE amount, so that all rubber compounds had the same concentration of curatives against summarized NR and CPE content in phr.

The elastomers are described in Table I. Other ingredients of the compound (in phr) were: a softener (aromatic oil: Plastyfikator P3, Silesian Refinery, Poland), 7.3; ZnO (Metallurgic Plant, Bedzin, Poland), 5.0; stearic acid (Nitrogen Plant, Kedzierzyn, Poland), 2.6; 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–Duslin PP (Duslo-Sala, Slovakia), 0.2. Rubber chemicals were standard commercial-grade materials.

Preparation of rubber compounds and vulcanizates

Mixing was carried out in a laboratory Banbury-type internal mixer (Meccaniche Moderne, Italy; 2-L volume) at 40 rpm. The fill factor was 0.85, and at the start of mixing, the chamber was heated to 150°C. The compounding procedure was as follows: loaded into an internal mixer were a raw rubber, additives, and CPE except curatives, after which carbon black and softener were added. The batches were dumped at 160°C. Compounding was finished (introduction of curatives) on the mixing mill (laboratory type with a friction ratio of 1 : 1.04) at a temperature not exceeding 80°C. Total mixing time was 4.5 min.

Test specimens were cured in respective molds in an electrically heated press with a table of 400 × 400 mm at 150°C for an optimum cure time (t_{90}), which was determined by an oscillating disk rheometer (Monsanto R100, St. Louis, MO).

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 procedure is as follows: the testing specimen was put into the measuring cell of the thermostatic chamber. It was frozen without pressing under a scanning rate of about 4°C/min, starting from room temperature usually to −120°C; next, the specimen was stored for 10–15 min to equalize a thermal field within the specimen. To obtain the thermomechanical curve (TMC), the stylus with a stable but small load was moved down to contact the surface of the specimen and the material was heated. For crosslinked polymers, the applied load was directly proportional to the modulus of elasticity.

For dynamic mechanical thermal analysis (DMTA) a Polymer Laboratory (Poole, UK) Analyzer MK III was used. The tests were done in bending mode at a frequencies of 1 and 10 Hz in a range of temperature from −90 to +240°C, at a heating rate of 2°C/min. DMTA software was used for data acquisition by computer.

Attenuated total reflection–infrared (ATR-IR) spectra were recorded in a Bruker spectroscope (Bruker Instruments, Billerica, MA) using the total reflection method and KRS-5 crystal.

Static hysteresis was measured at room temperature (21°C) using an Instron tensile testing machine (Instron Ltd. Corp., High Wycombe Bucks, UK). Loading was performed in 10 cycles running from zero to a maximum loading of 1.8 kN or 1.2 MPa and back to zero at a compression rate of 10 mm/min. Hysteresis loss was measured by subtracting the area under the force–retraction curve from the area under the force–deformation curve. Hysteresis loss ratio was calculated as the ratio of hysteresis loss to the area under the force–deformation curve.

Heat generation and fatigue resistance were tested in a Goodrich-type flexometer (model FR-2, Metallist, Leningrad, Russia) in which the specimen was com-

TABLE II
Influence of CPE on Curing Characteristics at 150°C

Curing characteristic	Content of CPE (phr)				
	0	5	10	15	20
t_2, min	1 min, 38 s	1 min, 23 s	1 min, 23 s	1 min, 30 s	1 min, 30 s
t_{90}, min	2 min, 30 s	2 min, 23 s	2 min, 23 s	2 min, 30 s	2 min, 53 s
M_{90}, dNm	62.5	66.0	66.0	60.0	57.5
M_{max}, dNm	68	71.5	71.5	65.0	62.0

pressed at a frequency of 30 Hz at both room temperature and 40°C. Schob elasticity was measured according to ISO 4662:1986 using rebound resilience tester (Zwick, Germany; model 5103).

Tensile strength, elastic modulus, and elongation at break were measured according to ISO 37:1994 and tear resistance according to ISO 34-1:1994 (an unnicked 90° angle specimen). An Instron 4466 Universal Testing Machine was used to measure these properties.

Aging of the specimens was performed in an air-circulating heating oven operated at 70°C for 144 h according to ISO 188:1998 (model UT6060 Heraceus Instruments GmbH, Hamau, Germany).

RESULTS AND DISCUSSION

Mixing and curing

The mixing torque, which characterizes the blending in the internal mixer, was increased by the addition of 5 phr of CPE, but did not change significantly by further increases in its amount.

CPE slightly influences the curing process by causing some changes in t_2, t_{90}, and rheometric modulus (Table II). Shortening of t_2 as the content of CPE in the rubber compound increases is small and irregular. For t_{90} a substantial extension of this time for rubber compound with 20 phr of CPE was observed. A comparison of the cure–rate indices ($t_{90} - t_2$) indicates that the presence of CPE can cause slower crosslink formation if the CPE is present in sufficiently large proportions.

CPE, which has a lower degree of unsaturation than that of NR, does not participate in the vulcanization reaction and does not become part of the network structure created by sulfidic junctions. Variations in curing characteristics, observed in this study, also imply that it is possible to suppose that during mixing or vulcanization a detachment of Cl^- from CPE molecules occurs. This initiates an uncontrolled thermal dehydrochlorination with an ion-radical mechanism. Stearic acid and ZnO influence this process.[1] This process could be a reason for some uncontrolled reaction between NR and CPE molecules, manifesting itself in compound behavior during curing process, although analysis of ATR-IR spectra did not confirm this.

An increase in CPE content in rubber compounds causes changes, to some extent, in mixing conditions, likely because viscosity and related shear stresses, ductility at compounding conditions, and the resulting continuity of NR and CPE phases all differ substantially.[7] This could be one of the reasons for variations in rubber structure and related rheometric modulus and some other properties discussed below.

Mechanical properties

A systematic decrease in elastic modulus and increase in elongation at break is observed with increase in

TABLE III
Influence of CPE on Properties of Cured Rubber

| Mechanical property	Content of CPE (phr)				
	0	5	10	15	20
Tensile strength, MPa	22.1	21.4	19.2	20.9	19.9
M 100, MPa	4.2	4.0	4.2	3.9	3.5
M 200, MPa	7.2	6.6	6.8	6.2	5.6
M 300, MPa	15.5	13.5	13.9	12.3	10.9
Elongation at break, %	540	590	530	630	650
Oven ageing 7 days, 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 (Goodrich Test)	30.4	33.3	33.5	32.9	34.0
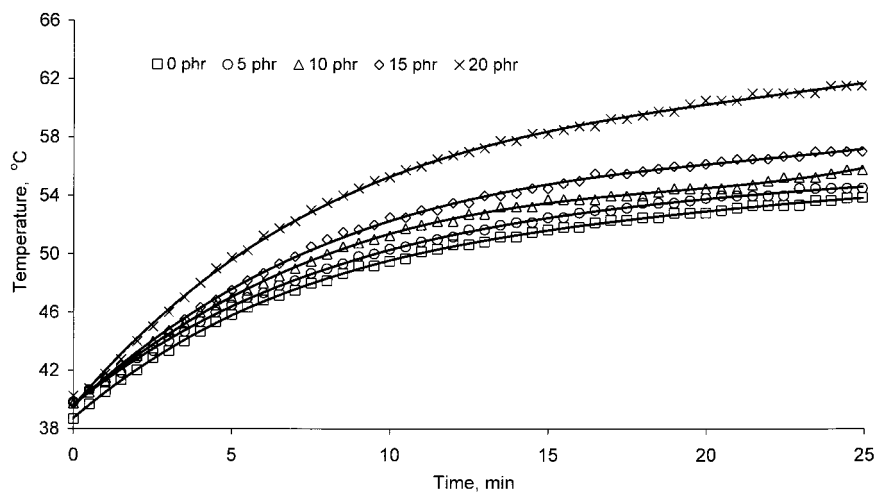
Figure 1 Dependency of heat generation in Goodrich test on CPE content.

CPE content (Table III) because CPE does not participate in a network structure created by sulfidic junctions, as explained above. Simultaneously, a decrease in tensile strength is observed. However, even for 20 phr of CPE, this change is small (<10%).

It is generally accepted that the modulus of elasticity in tension of cured rubbers and Monsanto rheometric modulus M_{90}, measured during determination of curing kinetics, are correlated. Here we observed that for compounds with 5 and 10 phr of CPE these two values do not change in the same way. Decreases of moduli at different standard elongations were observed when changes in M_{90} for compounds with 5 and 10 phr of CPE were random.

The influence of CPE on tear resistance was not observed. Simultaneously, adding even 5 phr of CPE improves the resistance of cured rubber to heat ageing, producing less of a change in tensile strength and elongation at break.

The influence of added CPE (5 phr) on heat generation in Goodrich test (Fig. 1) and hysteresis losses (Fig. 2) is clearly visible.

The vulcanizate of NR filled with carbon black N330, without CPE taken as reference, shows the glass-transition temperature (T_g) at $-30.2°C$ at a frequency of DMTA test 1 Hz. The tan δ, which is a measure of internal friction, is 0.83.

Incorporation of CPE influences the dynamic mechanical properties of the tested vulcanizates. An increase in CPE content produces a small increase in the E' value (Fig. 3), the most visible of which is in the range of temperatures between -20 and $+5°C$. A decrease in the E' value with temperature increase is not sharp. Simultaneously, it is less steep with increasing CPE content.

In addition, with increasing CPE content a decrease in the value of tan δ [Fig. 4(a)] and some shift in T_g toward a lower temperature are observed. The lower
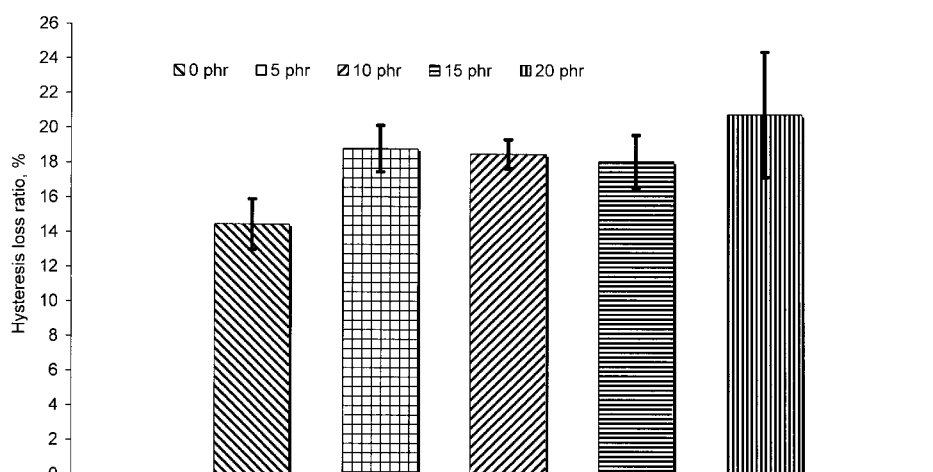

Figure 2 Dependency of hysteresis losses at static compression on CPE content.
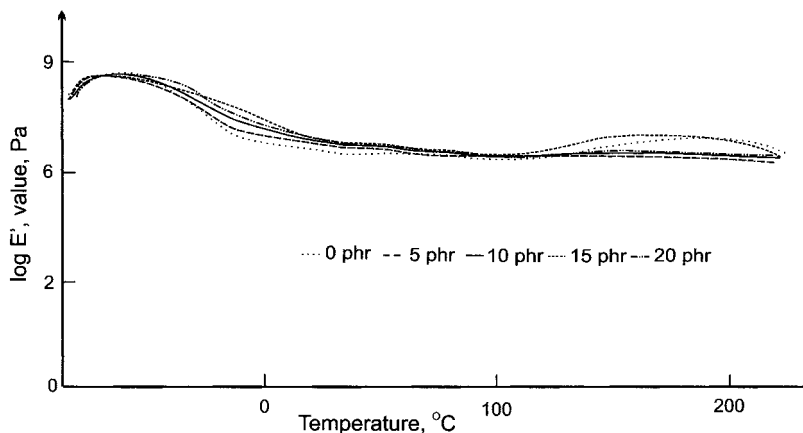
Figure 3 Dependency of E' value at 1 Hz evaluated at bending mode during DMTA test on CPE content.

tan δ values may be attributed to changes in crosslink density. However, in future research the reason for some reduction in T_g with increasing content of CPE should be elucidated.

The transition peak for CPE is not prominent upon addition of 5 phr. When the content of CPE is 10 phr and higher, a second relaxation transition is observed. In the experiment under discussion two relaxation processes are visible when CPE is added in a quantity of 10 phr, further confirming the limited compatibility of the tested polymers. When specimens were tested at

a frequency of 10 Hz [Fig. 4(b)], the value of T_g was higher than that at 1 Hz. This confirms a well-known fact that testing frequency influences the value of T_g.

Changes in the mechanical properties of the cured rubber upon addition of CPE do not arise solely from variations in crosslinking density (Table IV), although it is possible to expect that they should also result from some reorganization in topological structure and/or from changes in concentration of the most thermally stable rubber/carbon black chemosorptive structures.
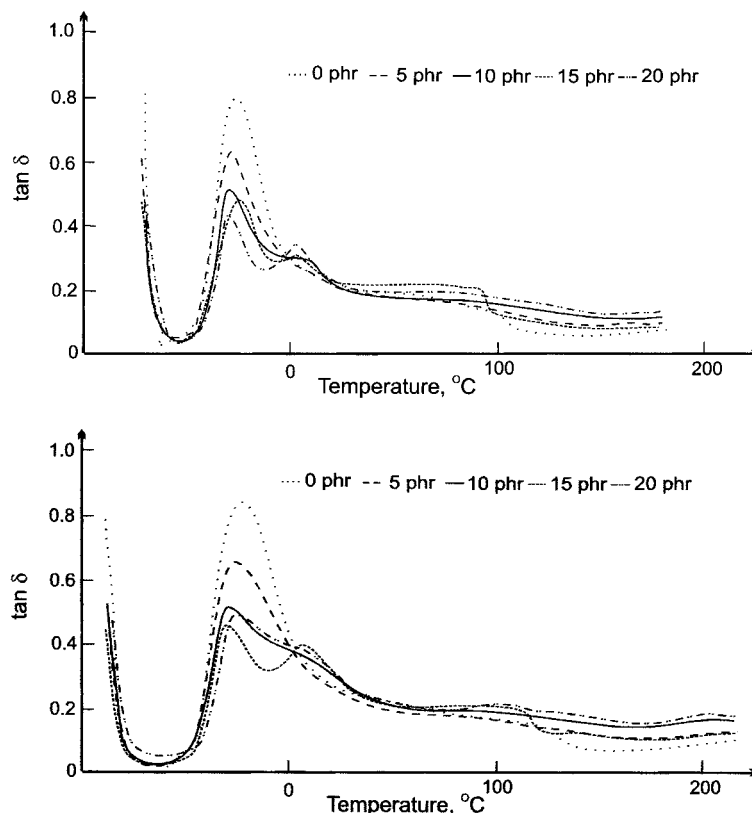

Figure 4 Dependency of loss tangent tan δ at (a) 1 Hz and (b) 10 Hz evaluated at bending mode during DMTA test on CPE content.

TABLE IV
Influence of CPE on Selected Properties of NR/CPE Master Batch

Analyzed parameter[a] (95% confidence limit)	Content of chlorinated polyethylene, phr				
	0	5	10	15	20
Low-temperature region					
T'_g, °C (±3–5)	−67	−71	−62	−67	−64
$\alpha_1 \times 10^5$, deg⁻¹ (±10%)	6.58	6.50	9.50	7.69	10.42
$\alpha_2 \times 10^5$, deg⁻¹ (±10%)	21.74	17.32	21.56	21.04	28.18
$V_f = 3\Delta\alpha T_g$ (±10%)	0.094	0.066	0.076	0.083	0.111
$\bar{M}'_n \times 10^{-3}$ (±10%)	5.00	2.74	0.51	4.15	25.24
$\bar{M}'_w \times 10^{-3}$ (±10%)	6.62	3.67	0.65	5.37	32.7
K (±10%)	1.33	1.34	1.27	1.29	1.30
φ' (±10%)	0.33	0.24	0.13	0.51	0.59
Intermediate region					
T_g, °C (±3–5)	−15	−32	−39	−46	−47
$\alpha_3 \times 10^5$, deg⁻¹ (±10%)	33.32	−16.81	32.50	21.04	28.18
T_f, °C (±3–5)	—	—	—	8	−15
$\bar{M}''_n \times 10^{-3}$ (±10%)	15.71	11.42	10.24	4.53	33.46
$\bar{M}''_w \times 10^{-3}$ (±10%)	21.64	5.67	13.83	6.13	45.17
K (±10%)	1.38	1.37	1.35	1.35	1.35
φ'' (±10%)	0.60	0.69	0.82	0.49	0.41
High-temperature region[b]					
T_{htt}, °C (±3–5)	—	22	−8	—	—
T'''_m, °C (±3–5)	31	—	—	—	—
T_f, °C (±3–5)	39	34	−5	—	—
ΔT_f, °C (±3–5)	8	12	3	—	—
$\bar{M}'''_n \times 10^{-3}$ (±10%)	5.0	5.6	0.42	—	—
$\alpha_4 \times 10^5$, deg⁻¹ (±10%)	76.92	−16.81	32.50	—	—
φ''' (±10%)	0.07	−0.07	0.05	—	—

[a] K, coefficient of polydispersity; $\bar{M}_n$, the number-average molecular weight; $\bar{M}_w$, the weight-average molecular weight; T_f, temperature of the beginning of molecular flow; T_g, the glass-transition temperature; T_{htt}, temperature of the high-temperature transition; T_m, temperature of the beginning of melting process; V_f, the free volume; α_1, the coefficient of linear thermal expansion in a glassy state; α_2, the coefficient of linear thermal expansion in a high-elastic state, low-temperature region, α_3, the coefficient of linear thermal expansion in a high-elastic state, intermediate-temperature region; α_4, the coefficient of linear thermal expansion in a high-elastic state, high-temperature region; φ', a share of a low-temperature amorphous region; φ'', a share of an intermediate-temperature region; φ''', a share of a high-temperature amorphous region, $\Delta T = T_f - T_m$.
[b] Parameters of a high-temperature region correspond to a glassy state for compound without CPE.

Observed trends of changes in rubber properties agree with literature data. Because of this, they could be used for comparison with characteristics of rubber structures.

Topological and molecular characteristics

An NR master batch has a semicrystalline complex structure, well known from numerous studies, which was also observed by our TMA investigations. Here, one could expect that the high-temperature region may act like some networking junctions of low-temperature regions. Some molecular and topological characteristics of a structure of NR filled with carbon black N330 rubber compound were described earlier.[10]

We also tested NR/BR (70 : 30 wt %) vulcanizates filled with the same carbon black.[11] Formulations of those cured rubbers also contained sulfur and CBS as a curing system. Separation of their topological structure into low- and high-temperature regions was visible after 20 min of curing.

The 1,4-*trans* isomer present in neat NR, which has a much higher interaction energy than that for 1,4-*cis* isomer, could also be preserved after introduction of the curing system and after the vulcanization process, although its concentration can change. If it is true, it is reasonable to accept that the 1,4-*trans* fraction of the rubber influences the formation of thermally stable cluster-type associates. It means that such cured rubbers have to be characterized by at least two topological regions resulting from differences in interaction energies and differences in structures of the chemical network. We observed that this rubber has two topological regions, as expected.

If the assumptions formulated above are true, the rubber network in a low-temperature region could be arranged in such a manner that its branching junctions result 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 structures under the influence of both thermal energy and

stress, what are well-known facts from kinetics of the curing and aging processes, and kinetics of the stress relaxation process.

In the current investigation, when polar CPE was introduced into an NR compound, one should expect its influence on formation of the physical network structure, particularly in cluster-type associates acting as additional junctions. With the help of TMA it was found that introduction of CPE to the tested filled rubber compound influences the dynamics of forming its molecular and topological structures. Figure 5 and the data of Table IV show the dynamic of formation of topological regions content in a master batch. There is a clear tendency of transformation of initial topological structure that has three regions to a structure that has two regions as the content of the modifier increases. Adding more than 10 phr CPE rapidly reduces the weight share of an intermediate topological amorphous region and causes the growth of a portion of a low-temperature topological region. The number-average molecular weights of the chain fragments between the junctions in a pseudo-network of low-temperature and intermediate-temperature topological regions have minimum values at 10 and 15 phr of CPE, respectively (Fig. 6).

As expected, introduction of CPE to the tested rubber compound also changes the dynamic of forming the molecular and topological structures of vulcanizates (Table V). However, here this influence is not so visible as for the master batch. Because macromolecules of CPE are not included in the created network of cured rubber as chemical branching junctions (the conclusion from IR spectra), we suppose that their role is limited to changes in concentration of the most thermally stable rubber/carbon black chemosorptive structures and/or polymer/polymer ordered domains
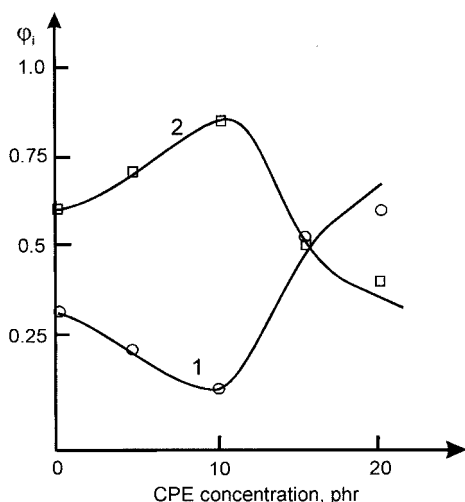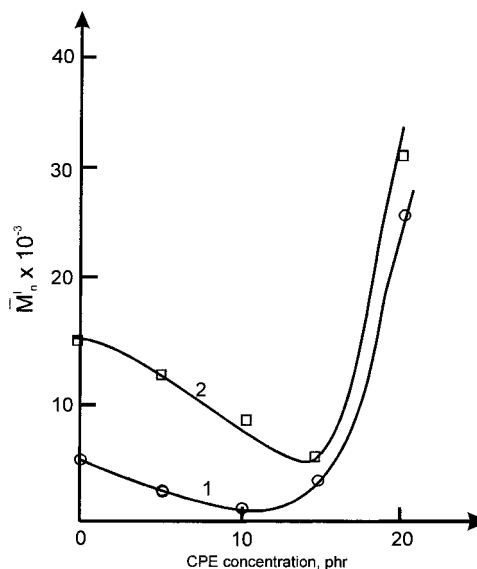

Figure 6 Dependency of the number-average molecular weight of the chain fragments between the junctions of a pseudo-network of (1) low-temperature and (2) intermediate-temperature regions in the tested master batch on CPE content.

and, as a result, in changes in cluster-type associates of both structure and content.

Correlation between investigated parameters

For cured rubbers with different ratios of CPE to NR (being incompatible and not reacting with each other's polymers), some characteristics of a structure obtained by using TMA correlate satisfactorily with mechanical properties measured at static and dynamic conditions (Table VI; magnitudes > 0.7 are given in bold letters). It was also noticed that the strength of correlation depends on which characteristics have been compared. These results support our previous preliminary conclusion[12,13] about the suitability of TMA to study some of the underlying reasons for changes in rubber properties, but formulated after discussion of characteristics of NR/ENR (compatible and co-crosslinkable polymers) cured rubber with another structure of the network than that in rubber in the present investigation. However, because of the limited number of experimental points, some dispersion in evaluated coefficients of correlation against values expected for larger amounts of experimental data should be considered.

Figure 5 Dependency of a share of (1) low-temperature and (2) intermediate regions in a tested master batch on CPE content.

CONCLUSIONS

1. Changes in the mechanical properties of the blend upon addition of CPE do not arise solely from some reorganization in its topological structure.

TABLE V
Influence of CPE on Properties of NR/CPE/Carbon Black Vulcanizates

Analyzed parameters[a] (95% confidence limit)	Content of chlorinated polyethylene, phr				
	0	5	10	15	20
Low-temperature region					
T'_g, °C (±3–5)	−69	−64	−67	−65	−64
$\alpha_1 \times 10^5$, deg^{-1} (±10%)	5.75	7.40	4.65	6.37	3.74
$\alpha_2 \times 10^5$, deg^{-1} (±10%)	27.40	27.78	27.40	28.57	22.22
$V_f = \Delta\alpha T_g$ (±10%)	0.132	0.128	0.139	0.139	0.116
$\bar{M}'_n \times 10^{-3}$ (±10%)	6.42	7.09	6.85	7.72	10.24
$\bar{M}'_w \times 10^{-3}$ (±10%)	10.34	11.82	11.64	13.24	16.99
K (±10%)	1.61	1.67	1.70	1.72	1.66
T_∞, °C (±3–5)	54	86	82	87	71
$\nu_c \times 10^4$, mol/cm^3 (±10%)	1.43	1.30	1.34	1.19	0.90
High-temperature region					
T_{htt}, °C (±3–5)	122	137	131	133	129
$\alpha_3 \times 10^5$, deg^{-1} (±10%)	−35.7	−32.2	−37.0	−35.7	−33.3
$\bar{M}''_n \times 10^{-3}$ (±10%)	20.81	19.25	19.70	20.63	27.14
$\bar{M}''_w \times 10^{-3}$ (±10%)	42.83	37.70	40.09	42.08	54.49
K' (±10%)	2.06	1.96	2.04	2.04	2.01
T_f, °C (±3–5)	232	234	232	241	237
φ''_{top} (±10%)	0.598	0.604	0.596	0.600	0.590
T''_∞, °C (±3–5)	219	215	217	217	218
$\nu_c \times 10^4$, mol/cm^3 (±10%)	0.44	0.48	0.47	0.45	0.34
Swelling in TGF–toluene					
$\nu_Q \times 10^4$, mol/cm^3	0.68	0.48	0.13	0.16	0.19

[a] K, coefficient of polydispersity; $\bar{M}_n$, the number-average molecular weight; $\bar{M}_w$, the weight-average molecular weight; T_f, temperature of the beginning of molecular flow; T_g, the glass-transition temperature; T_{htt}, temperature of the high-temperature transition; T_m, temperature of the beginning of melting process; V_f, the free volume; α_1, the coefficient of linear thermal expansion in a glassy state; α_2, the coefficient of linear thermal-expansion in a high-elastic state, low-temperature region; α_3, the coefficient of linear thermal expansion in a high-elastic state, intermediate-temperature region; α_4, the coefficient of linear thermal expansion in a high-elastic state, high-temperature region; φ', a share of a low-temperature amorphous region; φ'', a share of an intermediate-temperature region; φ''', a share of a high-temperature amorphous region, $\Delta T = T_f - T_m$; φ''_{top}, a share of topological junctions; ν_c, crosslinking density calculated from TMA; ν_Q, crosslinking density calculated from swelling.

2. Because macromolecules of CPE are not included in the created network of cured rubber as the chemical branching junctions, we suppose that their role is also related to changes in concentration of the most thermally stable rubber/carbon black chemosorptive structures and/or poly-

TABLE VI
Correlation Coefficients between Structural and Physical Characteristics of Cured Rubber Based on a Blend of Natural Rubber and Chlorinated Polyethylene[a,b]

Correlated value	φ'	$\bar{M}'_{n(n)}$	K'	φ''	$\bar{M}''_{n(n)}$	K''	$\bar{M}_{n(n)}$	$\varphi'/\bar{M}'_{n(n)}$	$\varphi''/\bar{M}''_{n(n)}$	$\varphi'/\bar{M}'_{n(n)} + \varphi''/\bar{M}''_{n(n)}$
Elasticity modulus										
M 100	0.299	**0.736**	**0.739**	−0.299	0.455	−0.338	0.533	**−0.822**	−0.426	**−0.728**
M 200	0.492	**0.863**	0.594	−0.492	0.643	−0.258	**0.707**	**−0.917**	−0.620	**−0.857**
M 300	−0.370	**−0.786**	**−0.692**	0.370	−0.525	0.311	−0.599	**0.861**	0.498	**0.778**
M 200 − M 100	−0.397	**−0.863**	−0.562	0.397	−0.626	0.368	−0.696	**0.929**	0.594	**0.858**
M 200/M 100	−0.185	−0.646	**−0.804**	0.185	−0.335	0.387	−0.420	**0.746**	0.303	0.634
Tensile strength	−0.582	−0.418	−0.567	0.582	−0.298	−0.031	−0.322	0.408	0.294	0.387
Elongation at break	0.269	**0.834**	0.279	−0.269	0.663	−0.349	**0.722**	**−0.896**	−0.636	**−0.847**
tan δ at 1 Hz for β_1	−0.318	−0.589	**−0.859**	0.318	−0.320	0.122	−0.390	0.670	0.309	0.581
tan δ at 10 Hz for β_1	−0.309	−0.579	**−0.865**	0.309	−0.307	0.130	−0.378	0.661	0.295	0.570
Goodrich test at room temperature	0.278	0.622	0.647	−0.278	0.346	−0.563	0.419	−0.685	−0.296	−0.588
Goodrich test at 40°C	**0.786**	**0.979**	0.220	**−0.786**	**0.907**	−0.088	**0.936**	**−0.963**	**−0.897**	**−0.978**

[a] φ' and φ'' are shares of low- and high-temperature regions; $\bar{M}'_{n(n)}$ and $\bar{M}''_{n(n)}$ are number-average molecular weights between the junctions in low- and high-temperature regions; $\bar{M}_{n(n)} = \varphi'\bar{M}'_{n(n)} + \varphi''\bar{M}''_{n(n)}$; K is the coefficient of polydispersity; M 100, M 200, and M 300 are elasticity modulus at 100, 200, and 300% elongation, respectively.
[b] Values > 0.7 are in **bold type.**

mer/polymer ordered domains and, as a result, in changes in both structure and content cluster-type associates.

3. For cured rubbers with different ratios of CPE to NR, some characteristics of a structure obtained by using TMA correlate with the mechanical properties measured at static and dynamic conditions. The strength of correlation depends on which characteristics have been compared. This supports our previous conclusion about the suitability of TMA to study some of the underlying reasons for changes in rubber properties.

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