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THE ASSESSMENT OF THERMAL STABILITY OF ELASTOMERIC BLENDS OF NR AND SBR LATEX BY USING THE IR SPECTROSCOPY

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Abstract. *All known polymeric materials are more or less subject to degradation. A knowledge of stability of polymeric materials is essential for their optimum treatment and application. For this purpose the testing of degradation and stabilization of polymers is an integral part of the science of polymers and polymeric engineering.*

The anticipation and following of the process of degradation in pure model polymeric composition is relatively simple, whereas in practice this problem is more complex in polymeric mixtures due to the system complexity.

Elastomeric blends of natural latices (NR) and styrene-butadiene rubber (SBR) rubber served as an example to test the influence of thermo-oxidative destruction on physical and mechanical properties of these blends. In connection with this, chemical changes were identified by using the IR spectroscopy.

Key words: *The latices of natural rubber, the latices of styrene-butadiene rubber, blends, mechanical properties, the IR spectroscopy, thermo-oxidative destruction*

1. INTRODUCTION

The term degradation of macromolecules means change in physical properties of polymer caused by chemical reactions of opening and/or creating bonds in the basic and/or lateral chain of macromolecules. Degradation, as such, is not necessarily an unwanted process. In some cases, depending on the goal, the making and/or opening of chemical bonds can be a desire and quantization of these processes is one of the most important tasks in polymer structuring. Whereas the anticipation of degradation processes in pure, structurally and chemically well-defined polymers is possible, in polymer compounds with a number of ingredients this anticipation is a complex problem.

The blending of rubbers in the stage of latex in this context, due to specific colloidal

dispersive nature, is a particular problem.

In the stage of latex compound preparation, because of applied shearing forces, according to some authors [3], "when the content of SBR in a compound is less than or equals 50%, the domains of SBR sustain agglomeration, and then the so-called SBR microfloculation occurs."

Keeping in mind that, in the stage of compound preparation, it is practically impossible to avoid shearing forces, the agglomeration, will unavoidably occur. That is why the phase homogeneity of latex mixtures is not to be expected, regardless of the satisfaction of other requirements of miscibility on the molecular level (solubility parameter, a similar chemical structure etc).

This idea about morphological structure induces us to infer that mechanical properties of latex mixtures are very dependent on the manner of phase coupling, that is on the processes occurring on the interface.

Some authors [5] think that an entirely new phase, with a significantly changed level of structure, is being formed on the interface. This phase is generated by co-vulcanization, segmental diffusion and segment intertwining in the stage of entanglement.

This fact shows that destructive processes of blends cannot have additive properties and that the behavior of blends cannot be predicted on the basis of the behaviour of pure components. Also the chemical processes which occur on the interface during, destruction play.

2. EXPERIMENTAL

2.1. Materials

The materials used during the operation are the following: centrifuged NR latex of 60% (Revultex, Malezia) and carboxylic styrene butadiene latex with different content of butadiene (28%; 44%; 72%), Revinex 30B40, Revinex 91Y40 and Revinex 76D41, Produced by "YUGOLATEX" Čačak (Table 1). Sulphur, ZnO and Zinc Diethyl Dithiocarbonate are commercial products and are used as a 50% water dispersion.

Table 1. The properties of carboxylic SBR latex

Type of latex	REVINEX 30B40	REVINEX 91Y40	REVINEX 76D41
Average diameter of particles (nm)	210	210	210
Content of dry matter (%)	50	50	50
Density (kg/m ³)	1020	1010	970
Viscosity (Pax3)	125	135	135
Surface stress	45	50	38
pH	7.5 – 8.0	8.0	8.5 – 9.0

The formulations of latex mixtures are given in Table 2. Index following a determined letter mark refers to volume ratio of up to 100 in relation to another component

Table 2. Formulation of latex compounds

Type of compound	N ₁₀₀	NA ₁₀	NA ₂₀	NA ₃₀	NA ₅₀	NA ₈₀	NA ₁₀₀	NB ₁₀	NB ₂₀	NB ₃₀	NB ₅₀	NB ₈₀	NB ₁₀₀	NC ₁₀	NC ₂₀	NC ₃₀	NC ₅₀	NC ₈₀	NC ₁₀₀
NR latex	100	90	80	70	50	20	0	90	80	70	50	20	0	90	80	70	50	20	0
REVINEX 30B40		10	20	30	50	80	100												
REVINEX 91Y40								10	20	30	50	80	100						
REVINEX 76d41														10	20	30	50	80	100
Sulphur	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
ZnO	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
ZDEC	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4

2.2. Preparation of samples

Compounds were prepared by well homogenizing component latexes first, and then by adding ingredients. Afterwards mixing was continued. Well homogenized mixtures were let to stand for 24 hours for removal of air bubbles and then they were poured into shallow round dish made of glass on the water bath (50 ± 1 °C), where they were let to stand for 24 hours. The samples in 2 mm thick dishes from which the water had evaporated, were then entangled in the air oven at 110 °C for 30 minutes [4].

Samples for the IR photographing were prepared in an identical way, but the thickness of the film was ~ 0.1 mm. After the entanglement, this film was set in a frame made of alluminium foil with a round opening. Before any treatment (agein, UV radiation), the surplus unreacted ingredients had been extracted by acetone in the Soxhlet apparatus for five hours.

2.3. The determination of mechanical properties

The mechanical properties of vulcanizing ingredients of experimental compounds were determined in accordance with ASTM D418, on standard test samples in the form of an dumbbell oar, at 25 °C and at speed of the moving head of the breaking machine (Monsanto tensometer 10) of 500 mm/min. The hardness was determined by the ASTM 2240 method.

2.4. The IR spectroscopy

IR spectres were photographed on the sample in the form of a membrane (2.2) on the Perkin – Elmer spectrophotometer, the 882 model. The IR photographing was done on the three types of samples:

1. In the original state
2. After the treatment $24^h/70$ °C, where
3. After the treatment $96^h/70$ °C
4. UV radiation 10 hours

The photographing was done successively on the same samples, so that the times of treatments are added.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties of vulcanizing ingredients

The results of physical–mechanical measures before and after ageing are shown in Table 3. The elongation at break and tensile strength of the NR latex vulcanizate ingredients before ageing (630%, 27 Mpa) is greater than that of blend compounds. In Pa compounds with the same ratio of NR/SBR the elongation at break is increased and the tensile strength is coming down with an increase in butadiene content in SBR copolymer.

The modulus of all compounds before ageing are greater than those of pure NR, and they are getting higher with an increase in the portion of SBR in the mixtures, which is most distinct in SBR compounds with the highest content of styrene in SBR copolymer.

Hysteresis losses and the hardness of samples are going up with an increase in the portion of SBR in the mixtures.

The density of vulcanizing ingredients is well aligned with additivity, which is shown by the homogeneity of mixtures and the absence of gas inclusions.

After ageing (24^h/70°C), physical–mechanical properties change significantly. In all samples the elongation at break is smaller after ageing whereas the moduli are bigger.

In all blends the contribution of individual properties of component elastomers is evident. The thermoplastic nature of SBR, which particularly appears in copolymers with higher content of styrene, is more apparent in NR/SBR compounds with higher content of SBR (a decrease in elongation at break, tensile strength, a decrease in hysteresis and hardness), which is the result of the coupling of phases generated from the different kinetics of cure. The SBR phase in the NR matrix here behaves as a filler so that thermooxidative processes play an important role in the phase boundary (the interface).

Table 3. Physical-mechanical properties of vulcanizate before and after ageing

Composition		N ₁₀₀	NA ₁₀	NA ₂₀	NA ₃₀	NA ₅₀	NA ₈₀	NA ₁₀₀	NB ₁₀	NB ₂₀	NB ₃₀	NB ₅₀	NB ₈₀	NB ₁₀₀	NC ₁₀	NC ₂₀	NC ₃₀	NC ₅₀	NC ₈₀	NC ₁₀₀
Properties																				
Elongation at break, (%)	BA	630	567	526	478	358			615	561	494	365	288	181	608	576	491	201	134	
	AA	585	545	506	457	276			575	423	456	344	243	165	570	520	514	379	165	
Change (%)	Δ	-7.1	-3.9	-3.8	-4.4	-23			-6.5	-6.8	-7.7	-5.8	-16	-8.8	-6.3	-9.7	4.7	89	23	
Tensile strength, (MPa)	BA	27	23.7	21.4	17.2	13.2			22.8	20.5	16.4	9.7	9.9	5.2	23.7	19.3	13.8	4.3	3.45	
	AA	25.8	22.8	20.6	17	15.1			24.9	20.9	17.1	11.2	10.2	6.3	23.2	18.2	15.5	7.4	3.1	
Change (%)	Δ	-4.4	-3.9	-3.6	-1.16	14.3			9.21	1.95	4.3	16.1	3.0	22.1	-2.1	-5.7	12.3	72.1	-10.1	
Modulus 100%	BA	1.26	1.85	2.8	4.2	7.6			1.4	1.6	2.0	2.45	3.6	3.6	1.28	1.3	1.53	2.42	2.8	
	AA	1.28	2.0	3.14	4.6	9.3			1.5	1.8	2.4	3.1	4.72	5.1	1.3	1.5	1.55	1.7	1.1	
Change (100%)	Δ	1.6	9.7	13.4	9.0	22.4			6.4	12.3	19.2	24	32.2	41.3	3.9	15.4	1.3	-29.8	-6.1	
Modulus 200%	BA	2	2.96	4.14	5.7	8.9			2.2	2.6	3.4	4.2	6.0		2.0	2.1	2.5	4.3		
	AA	2.1	3.3	4.7	6.4	11.5			2.5	3.15	4.25	5.4	8.1		2.2	2.5	2.5	2.84		
Change (%)	Δ	5	10.5	14	11.4	29.2			11.7	19.8	26.5	29.1	33.7		6.4	18.8	-0.4	-33.3		
Modulus 300%	BA	2.98	4.46	6	7.8	11.3			3.32	4.1	5.3	6.86		3.0	3.19	4.05				
	AA	3.25	4.93	6.9	9				3.9	5.1	7	9		3.4	3.9	3.9	4.6			
Change (%)	Δ	9.1	10.5	15.2	15.4				16.6	23.4	32	31.2		12.6	22	-2.96				
Hardness, Sh A	BA	49	57	66	76	82			50	54	59	65	71	74	47	50	55	60	58	
	AA	48	55	56	82	84			52	54	59	67	75	81	50	50	54	62	58	
Change (ShA)	Δ	-2.04	-3.5	0	7.9	2.4			4	0	0	3.1	5.6	9.5	6.4	0	-1.8	3.3	0	
Stress-strain hysteresis (%)		33.5	50.4	72	71	95.6			33.4	40.4	47	69	76.7	82	35.5	36.6	39	26	22.7	

BA - Before ageing; AA - After ageing

3.2. The IR photographing

The apsorbances which are characteristic of component rubber can be seen on IR photographs. Table 4 shows characteristic absorbances of pure NR and SBR and NR/SBR blends as well as a change of their relative optical density [6]. What was used as the inner standard were the apsorbances on 1378 cm^{-1} coming from symmetrical deformation vibrations (δ_s) the CH_3 group and on 700 cm^{-1} which are attributed to skeleton deformation vibrations ($\Phi_{\text{C=C}}$) of the benzene ring. [2]

Thermooxidative processes cause a change of band intensity on 1721 cm^{-1} which comes from valence vibrations of the C=O group on $\sim 3300\text{ cm}^{-1}$ which is also attributed to valence vibrations of the O—H bond of hydroperoxide, hydroxide and carboxyl compounds as destruction products.

By comparing the data from Table 4, it can be seen that the growth of relative optical density of absorbances on 1721 cm^{-1} and 3300 cm^{-1} is the most distinct in blends with the highest content of styrene in copolymer SBR and that it declines with an increase in the butadiene content. By the analysis of the UV radiation influence, the most distinct change has been recorded in blends with the highest content of styrene in copolymer SBR and it declines with an increase in the butadiene content, judging by the absorbances on 1721 cm^{-1} and 3300 cm^{-1} .

Table 4. Relative optical densities of characteristic absorbances of the IR spectrum of NR vulcanizing ingredients and SBR mixtures.

Mixture	Relative optical density		D_{1378}	D_{700}	D_{1378}	D_{1721}	D_{3294}	D_{838}	D_{890}	D_{1735}	D_{3024}	D_{3033}	D_{570}	D_{500}	D_{438}
	Regime	D_{1378}													
N ₁₀₀	Unaged	1.18					0.085	0.559	0.109	0.027	0.195	0.048	0.195	0.07	0.212
	Aged 70°C/24 ^h	1.27					0.089	0.564	0.102	0.038	0.181	0.067	0.197	0.063	0
NA ₂₀	Unaged	1.43	1.125	1.27	0.038	0.111	0.603	0.076	0.038	0.126	0.063	0.256	0.08	1.01	
	Aged 70°C/24 ^h	1.404	1.08	1.3	0.057	0.102	0.563	0.067	0.052	0.119	0.092	0.232	0.077	0.0055	
	Aged 70°C/96 ^h	1.435	1.07	1.34	0.11	0.129	0.52	0.058		0.112	0	0.231	0.088	0	
	UV radiation 10 ^h	1.306	1.05	1.24	0.143	0.161	0.522	0.062		0.119	0	0.243	0.099	0	
NB ₂₀	Unaged	1.475	0.942	1.56	0.035	0.107	0.584	0.076	0.038	0.13	0.065	0.235	0.076	0.0248	
	Aged 70°C/24 ^h	1.485	0.927	1.6	0.056	0.098	0.554	0.059		0.106	0	0.233	0.08	0.0258	
	Aged 70°C/96 ^h	1.38	0.903	1.53	0.11	0.13	0.551	0.064		0.116	0	0.233	0.08	0.0258	
	UV radiation 10 ^h	1.386	0.911	1.52	0.125	0.139	0.527	0.061		0.116	0	0.229	0.073	0.0209	
NC ₂₀	Unaged	1.025	0.288	3.55	0.032	0.097	0.542	0.066	0.04	0.122	0.074	0.212	0.077	0.0185	
	Aged 70°C/24 ^h	1.34	0.29	3.56	0.047	0.101	0.54	0.062	0.056	0.115	0.104	0.21	0.075	0.0192	
	Aged 70°C/96 ^h	1.063	0.304	3.5	0.089	0.121	0.53	0.063	0.093	0.119	0.175	0.199	0.086	0.0071	
	UV radiation 10 ^h	1.046	0.292	3.58	0.098	0.131	0.48	0.58	0.105	0.121	0.219	0.201	0.067	0	

4. CONCLUSIONS

1. The presence of the presumed thermooxidative processes as well as their influence on physical-mechanical properties have been recorded.
2. The most apparent influence of thermooxidative processes has been recorded in compounds with the highest NR content.
3. The synergetic effect of blending is the result of phase coupling
4. The IR spectroscopy can be used for a relative assessment of the influence of thermooxidative processes on the destruction of NR and SBR elastomeric compounds.

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OCENA TERMIČKE STABILNOSTI ELASTOMERNIH BLENDI LATEKSA NR I SBR KAUČUKA IR SPEKTROSKOPIJOM

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Svo poznati polimerni materijali u većoj ili manjoj meri podložni su destrukciji. Poznavanje stabilnosti polimernih materijala je neophodno za njihovu optimalnu preradu i primenu. Iz tih razloga ispitivanje degradacije i stabilizacije polimera predstavlja integralni deo nauke o polimerima.

Predviđanje i praćenje procesa degradacije kod čistih modelnih polimernih kompozicija je relativno jednostavno, dok je kod polimernih smeša u praksi taj problem daleko složeniji zbog složenosti sistema.

U radu je na primeru elastomernih blendi lateksa prirodnog (NR) i stiren butadienskog (SBR) ispitan uticaj termooksidativne destrukcije na fizičko-mehanička svojstva ovih blendi a IR spektroskopijom identifikovane hemijske promene u vezi s tim.

Ključne reči: *lateks prirodnog kaučuka, lateks stiren butadienskog kaučuka, blende, mehanička svojstva, IR spektroskopija, termooksidativna destrukcija*