Synthesis and Modification of Fillers with Derivatives of Benzoic Acids

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Summary: The subject of this research work was an effect of liquid crystals on the properties of filled elastomer systems. Both commercially available and own synthesized liquid crystals were used. The elastomer was ethylene-propylene rubber, while precipitated silica and calcium carbonate were used as fillers. The liquid crystals were deposited on the surface of the fillers from solution. Their effect on the mechanical properties of the vulcanizates was studied.

1. Introduction

Liquid crystals (LCs) have attracted a lot of attention and have found wide range of application [1-3]. Thanks to their particular properties (optical and rheological anisotropy) LCs are used for modification of polymers and fillers[4-10]. We have assumed that a liquid crystalline layer adsorbed at a surface of filler and simultaneously grafted onto an elastomer matrix should act as some kind of damping element which would be able to dissipate critical stresses occurring in the system.

Derivatives of benzoic acid exhibit liquid crystalline properties [4].

We have seen a possibility to insert them at the interface with the use of functional groups present in their molecules.

2. Materials

The following derivatives of benzoic acid, Dutral (CO-054(Montedison Co.) as an elastomer, fillers and adhesion promoter were the objects of our studies:

- commercially available product –4-octyloxy benzoic acid (LC_1) (Aldrich Co., purity 98 w.%).Products synthesized at our laboratory: 4-allyloxybenzoic acid(LC_2), 4-(7-octene)oxy benzoic acid(LC_3) and 4-(9-decylene)oxy benzoic acid(LC_4) (all of them purity above 95 w.%).
- fillers - calcium carbonate Socal NZ(Socal Co., specific surface S=20 m^2/g),precipited silica Ultrasil VN3 (Degussa Co., specific surface S=210m^2/g).
- The adhesion promoter was N-2-aminoethyl-3-aminopropyltrimetoxysilane (DAMS, Unisil Co.)

3. Experimental

Synthesis of the LCs compounds was performed on the basis of Williamson's reaction of esters formation [4]. Spectroscopic data of the products, the Rf coefficients, and

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yields values are given in Table 1. The samples analyzed with the use of Avance DPX-250(250MHz) aparatus with DMSO-D_6 or $CDCl_3$ solutions. IR spectra were recorded with the BioRAD FTS spectrometer. TLC chromatograms were prepared with the DC-Aurolle Kieselgel's plate (F_{254} Merck Co.) .

The calcium carbonate and the silica were coated with the LC compounds from dioxane solutions (the silica had been earlier covered with a monolayer of N-2-aminoetyl-3-aminopropyl-trimetoxy-silane (DAMS).

Table 1. Spectroscopic data, Rf coefficient of products and yield of reactions.

	Rf ($CHCL_3$)	**^{1}H NMR δ(ppm)**	**IR**	**Yield [%]**
LC_2	**0,13**	**(DMSO(d_6);TMS): 2.45(s,3H,CH_3) 4.32-4.34 (m,2H,CH_2O),4.97-5.22(m,2H,CH_2=),5.70-5.80(m,1H,HC=),6.86-6.90(m,2Har),8.18-8.22 (m,2Har).**	3340-3600 cm^{-1} (OH), 1712 cm^{-1} (C=O)	**73**
LC_3	**0,13**	**($CDCl_3$;TMS):1.254-1.254 - 1.51(m,7H,-CH_3-$(CH_2)_2$-), 1.76-1.84(m,2H,CH_2) , 2.03-2.176 (m,2H,CH_2),3.99-4.05(t,2H,CH_2O), 4.92-5.05 (m,2H,CH_2=), 5.76-5.87(m,1H,-HC=), 6.91-6.95(m,2Har), 8.02 - 8.08 (m,2Har).**	2950-3164 cm^{-1} (OH), 1703 cm^{-1} (C=O)	**57,6**
LC_4	**0,15**	**($CDCl_3$;TMS):1.38-2.06(m,14H,-$(CH_2)_7$-) 4.02 (t,2H,CH_2O),4.92-5.03(m,2H,CH_2=),5.80-5.90(m,1H,-HC=),6.91-6.94(m,2Har),8.02-8.06 (m,2Har).**	2800-3100 cm^{-1} (OH), 1670 cm^{-1} (C=O).	**35,6**

The modified fillers were dried in a vacuum dryer for 48 hours. Rubber mixes with the use of modified fillers were prepared by a two rolling mill. Flow energy was calculated from the curves of viscosity versus temperature. Rheological measurements have been made with the Brabender apparatus at shear rate 10[s^{-1}]

The samples were vulcanized at 160 ^{0} C. Time of vulcanization was determined with the WG-02 rheometer. Vulcanization rate was measured according to the Standard ISO

037. Stress at elongation 300% (σ_{300}), tensile strength (TS) , time of relaxation and elongation at break were measured with Zwick machine (model 1415). Crosslink density was calculated from equilibrium swelling values in toluene and in toluene under ammonia atmosphere. Crosslink density , time of relaxation and mechanical properties of EPM vulcanizates filled with silica or calcium carbonate are given in Table 2-4.

Table 2. Crosslink density and mechanical properties of EPM vulcanizates filled with silica.

LC Content per 30 g of silica	$\nu*10^{-5}$ [mol/cm^3]	$\Delta\nu*10^{-5}$ [mol/cm^3]	M_{min} [dNm]	ΔM. [dNm]	Flow energy [J/molK]	σ_{300}	TS [MPa]	$\varepsilon_{\%}$ [%]
0	**6,42**	**0,51**	**50,8**	**28,3**	**916**	**1,9**	**10,30**	**739**
0,5 LC_1	10,17	1,86	24,0	37,0	712	2,8	10,1	645
1 LC_1	10, 96	2,35	18,2	36,4	700	2,1	10,9	606
3LC_1	11,2	2,9	16,4	35,3	687	1,8	10,8	584
0,5LC_2	3,2	0,3	33,5	52	-	1,73	11	712
1 LC_2	6,5	1	38,7	71	-	1,46	10,2	>1000
3 LC_2	6,8	1,1	41,2	92	-	2,08	8,35	>1000
0,5LC_3	8,92	0,84	42,4	44,7	739	3,3	11,82	688
1LC_3	10, 43	2,09	30,9	53,5	685	3,7	13,87	646
3LC_3	11,49	2,54	23,9	54,4	676	3,8	10,90	566
0,5LC_4	2,3	0,5	34,2	51,3	-	1,54	11,2	750
1LC_4	1,9	0,3	38,2	46	-	1,21	9,4	>1000
3LC_4	3,8	0,3	37	74	-	1,9	6,2	676

ν- crosslink density of the vulcanizates, Δν– decrease in crosslink density under the influence of ammonia, σ_{300}- stress at elongation 300 %, R_r – tensile strength, ε_r – elongation at break.

Table 3. Crosslink density and mechanical properties of EPM vulcanizates filled with calcium carbonate.

LC Content per 30g of chalk	$\nu*10^{-5}$ [mol/cm^3]	$\Delta\nu*10^{-5}$ [mol/cm^3]	M_{min} [dNm]	ΔM [dNm]	σ_{300}	TS [MPa]	$\varepsilon_{\%}$ [%]
0	**6,21**	**0,44**	**21,5**	**60,3**	**1,6**	**2,75**	**653**
1 LC_1	2,06	0,03	20,2	58,8	1,5	2,75	671
2 LC_1	3,74	0,20	14,5	48,1	1,3	2,97	705
4 LC_1	1,98	0,12	8,5	22,5	1,1	3,44	873
1LC_2	7	0,6	38,7	109	2,2	5,85	664
2LC_2	7,5	0,4	33,5	123	3,2	6,07	474
1LC_4	6,8	0,4	43,7	106	2,3	8,00	784
2LC_4	7,2	0,3	36,7	115	2,8	11,7	731

Abbreviations are the same as in table 1.

Table 4. A ratio of relaxation times of elastomers filled with silica or chalk(t_0) to elastomers filled with modified **silica** or chalk (t_m).

LC Content per **30**/40 phr of filler	t_0/t_m
2 LC$_2$	**1,4**
1LC$_3$	**2,6**
1LC$_4$	**1,5**
1LC$_2$	1,1
1LC$_4$	1,26

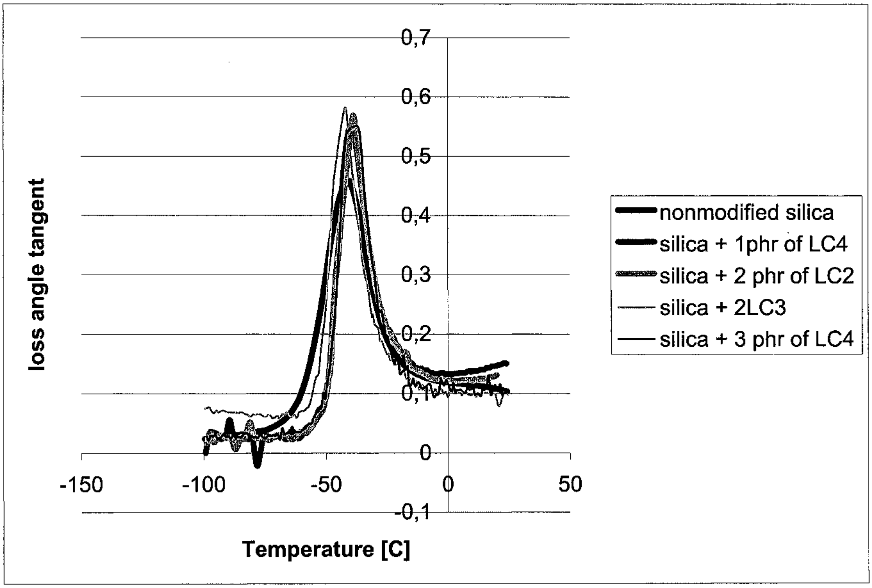

Figure 1. Curves of loss angle tangent versus temperature for elastomers filled with modified and nonmodified silica.

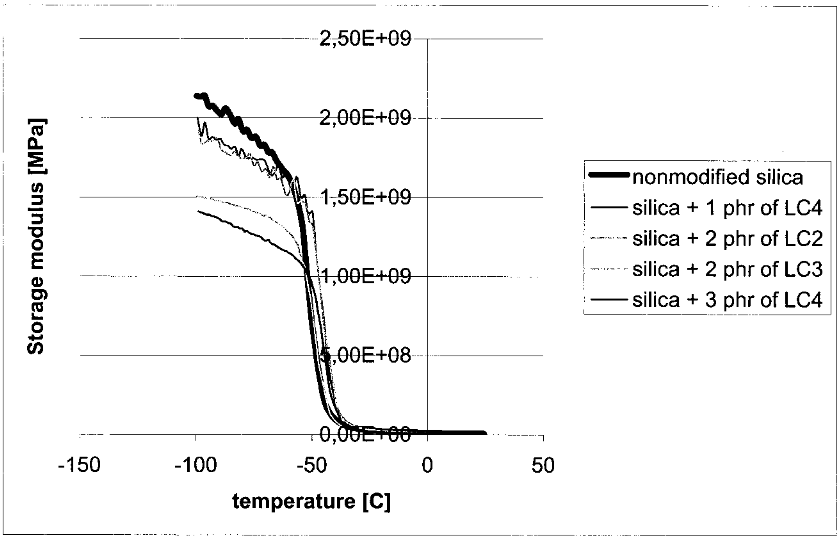

Figure 2. Curves of storage modulus versus temperature for elastomers filled with modified and nonmodified silica.

4.Discussion of Results

An effect of derivatives of benzoic acids on the properties of ethylene-propylene copolymer has been investigated. An increase in the concentration of 4-octyloxy benzoic acid or 4-(7-octene)oxy benzoic acid in elastomers filled with silica leads to a rise in their crosslink density and stress at 300% elongation.

In the case of these two modifiers an interaction between the elastomer and fillers become stronger what is confirmed by a change in the crosslink density ($\Delta\nu$). In the case of the elastomer containing fillers modified with 4-allyloxybenzoic acid or 4-(9-decylene)oxy benzoic acid no increase in their crosslink density has been observed. The biggest effect on the tensile strength has been detected for vulcanizates containing fillers modified with 4-(7-octene)oxy benzoic acid.

An increase in the concentration of LC_2 and LC_4 in EPM elastomer filled with chalk causes an increase in its crosslink density and stress at 300% elongation. An increase in the concentration of LCs compounds causes an increase in the tensile strength reaching maximum value for 2 phr of LC_4 compound.

Vulcanizates filled with silica or modified silica have similar glass temperature although a width and height of loss angle tangent peak have been changed as a results of addition of LCs compounds.

The measurements of viscosity versus temperature have shown that LCs seems to plastize the elastomer. They tend to diminish its flow energy. All the vulcanizates has shown lower time of relaxation.

In vulcanizates with LC modified fillers quicker dissipation of stresses takes place which causes increase in their tensile strength.

Conclusion

Application of liquid crystalline substances and particularly, containing functional groups reactive toward a solid phase particles and the elastomer matrix influences positively a activity of fillers. A mechanism of the effect has been proposed.

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