Macromol. Symp. ***194***, *287–294 (2003)*

Modification of Precipitated Calcium Carbonate to Improve Its Activity toward Elastomers

M. Lipińska, M. Zaborski, L. Ślusarski*
Department of Chemistry, Institiut of Polymers, Technical University of Lodz
ul. Stefanowskiego 12/16, 90-924 Łódź, Poland

Summary: Surface area of precipitated calcium carbonate was modified by using difuncional compounds f.e. : hydroxyacids, aminoacids, unsaturated acids, their derivatives and silanes. We observed the influence of the degree of surface coverage ratio of calcium carbonate on the properties of modified filler, particularly its surface free energy. As a result of the modification, the dispersive component of surface energy and its specific interactions parameter S_f decreased. The investigations showed that the modification of calcium carbonate with difuncional compounds increased the adsorption of dibutyl phthalate on its surface. The activity of modified fillers in ethylene-propylene copolymer, butadiene-acrylonitrile copolymer and carboxylated butadiene-acrylonitrile copolymer was studied. We tried to modify $CaCO_3$ by using hydroxyacids and proadhesive silanes substances so that interactions between fillers particles increased. As the result of these modifications the absorption of dibutyl phthalate increased what could indicate a higher tendency to create $CaCO_3$ own structure.

Introduction

Precipitated calcium carbonate (PCC) is widely used as an inactive filler of thermoplastics (polyolefines, polyamides) as well as elastomers. Before incorporation into polymers calcium carbonate is often surface treated to change the basic character of the particles surface induced by the presence of calcium cations on the surface of the calcium carbonate particles [1].

Commonly PCC is modified with higher fatty acids, a traditional reagent is stearic acid [2]. This modification leads to facilitation of dispersion in the polymer non polar matrix [3] as a consequence of the reduction of the calcium carbonate surface energy and of its polarity [3,4]. However, the ability of PCC to form specific interface interactions with hydrocarbon elastomers decreases [5]. The increase in PCC activity was achieved by modifying calcium carbonate with difunctional compounds e.g. aminoacids [6] or unsaturated acids, especially sorbic acid [7]. We studied the effect of the modification of calcium carbonate on the activity of this filler in butadiene-acrylonitrile rubber (NBR) and ethylene-propylene copolymer (EPR). The modifiers of PCC belong to four groups of compounds (unsaturated acids, hydroxyacids, silanes, aminoacids and their derivatives). The influence of the treatment on the mechanical properties of NBR and EPR vulcanized composites and the surface energy of calcium carbonate were investigated.

CCC 1022-1360/00/$ 17,50+.50/0

Materials

The object of our studies was a butadiene-acrylonitrile rubber (NBR, Nipol N-41 produced by Nippon Zeon Co.) containing 21% acrylonitrile and an ethylene-propylene copolymer (EPR, Dutral CO 054 manufactured by Montedison , Ferrara, Italy). NBR was crosslinked by sulfur in presence of mercaptobenzothiazole (MBT), (NBR-100 phr, ZnO-5 phr, St.A.-1 phr, S-2 phr, MBT-3 phr), EPR was crosslinked with dicumyl peroxide (DCP), (EPR-100 phr, DiCuP-5 phr). Rubber mixtures were made by a laboratory two-roll mill at a temperature of approximately 35°C. The conditions of vulcanization were determined by WG-2 rheometer. The samples were vulcanized at 160°C for the time necessary for a torque increase of moment of the rheometer by 90% ($\tau_{0,9}$). Calcium carbonate with a 20m^2/g specific surface produced by Solvay (Socal U1R07, Socal 31) were used as fillers. It was modified with compounds such as hydroxyacids, silanes, unsaturated acids . For this purpose 2 mmol of modifying substance was dissolved in 300ml of solution (ethanol, acetone or distilled water). Then 100g of calcium carbonate was added to the solution and the reagents were mixed for fifteen minutes at room temperature. After this the solution was evaporated at 50°C, the modified filler was washed with distilled water to remove the remaining solvent. The modified calcium carbonate was dried at 100°C in a vacuum oven for 72h. The surface properties of calcium carbonate were determined by inverse gas chromatography (IGC).The IGC measurements at infinite dilution were performed with a commercial equipment (Perkin Elmer) fitted with a flame ionization detector of high sensitivity. The dispersive component of the surface energy of solids (γ_s^D) was calculated according to Dorris and Grey [8] from the retention times of a series of n-alkanes. The contribution of specific interactions was computed using the method proposed by Papirer [9,10].

Results and Discussion

As a result of the modification of precipitated calcium carbonate with aminoacids the dispersive component (γ_s^D) of its surface energy decreased (table 1), but from our studies it follows that the value of this parameter increased for the modification with aminoacid such as phenylalanine. The lowest value of dispersive component of the surface energy was obtained in the case of calcium carbonate modified with aminocapronic acids (γ_s^D = 38.6 mJ/m^2 at 20°C).

Table 1. Surface properties of modified calcium carbonate. Dispersive components of surface energy γ_s^D at 20°C Morphology indexes Im, I^*m and DBP absorption index.

Type of treatment	γ_s^D (mJ/m^2)	Im	I^*m	DBP(g/100g)
Untreated Socal 31	84.2	1.48	1.47	55.4
Aminocapronic acid	38.6	1.86	1.97	70.4
Asparagine	53.9	1.55	1.53	64.8
Arginine	56.7	1.42	1.42	61.3
Lisyne	70.7	1.33	1.38	58.8
Histidine	61.1	1.58	1.49	63.8
Cystine	49.4	1.33	1.50	61.4
Phenylalanine	96.8	0.95	1.08	51.2
Leucine	41.2	0.87	1.12	50.8
Tyrosine	41.2	1.37	1.31	60.5

Im, I^*m - morphology indexes defined as a ratio of retention volume of octane to trimethyl-2,3,4-pentane and dimethyl-2,5-hexane, respectively.

From data compiled in table 2, it appears that the modification of precipitated CC with compounds such as hydroxyacids or silanes decreases in most case the dispersive component γ_s^D of its surface free energy. A different effect (increase of γ_s^D) was observed in case of modification with monoallyl maleate. The lowest value of γ_s^D were obtained for calcium carbonate modified with vinyltrietoxysilane (VES) and monoallyl maleate + VES.

Table 2. Surface properties of modified calcium carbonate. Dispersive components of surface energy γ_s^D at 20°C Morphology indexes Im, I^*m and DBP absorption index.

Type of treatment	γ_s^D (mJ/m^2)	Im	I*m	DBP(g/100g)
untreated Socal U1R07	72.8	1.30	1.43	42.44
monoallyl maleate	104.7	3.47	2.28	51.93
vinyltriethoxysilane VES	49.9	1.30	1.45	46.21
monoallyl maleate + VES	46.9	2.01	1.96	55.41
citric acid	60.7	1.82	1.85	44.20
DAMS	52.5	1.49	1.69	44.11
citric acid + DAMS	66.4	1.81	1.99	52.84

Im, I*m – morphology indexes definied as the ratio of retention volume of octane to trimethyl-2,3,4-pentane and dimethyl-2,5-hexane, respectively.

DAMS - N-2-aminoethyl-3-aminopropyltrimethoxysilane

We have indicated the morphology indexes Im, I*m which provide an information on the roughness of the fillers particles surface (table 1÷2). The highest differences in morphology indexes were observed in case of the calcium carbonate modification by using monoallyl maleate or aminocapronic acid as modifying agents what could suggest that the surface morphology of filler was more irregular and inhomogeneous. The calcium carbonate modified with phenylalanine or leucine characterized lower morphology indexes, in this case the morphology of surface is more homogeneous. The calcium carbonate modifications led in most cases to an increase dibutyl phthalate adsorption (table 1÷2). This effect was the highest for calcium carbonate modified with aminocapronic acid what could suggest that in this way we were able to obtain the filler with the highest degree of porosity and ability to create $CaCO_3$ own structure in elastomer matrix.

We tried to modify $CaCO_3$ by using two of modifing agents (hydroxyacids and proadhesive silanes substances) so that interactions between fillers particles increased. In this case we observe the increase of dibutyl phthalate absorption (table 3). The fillers modified in this way were used in NBR vulcanizates.

Table 3. Values of DBP absorption index (g/100g CC).

Type of treatment (*)	DBPA (g/100g CC)
untreated Socal U1	40.1
3,5-dihydroxybenzoic acid	39.4
3,5-dihydroxybenzoic acid +DAMS	45.3
3,5-dihydroxybenzoic acid + VES	44.2
3,5-dihydroxybenzoic acid + IPS	42.0

(*) concentration of modyfing agents – 0.2 mmole/g CC

DAMS - N-2-aminoethyl-3-aminopropyltrimethoxysilane

VES – vinyltriethoksysilane

IPS - 3-isocyanatepropyltriethoxysilane

Table 4. Crosslink density of NBR vulcanizates filled with CC modified by using aminoacids.

Vulcanizates	$\nu\ 10^5$ [mole/cm^3]	$\Delta\nu\ 10^5$ [mole/cm^3]	$\Delta\nu/\nu$ [%]
Unfilled	5.36	0.23	4.3
Untreated Socal 31	4.55	1.12	24.5
Aminocapronic acid	7.16	1.22	17.1
Asparagine	5.92	1.89	31.9
Arginine	6.06	0.77	12.7
Lisyne	7.20	2.08	28.9
Histidine	5.89	1.06	17.9
Cystine	5.94	1.29	21.7
Phenylalanine	4.98	0.30	5.9
Leucine	6.09	0.02	0.4
Tyrosine	6.24	0.38	6.1

$\nu\ 10^5$ - crosslink density calculated from equilibrum swelling in toluene,

$\Delta\nu\ 10^5$ – decrease of crosslink density under ammonia treatment.

The activity of modified fillers was studied in butadiene-acrylonitrile copolymer (NBR) as well as in ethylene-propylene copolymer (EPM). Calcium carbonate modified by aminoacids increased the crosllink density of NBR vulcanizates (table 4).

Our investigations showed that the modifications of calcium carbonate with different concentration of 3,5-dihydroxybenzoic acid (DHBA) decreased crosslink density of filled NBR vulcanizates (table 5). As the results of application of DAMS as second modifying agent the crosslink density of NBR vulcanizates increased (table 5).

From table 6 it follows that application of silanes as modifing agents decreased crosslink density of NBR vulcanizates.

Table 5. Crosslink density ν 10^5 [mole/cm^3] and decrease of crosslink density under ammonia treatment Δν 10^5 [mole/cm^3] of NBR vulcanizates filled with calcium carbonate modified by 3,5-dihydroxybenzoic acid (#) or 3,5-dihydroxybenzoic acid + DAMS (*).

Concentration of modyfing agents [mmole/g CC]	(#) DHBA ν 10^5 / Δν 10^5 [mole/cm^3]	(*) DHBA + DAMS ν 10^5 / Δν 10^5 [mole/cm^3]
0	5.99 / 1.30	5.99 / 1.30
0.05	5.65 / 1.29	16.77 / 3.24
0.1	4.56 / 0.87	16.13 / 1.35
0.2	4.65 / 1.14	21.11 / 2.20
0.3	4.38 / 1.19	23.59 / 6.43
0.4	5.38 / 1.12	21.91 / 5.53

DAMS - N-2-aminoethyl-3-aminopropyltrimethoxysilane

Table 6. Crosslink density ν 10^5 [mole/cm^3], decrease of crosslink density under ammonia treatment Δν 10^5 [mole/cm^3] and mechanical properties of NBR vulcanizates filled with calcium carbonate modified by 3,5-dihydroxybenzoic acid or 3,5-dihydroxybenzoic acid + silanes.

Vulcanizates	ν 10^5 [mole/cm^3]	Δν 10^5 [mole/cm^3]	σ_{100} MPa	TS MPa	EB %	**W1** (kJ/m^2)	**W5** (kJ/m^2)
unfilled	5.36	0.23	0.93	2.55	446	5.4	2.1
untreated Socal U1	5.99	1.30	1.33	7.62	600	9.9	3.3
3,5-dihydroxybenzoic acid	4.65	1.14	1.11	5.77	689	6.0	2.2
3,5-dihydroxybenzoic acid +DAMS	21.11	2.20	2.24	9.36	330	33.6	2.0
3,5-dihydroxybenzoic acid + VES	9.71	0.85	1.49	5.47	420	5.1	1.5
3,5-dihydroxybenzoic acid + IPS	10.33	0.40	1.64	6.19	360	13.4	2.9

(*) concentration of modifying agents – 0.2 mmole/g CC

DAMS - N-2-aminoethyl-3-aminopropyltrimethoxysilane,VES – vinyltriethoxysilane

IPS - 3-isocyanatepropyltriethoxysilane

σ_{100} – 100% modulus, TS – tensile strength, EB – elongation at break, W1 – hysteresis during 1st strain, W5 - hysteresis during 5th strain

We also studied the strengthening effect of modified fillers by using maleates and vinyl silane in ethylene-propylene copolymer. We observed the increased crosslink density of EPM vulcanizates filled with modified CC. From table 8 it follows that crosslink density decreases considerably under ammonia treatment in the case of the modification with monoallyl maleate and vinyltriethoxysilane. As is shown in table 7 application of DAMS and DHBA as modifing agents caused increase of modulus at 100% and hysteresis in comparision to the modification in which we used only DHBA.

Table 7. Mechanical properties of NBR vulcanizates filled with CC modified by different concentrations (mmole/gCC) of DHBA and DAMS.

vulcanizates	σ_{100} MPa	TS MPa	EB %	**W1** (kJ/m^2)	**W5** (kJ/m^2)
Socal U1	1.33	7.62	600	9.9	3.3
DHBA (0,05)	1.06	5.09	641	6.8	2.2
DHBA (0,05) + DAMS (0,05)	1.80	9.63	463	20.0	1.8
DHBA (0,1)	1.12	7.59	707	7.0	2.6
DHBA (0,1) + DAMS (0,1)	1.83	9.78	427	17.5	2.1
DHBA (0,2)	1.11	5.77	690	6.0	2.2
DHBA (0,2) + DAMS (0,2)	2.62	9.43	301	33.6	2.0
DHBA (0,3)	1.11	5.77	679	6.0	2.1
DHBA (0,3) + DAMS (0,3)	2.08	8.56	386	20.6	2.2
DHBA (0,4)	1.08	5.69	675	6.2	2.2
DHBA (0,4) + DAMS (0,4)	2.28	9.78	356	20.1	1.9

DHBA - 3,5-dihydroxybenzoic acid, DAMS - N-2-aminoethyl-3-aminopropyltrimethoxysilane

σ_{100} – 100% modulus, TS – tensile strength, EB – elongation at break,

W1 – hysteresis during 1st strain, W5 - hysteresis during 5th strain

Calcium carbonate modified by using maleates and silanes containing unsaturated C=C bond was used as a filler in ethylene-propylene copolymer (EPM) crosslinked with dicumyl peroxide. Fillers modified in this way caused increase of modulus 100% and loss histeresis of vulcanizates (table 8).

Table 8. Crosslink density ν 10^5 [mole/cm^3], decrease of crosslink density under ammonia treatment $\Delta\nu$ 10^5 [mole/cm^3] and mechanical properties of EPM vulcanizates filled with modified calcium carbonate.

vulcanizates	ν 10^5 [mole/cm^3]	$\Delta\nu$ 10^5 [mole/cm^3]	σ_{100} MPa	TS MPa	EB %	**W1** (kJ/m^2)	**W5** (kJ/m^2)
unfilled	3.05	0.54	0.70	1.23	357	7.10	2.51
Socal U1R07	4.14	0.13	0.97	2.87	659	8.32	2.20
Monoallyl maleate	11.49	2.31	1.57	6.18	604	13.97	4.11
Monododecane maleate	7.18	0.78	1.41	7.65	805	11.96	4.49
vinyltriethoxysilane	9.56	1.23	1.49	6.85	729	13.82	4.30

σ_{100} – 100% modulus, TS – tensile strength, EB – elongation at break,

W1 – hysteresis during 1st strain, W5 - hysteresis during 5th strain

Conclusion

From the presented results it follows that the modification of precipitated calcium carbonate led to an increase the absorption of dibutyl phthalate on its surface and morphology indexes Im, I^*m of fillers what could indicate higher porosity of filler surface and higher tendency to create $CaCO_3$ own structure The dispersive components of surface free energy (γ_s^D) decreased for the samples modified by hydroxyacids and silanes. This effect was not observed for the samples modified by unsaturated acid such as monoallyl maleate or phenylalanine. In these cases the dispersive components of surface energy (γ_s^D) increased. The modifications also influenced the crosslink density of the vulcanizates. The EPM vulcanizates filled with calcium carbonate modified with monoallyl maleate and vinyl silane were characterized by an increase of the crosslink density. The modifications with aminoacids had the same effect in the case of NBR vulcanizates .

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