

Surface Migration of Carboxylic Acid in Styrene–Butadiene Rubber and Its Tribological Consequences

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ABSTRACT: Surface migration of the carboxylic acids ($C_{10}H_{21}COOH$, $C_{11}H_{23}COOH$, $C_{12}H_{25}COOH$, $C_{15}H_{31}COOH$, $C_{16}H_{33}COOH$, and $C_{17}H_{35}COOH$) in styrene–butadiene rubber (SBR) matrix was investigated together with its influence on tribological properties of the vulcanisates. Macro- and microtribological properties were correlated with properties that come from carboxylic acid addition to the samples. A plastifying effect was characterized by a decrease of the rubber glass transition temperature measured by the DSC method. Thickness of an acid bloom was directly determined from an indentation experiment and estimated from the DSC curve as well as from FTIR reflection spectra. Morphology of the bloom was studied using an AFM technique to characterize topography as well as microroughness of the bloom surface. Macrofriction was studied using block-on-ring tribometer. Microfriction was examined with a Nano Test apparatus, applying ball-on-plate

contact. Despite correlation found between plastification, morphology, and bloom thickness on the one hand, and tribologic properties of the rubber on the other hand, influence of the chain length of carboxylic acids on properties of the samples still needs further qualitative investigation. Tribological properties of SBR modified with carboxylic acids are the result of balance of two opposite effects: plastification of rubber—leading to an increase of friction and lubrication—which causes a decrease of friction of the rubber. Apart from plastifying and lubrication effects microroughness also plays an important role in friction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3368–3376, 2002

Key words: surfaces; rubber; morphology; indentation; atomic force microscopy (AFM)

INTRODUCTION

This article describes the surface migration of various carboxylic acids in a styrene–butadiene rubber (SBR) matrix, morphology of the bloom, and its interactions with the surface layer of the rubber. Structural aspects of carboxylic acids constitution are considered. Tribologic properties of SBR modified with a small amount of the acids are discussed from the point of view of composition and structure of the surface layer of the rubber sample. Despite the fact that phenomenon of rubber friction has been studied extensively for many years, less attention has been paid to the influence of material composition and structure. Usually mechanical aspects of friction are taken into consideration.^{1,2} Friction of elastomers strongly depends on their viscoelastic properties, especially concerning their surface layer.¹ Blooming of low molecular weight addi-

tives onto the surface of vulcanisate is well recognized in rubber technology, and has been already described by many authors.^{3–8} Many articles describe how to protect vulcanisates from the deteriorating action of ozone² or improve the adhesion of rubber mixes.^{6,9} Despite the fact that influence of structure and properties of low molecular weight compounds are discussed, for example, the higher melting point of paraffin the higher their migration rate,¹⁰ the influence of migration (blooming) on tribologic properties of the material is rarely discussed.^{11,12}

The ability of low molecular weight additives to migration in the rubber matrix is recognized as a function of two factors: solubility and diffusion.⁷ If more substance than its solubility limit is added to a rubber mix, an excess could migrate to the surface, forming a bloom. In this case solubility determines the rate of migration. Solubility of low molecular weight compounds in an elastomer matrix is a function of temperature and structure of their molecules. With an increase of temperature the solubility increases slowly stepwise up to the melting point of an additive. In the melting point its solubility increases dramatically.¹³ Structure of low molecular weight compounds strongly influences its solubility in rubber due to in-

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TABLE I
Composition of Rubber Mixes and Their Vulcanization Parameters

Component	Rubber Mix						
	SC	SC11	SC12	SC13	SC16	SC17	SC18
SBR 1500	100	100	100	100	100	100	100
DCP	4	4	4	4	4	4	4
CH ₃ (CH ₂) ₉ COOH	—	4	—	—	—	—	—
CH ₃ (CH ₂) ₁₀ COOH	—	—	4	—	—	—	—
CH ₃ (CH ₂) ₁₁ COOH	—	—	—	4	—	—	—
CH ₃ (CH ₂) ₁₄ COOH	—	—	—	—	4	—	—
CH ₃ (CH ₂) ₁₅ COOH	—	—	—	—	—	4	—
CH ₃ (CH ₂) ₁₆ COOH	—	—	—	—	—	—	4

Parameters of vulcanisation (ISO 3417): 160°C/15 min.

teractions with polymer chain such as hydrogen bonding, solvation, or other specific interactions. A degree of branching is also of great importance. Structure is used to be described by the solubility parameter and polarity of molecule/side groups.¹⁴ Amerongen also mentioned crystallization taking place on the surface as a possible driving force for migration,⁷ but there is no agreement among authors whether crystallization is the driving force or only a result of blooming. Choi found that wax bloom affects migration of antiozonants, probably due to causing disturbance of their crystallization.¹⁵ It seems that the ability of low molecular weight compound to crystallize facilitates its surface migration in amorphous rubber, but above melting temperature of the crystalline phase this effect disappears. The second important factor influencing the rate of migration mentioned above is diffusion, characterizing mobility of molecules together with their solubility in the rubber matrix at defined temperatures. Mobility of the molecules is also temperature dependent, and increases with an increase of temperature.^{7,13} Structure of a molecule determines its mobility in the rubber matrix. Some simple relations have been observed like those where mobility decreases with an increase of molecular weight⁸ and the presence of bulky side groups.¹⁶ Diffusion can also be affected by the presence of fillers. With an increase of a filler content an increase of activation energy of diffusion is observed.¹⁷ Commonly migration of additives is discussed, taking into consideration features of their molecules, i.e., solubility parameter values and mobility as a whole. This approach seems to be oversimplified, because, for example, amphiphilic substances or block copolymers could interact with a polymer matrix in a very specific, complex way.¹⁸

EXPERIMENTAL

Materials

Carboxylic acids R—COOH (where R is: C₁₀H₂₁, C₁₁H₂₃, C₁₂H₂₅, C₁₅H₃₁, C₁₆H₃₃, C₁₇H₃₅—at least of

95% wt purity) were admixed to styrene-butadiene rubber (SBR, Ker 1500, Z. Chem. Oswiecim, Poland) in the amount of 4 phr. Prior to processing the rubber was extracted with boiling acetone (48 h, Soxhlet apparatus) to remove antioxidants and other low molecular weight substances that can affect migration of the acids studied.¹⁵ Mixes were prepared with the laboratory two-roll mill (David Bridge Co.,UK). Each rubber mix was cured with 4 phr of dicumyl peroxide (DCP, 98% wt of purity, Merck-Schuhardt, Germany). The amount of 4 phr of DCP is larger than commonly used, and can result in grafting of carboxylic acids onto SBR macromolecules. However, the high content of the curing agent was necessary to obtain low elasticity of the sample, necessary to prepare very smooth surfaces for AFM study. To be sure that grafting of acids onto SBR chains does not affect acid concentration, the acid was also incorporated into rubber mixes in excess (4 phr). Samples were vulcanized in a steel mold at 160°C during time determined rheometrically (ISO 3417). The following symbols were adapted for the acids (the number of carbon atoms in a molecule): C11, C12, C13, C16, C17, C18, and for rubber mixes containing the adequate acid: SC11, SC12, SC13, SC16, SC17, SC18, respectively. The SC symbol was given to SBR cured with DCP, used as an unmodified reference. Table I contains formulations of rubber mixes and their vulcanization parameters. The acids were examined for thermal stability to be sure that their concentration in vulcanizates was the same as in the rubber mixes. The temperature of 5% mass loss was above 160°C (from 163°C for undecanoic acid to 205°C for stearic acid determined at the heating rate of 10°C/min.), so there is practically no degradation or evaporation of acids from the rubber during vulcanization.

Techniques

FTIR spectroscopy

FTIR spectra were used for determination of kinetic and yield of the surface migration of the carboxylic acids. Rate of migration was calculated as COOH

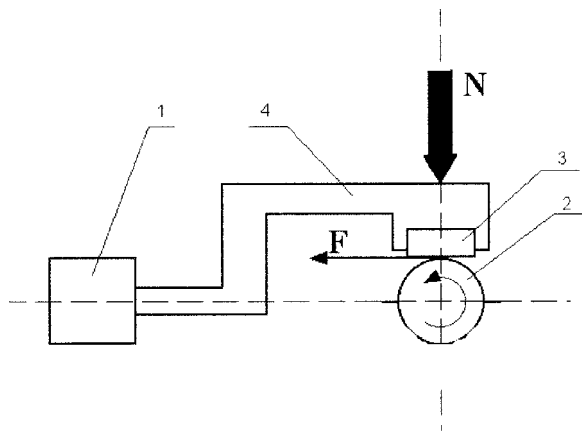


Figure 1 Scheme of the T-05 apparatus: 1—force detector; 2—rubber sample (ring); 3—steel counterface (block); 4—block holder.

group absorption at 1700 cm^{-1} related to the band at 696 cm^{-1} , originating from an aromatic ring in SBR. Experiments were carried out with FTIR spectrometer (BIO-RAD FTS 175C, Germany) equipped with an IRS microscopic accessory (Split-Pea, Harrick Scientific, USA) at ambient temperature, with a resolution of 4 cm^{-1} . Thickness of the surface layer penetrated by the IR beam was calculated according to eq. (1):¹⁹

$$d = \frac{\lambda}{2 \cdot \Pi \cdot n_1 \sqrt{\sin^2 \vartheta - \left(\frac{n_1}{n_2}\right)^2}} \quad (1)$$

where λ is the wavelength, ϑ is the angle between beam and the surface ($\vartheta = 45^\circ$), n_1 is the refraction index of the sample ($n_1 \approx 1.525^{21}$), and n_2 is the refraction index of the Si crystal ($n_2 \approx 3.76$).

The depth of the surface layer being analyzed depends on the absorption bands chosen. Calculated values for the wavelength considered are as follows: (1) 2920 cm^{-1} — $d = 0.4\text{ }\mu\text{m}$; (2) 2850 cm^{-1} — $d = 0.4\text{ }\mu\text{m}$; and (3) 696 cm^{-1} — $d = 1.6\text{ }\mu\text{m}$. It should be mentioned, however, that the calculated depth of penetration represents only c.a. 80% of the particular IR absorption. The rest of signal comes from a deeper layer of the rubber sample.

Macrotribological properties

Friction was determined with the block-on-ring T-05 tribometer (Institute for Terotechnology Radom, Poland). The 35-mm diameter rubber ring rotated against the flat block of stainless steel (Fig. 1). Measurements were carried out with rotational speed of $n = 1.0\text{ rps}$ (equivalent sliding speed was $v = 12\text{ cm/s}$) and normal load varying from 1.4 to 11.4 N, at room temperature (20^{+5}C). Friction force taken for the further calculations was a median value from 70 experi-

mental points obtained during the 2-min test. Accuracy of its determination falls in the range not exceeding 5%. Under experimental conditions the rubber is in a viscoelastic state, so changes in the friction force are caused by deformations of the rubber sample during friction test (stick-slip phenomenon). From the last three calibrations of the T-05 apparatus we find that differences in median of friction force for the same rubber sample is about 5%. Coefficient of friction was calculated according to the Amontons' formula:¹

$$\mu = \frac{T}{N} \quad (2)$$

where T is the friction force, N is the normal load.

Microindentation and microfriction

Microindentation of the surface layer as well as microfriction experiments were performed with a Nano Test 600 (Micromaterials Ltd., UK). Indentation experiments were carried out at ambient temperature (20^{+2}C) using a stainless steel spherical indenter of 1.5-mm diameter and a loading rate of 0.08 mN/s. Thickness of the bloom was calculated from the indentation loading-unloading hysteresis at the bent point (Fig. 2) in a way described below. Drawing line 1 on the plot tangentially to starting points (bloom) and line 2 tangentially to final points (SBR substrate), thickness of a bloom was determined from a crossing point of line 1 and 2. Thickness was taken as an average of three experiments, each performed at different point on the surface of sample. Microfriction experiments were run using the Nano Test apparatus, equipped with a friction attachment, operated with normal load of 5 mN and a sliding speed of 100 nm/s. Friction force between the sample and the stainless

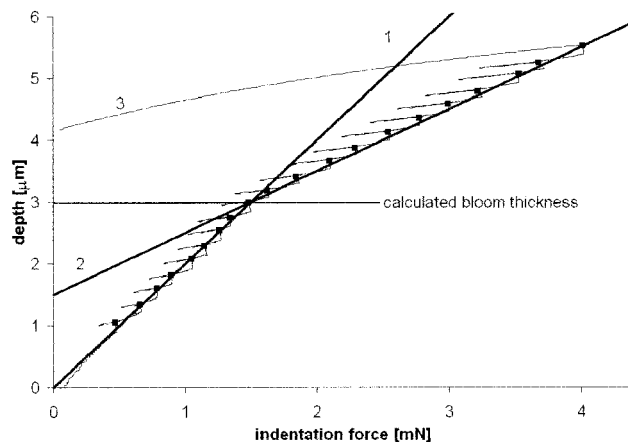


Figure 2 Method for bloom thickness determination from microindentation experiments. Line 1 is tangential to the starting point (bloom); line 2 is tangential to the final points (SBR substrate); line 3 is the unloading curve.

steel indenter (as above) was measured continuously along 500 μm . Data for analysis was taken as an average value of three experiments, each being run on other place of the sample.

Differential scanning calorimetry (DSC)

Thermal properties of the carboxylic acids and rubber samples were determined with DSC (TA Instruments Inc., USA). Rubber samples were prepared 3 days prior to the experiment, well enough to complete blooming of acids on the surface of rubber, as confirmed by the kinetics of migration determined with FTIR. Measurements were carried out under helium atmosphere with a heating/cooling rate of 10°C/min, following the loop: (1) heating from -100 to $+150^\circ\text{C}$ then, (2) cooling to -100°C and again (3) heating to $+150^\circ\text{C}$ and then (4) final cooling to the room temperature. The melting temperature (T_m) and enthalpy of melting (ΔH_m) of pure carboxylic acids as well as thickness of their bloom on the surface of SBR were calculated from the first heating, and any changes in a shape of a curve were not observed in the second one. The glass transition temperature (T_g) of rubber was also determined from the first heating curve. Migration yield was calculated as a ratio of enthalpy of the bloom melting to that of the pure acid, taking into account concentration of the acid in the sample.

Atomic force microscopy (AFM)

Surface morphology of the samples was studied with AFM (Nanoscope III, Digital Instruments, USA). Rubber specimens were prepared by pressing ($p = 50 \text{ g/cm}^2$ of material) a piece of rubber mix at 160°C between two glass plates, for 20 min, and then free cooling to 50°C (heating of an oven was turn off). At 50°C the samples were removed from the oven and stored for another 3 days in closed containers, allowing migration of the carboxylic acids to be completed. The temperature of 50°C for the sample was required to separate the sample from the glass plate very gently, avoiding large deformation of its surface layer, making the surface wavy and disabling AFM experiment. AFM images were made applying the tapping mode. The commercial silicon cantilevers with resonant frequency of 300 kHz were used at a scan frequency of 1 Hz, operating with a height and amplitude scale. AFM images provide both morphological and geometrical information. Values of the root mean square roughness (R_{ms}) of the surface, taken as the standard deviation of the height of an image area, were calculated together with an excess of the bloom surface over the area of image (S_{diff}) and bearing area (B).

TABLE II
Changes of Absorption at 1700 cm^{-1} Related to the Band at 696 cm^{-1} , versus Time after Vulcanization

Time (h)	SC11	SC12	SC16	SC17	SC18
3	0.17	0.26	1.52	1.36	1.17
72	0.28	0.88	4.03	4.04	3.70
384	0.30	3.73	4.24	4.38	4.32

RESULTS AND DISCUSSION

Influence of the carboxylic acid chain length on thickness and morphology of the bloom

The migration phenomenon can be characterized by two factors: yield of migration and the migration rate. Rate of migration, determined from FTIR spectra is given in Table II. Yield of migration is directly connected with the bloom thickness, whereas the migration rate determines morphology of the bloom on the surface of the rubber. The thickness of the bloom was calculated directly from microindentation experiments. Despite this, the bloom thickness was also estimated from FTIR spectra, applying the procedure described above or (2) from DSC curves determining the weight percentage of the acid in a part representing the bloom. All data are compared in Table III. It seems likely that thickness of the bloom can be connected with difference between values of solubility parameters of the carboxylic acids and the elastomer. Solubility parameters of the acids and SBR, calculated according to the method proposed by Hoftyzer and Van Krevelen,¹⁴ are given in Table IV. One can keep in mind, however, that this method does not consider hydrogen bonding. Figure 3 relates a difference of solubility parameters ($\Delta\delta$) between the matrix and the carboxylic acids and number of carbon atoms in the low molecular weight substances. Comparing the results of bloom thickness measurements to the calculated difference in solubility parameters between the rubber matrix and the low molecular weight substances one can expect that yield of migration should increase with an increase of chain length of the acids applied. However, no direct dependence between the difference in solubility parameters and the bloom thickness could be observed (Tables III and IV).

Morphology of the carboxylic acids blooms is strongly dependent on their chain length. Surface microroughness (R_{ms}) generally increases with an increase of number of carbon atoms in the acid molecule (Table III). C17, containing an odd number of carbon atoms in the molecule, does not follow the trend. Probably "odd" and "even" acids exhibit different thermodynamical properties.²⁰ The data for C11, however, following the trend, do not provide the final answer because of a very low bloom thickness being produced in this case. Also, an increase of the surface area (S_{diff}) of the rubber sample shows the same ten-

TABLE III
Thickness of the Bloom of Carboxylic Acids

Method Unit acid	Indentation (μm)	DSC ^b A (%)	FTIR		AFM		
			J (%)		^c (nm) R_{ms}	^c [%] S_{diff}	^d [%] B
			A2850/A700	A2910/A700			
C11	0.02 ^a	0	8	11	8	0.57	71
C12	0.2	1	86	84	35	1.7	25
C16	4.74	65	90	88	227	15	52
C17	4.47	55	92	90	129	13	44
C18	3.42	55	92	91	256	54	71

^a Data from AFM.

^b A—enthalpy of melting of a bloom related to the enthalpy of melting of pure carboxylic acid (% of acid added to rubber that was detected as bloom).

^c S_{diff} —the surface area of a bloom related to the plane area of an image.

^d B—bearing area (%).

J—absorption related to absorption at 696 cm^{-1} .

density as R_{ms} . The surface of the SBR substrate (Fig. 4) is very flat ($R_{\text{ms}} < 5\text{ nm}$, $S_{\text{diff}} < 0.2\%$), and contains holes originated from evaporated products of DCP decomposition. When carboxylic acid is added, its bloom covers the whole surface with a continuous layer. Topography of blooms produced by the acids of shorter backbones (C11 and C12) is very smooth. The blooms form flat crystals of terrace shapes. Topography of the blooms are presented in AFM images (Fig. 4). Figure 4(b) and (c) shows thin layers of the carboxylic acids covering the whole surface of rubber; however, a few bigger crystalline forms could also be recognized. The bloom is built of small round flakes, forming layers. The surface of the bloom produced by palmitic acid is of a mountain-like architecture. Shapes of the hills are round and smooth [Fig. 4(d)]. Heptadecanoic acid also forms mountain-like bloom, but shapes of the hills are in this case sharp and triangular [Fig. 4(e)]. Stearic acid forms a bloom of similar topography to heptadecanoic acid but the hills are higher and bigger [Fig. 4(f)]. The surface morphology of the blooming acids, represented by different topography (AFM), can originate either from their molecular superstructure or can as well be shaped by the rate of migration. To differentiate between the factors affecting the bloom morphology reference samples, prepared by deeping of SBR samples in diluted acetone

solution of carboxylic acids ($\sim 0.001\text{ wt } \%$), were studied. AFM images of the surface of reference samples were made to compare crystals being formed under unperturbed conditions to ones constituting the blooms. It was found that crystals habit of acids is independent of growth conditions. The same morphology of single crystals is observed in both cases. The surface of SBR coated with acids is very smooth, and any mountain-like structures were not observed. The mountain-like morphology of blooms most likely comes from conditions of crystals growth. The more rapid the migration, the higher the microroughness of the bloom on the surface being formed.

Influence of the melting temperature on ability to the surface migration

Blooming yield calculated from the DSC curves can be associated with the melting temperature of low molecular weight compound in the same way as described by Choi for paraffin waxes.¹⁰ The melting temperature and blooming yield for the carboxylic

TABLE IV
Melting Temperature (T_m), Enthalpy of Melting (ΔH_m) and Differences in Solubility Parameters ($\Delta\delta$) of the Acids and SBR, Calculated According to Van Krevelen and Hoftyzer¹⁴

Acid	T_m [$^{\circ}\text{C}$]	ΔH_m [J/g]	$\Delta\delta$ [$\text{J}^{0.5}/\text{cm}^{1.5}$]
C11	28.7	176.3	0.20
C12	45.2	186.4	0.35
C16	61.8	189.1	0.77
C17	61.8	205.2	0.84
C18	55.9	163.4	0.91

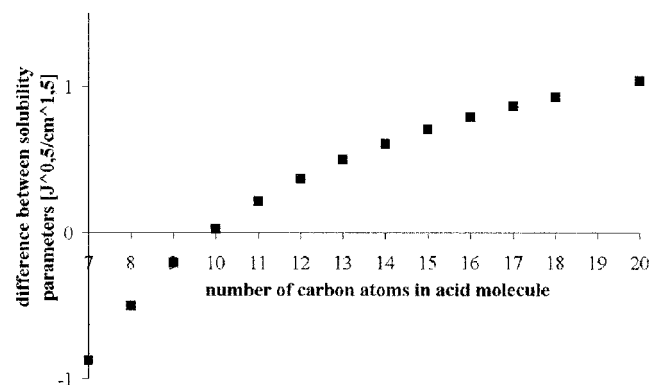


Figure 3 Relation between difference in solubility parameters of SBR and carboxylic acids ($\Delta\delta$), calculated according to Hoftyzer and Van Krevelen¹⁴ and number of carbon atoms in the carboxylic acid molecule.

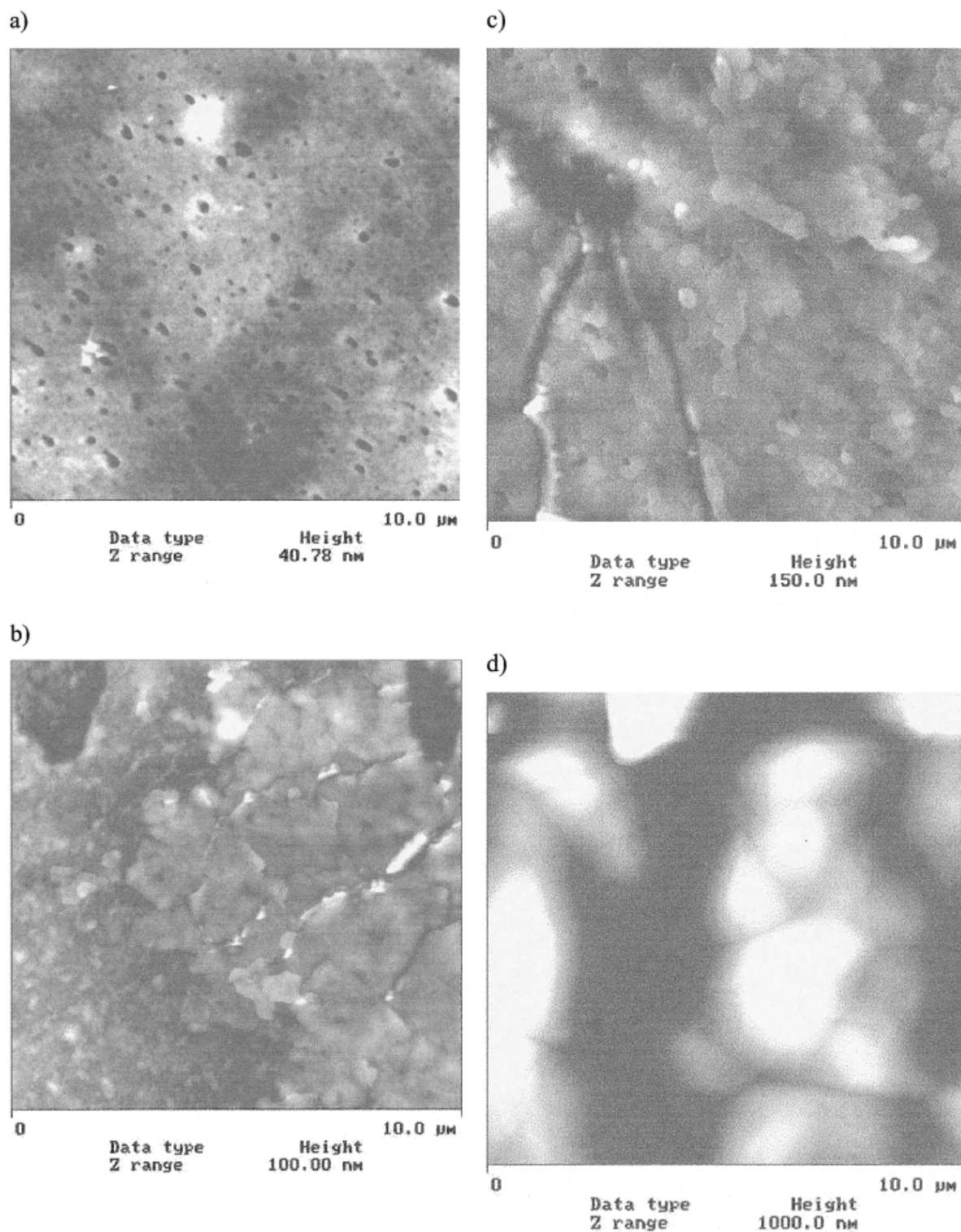


Figure 4 Topography of the surface of the SBR/4 phr of the carboxylic acid system AFM image, tapping mode, scanning rate of 1 Hz. (a) SBR substrate; (b) undecanoic acid (C11) bloom on the SBR substrate; (c) dodecanoic acid (C12) bloom on the SBR substrate; (d) palmitic acid (hexadecanoic acid) (C16) bloom on the SBR substrate; (e) heptadecanoic acid (C17) bloom on the SBR substrate; (f) stearic acid (octadecanoic acid) (C18) bloom on the SBR substrate.

acids studied are compared in Figure 5. Yield of migration depends on the melting temperature; however, character of the dependence has yet to be clari-

fied. Detection of the bloom by the DSC method, due to its dynamic character, requires an adequate difference between the melting temperature of the acid and

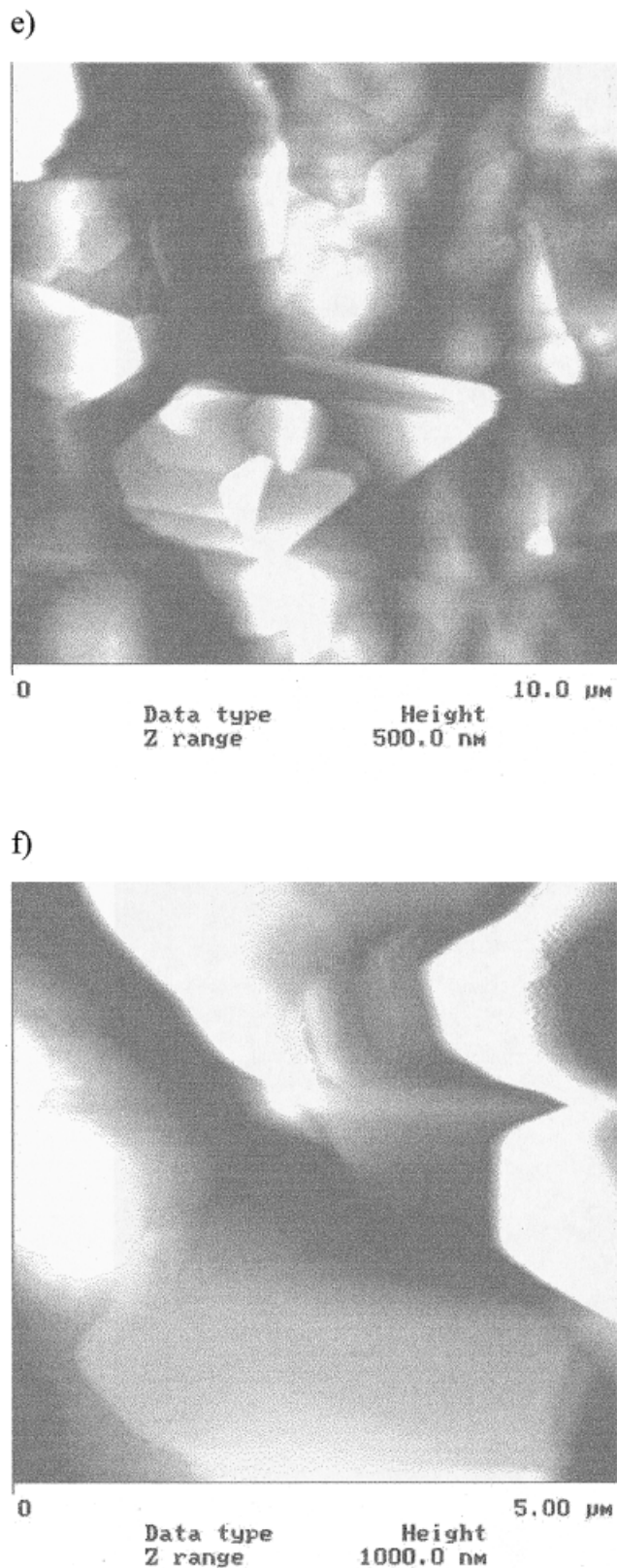


Figure 4 (Continued from the previous page).

the rubber sample (temperature of storing), ΔT . From our experimental experience it follows that under $\Delta T = 15^\circ\text{C}$ any bloom could hardly be detected by DSC.

Despite that, from comparison of solubility parameters of SBR and low molecular weight additives it can be concluded that with an increase of a chain length of the latter its solubility in the matrix decreases, so the migration yield should increase, which has not been confirmed experimentally. The migration yield increases up to 15 carbon atoms in a hydrocarbon rest (C16) and then sharply decreases, resembling previously mentioned melting temperature dependence (Fig. 5). The relation between the migration yield and the melting temperature can be explained by DSC data. Melted acid blooms swell the SBR substrate. After swelling the rubber matrix, carboxylic acids do not have enough time to migrate to the surface during DSC run, so no crystallisation peak was observed in curves representing the first cooling. Consequently, any melting peak was not observed during the second heating. This confirms that liquid acids have better solubility in SBR than the solid ones, making it clear why acids of lower melting temperature migrate with lower yields. In the case of acids of a longer backbone, C16–C18, their dissolved excess was cooled down in the rubber matrix, revealing an additional glass transition, like the effect around 0°C during the second heating. No shift of SBR glass transition in the second heating was detected in comparison to the first heating. This second glass transition probably comes from an overcooled acid phase that was left undissolved in the SBR matrix (Fig. 6). Overcooled carboxylic acids in the rubber matrix can form a separate phase, probably of a micellar structure. At the end of second glass transition a small endothermic effect is visible, probably due to disorientation of micellar structures of an overcooled acid phase.

Influence of the bloom structure on tribologic properties of rubber

Experiments in macroscale

Coefficient of rubber friction depends on the following factors: (1) external parameters, such as normal load,

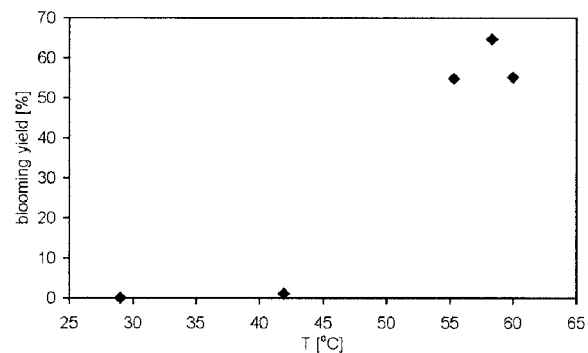


Figure 5 Blooming yield of carboxylic acids correlated with their melting points (DSC).

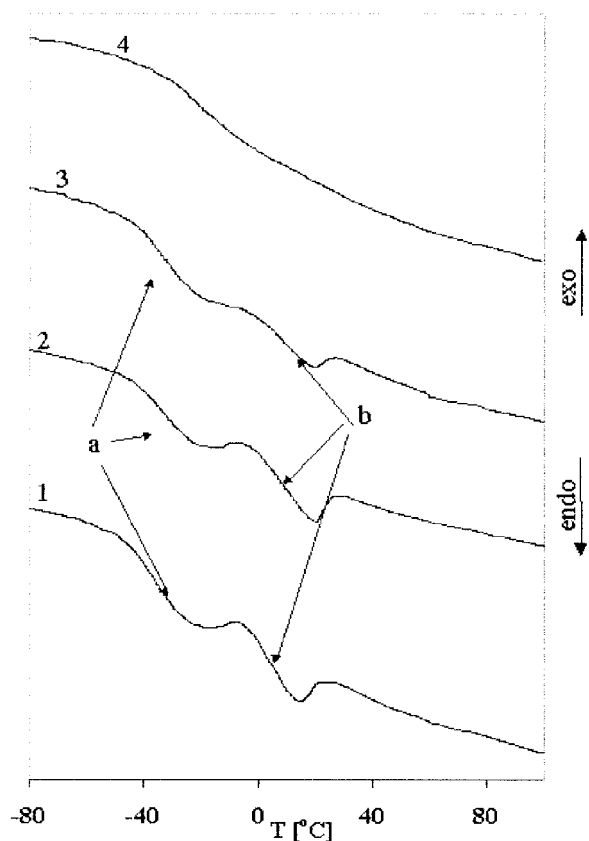


Figure 6 The second heating run (DSC) of SBR samples containing 4 phr of carboxylic acids; 1—C16, 2—C17, 3—C18, 4—SC; (a) the glass transition of the SBR matrix plastified with acids; (b) the glass transition of the over-cooled acid phase.

sliding speed, and type of contact geometry, as well as (2) structural factors, particularly coming from the surface layer¹ and influencing hysteresis and adhesion of a sample. In our studies an effect of plastification, the bloom thickness, and its morphology (topography) were taken into account. Plastifying effect was estimated from DSC curves as an decrease of the glass transition temperature of rubber. Carboxylic acids of shorter backbone cause larger plastification of the SBR substrate than the longer ones, but the relation is not linear Figure 7. Again, C17 exhibits a deviation. Thickness and morphology of the acid blooms discussed earlier (Table III and Fig. 4) stay in fair agreement with their ability to plasticise the rubber. Coefficients of rubber macrofriction measured for various samples are compared in Figure 8. Addition of C11 causes an increase in SBR friction, because of a plastifying effect prevailing over very a smooth surface and very thin lubricating layer of the bloom, covering the rubber sample. C12 forms the thicker bloom, resulting in lower degree of plastification at similar very smooth surface, so friction considerably decreases. C16 forms a thick bloom of high roughness, which, however, is not sharp. A low degree of plastification, together with

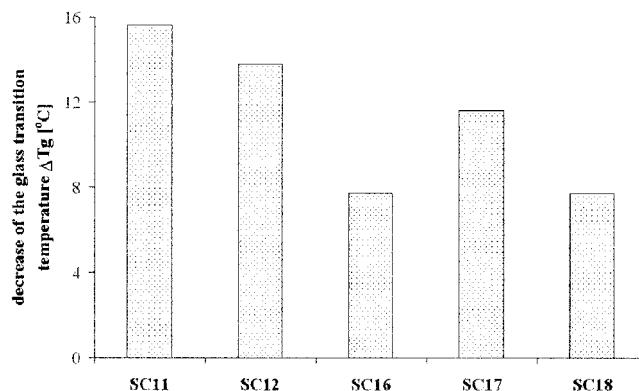


Figure 7 Plastification effect of carboxylic acids towards the SBR substrate, estimated from a decrease in the glass transition temperature; DSC, heating rate dT/dt 10°C/min; sample mass 10 mg.

the smaller contact area (limited to the area occupied by deformed a microrough bloom), makes the coefficient of the friction decrease. C17 and C18 also form thick and rough blooms; however, they are sharper. Sharp microroughness is the origin of an increase of friction, caused by the mechanical interaction of the sample with the counterface. A larger degree of plastification of the SBR substrate by C17 than C16 or C18 is responsible for the higher friction of SBR. A larger degree of plastification detected in the case of C17 is again supposed to originate from an odd number of carbon atoms in the molecule.

Experiments in microscale

In the microtribological experiments deformations accompanied friction are restricted to the thin layer of the material, so the friction force detected in this case originates exclusively from the surface layer of the rubber sample. When the layer of bloom is very thin, however, as in the case of C11 in SBR, the bulk elasticity of the rubber still plays a dominant role in fric-

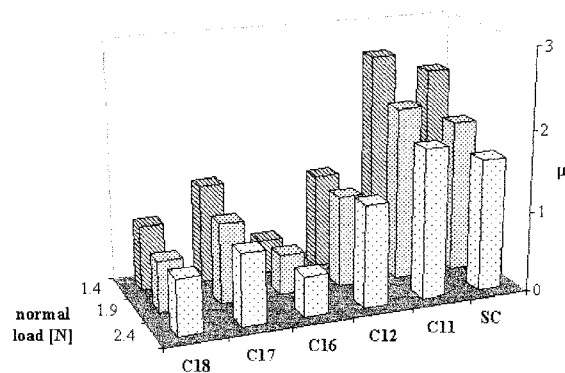


Figure 8 Comparison of the coefficient of friction (μ) measured for SBR modified with various carboxylic acids; experimental conditions: $T = 24^{\circ\pm 5}\text{C}$, macroscale block-on-ring contact (T-05), sliding speed $v = 12$ cm/s.

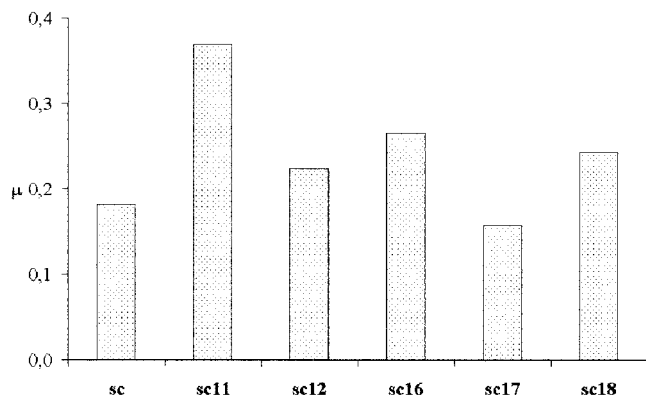


Figure 9 Comparison of microfriction behavior (μ) of SBR modified with various carboxylic acids; experimental parameters: normal load $N = 5$ mN, sliding speed $v = 100$ nm/s, $T = 20^{+2}$ C.

tion, being additionally enhanced by high plastification. It results in the highest friction among the samples studied (Fig. 9). With an increase of the bloom thickness (C12) the friction coefficient decreases, because interactions with SBR substrate becomes weaker and lubrication effect starts to prevail over plastification. In the case of carboxylic acids of a longer backbone (C16–C18), the bloom thickness is so high that contribution of the rubber bulk to friction measurements disappears. Differences in friction observed for SBR modified with palmitic, heptadecanoic, or stearic acid can be, in this case, explained by various microroughness and bearing area of the bloom surface (Table III). The higher and sharper the microroughness and the higher bearing area, the higher the coefficient of the friction.

CONCLUSIONS

The ability of carboxylic acids to migration in SBR matrix and formation of the bloom on the surface depends on solubility of the acids in the rubber. Solubility decreases with an increase of the melting temperature of low molecular weight additive.

An excess of the undissolved carboxylic acid can form a separate phase in the SBR matrix. This phase disappears when migration occurs, and a bloom of the acid is formed.

Topography of the bloom surface is dependent on the size of migrating molecule, but its microroughness increases generally with their backbone length.

Tribologic properties of SBR modified with a fatty acid are dependent on thickness and microroughness of the bloom formed as well as on its plastifying effect towards the matrix. The friction force increases with an increase of the degree of plastification, a decrease of thickness, and an increase of microroughness as well as a bearing area of the bloom formed.

From microtribological data it follows that in the case of a thick bloom (C16–C18) the coefficient of friction is determined by morphology. For carboxylic acids of shorter backbones (C11 and C12), producing much thinner blooms, the higher coefficient of the friction, in comparison to pure SBR, is a consequence of plastification of the rubber substrate. Probably when the bloom thickness stays in its medium range, both morphology and plastification effect would contribute to tribologic behavior of the rubber.

Despite the good correlation found between plastification–lubrication effect and tribologic properties, it is not clear why heptadecanoic acid exhibits so different a migration character as well as plastification effect compared to C16 and C18. The odd number of CH_2 groups in the chain probably produces various crystal morphologies, which can be responsible for the lower bearing area, and finally lowers the coefficient of the friction.

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