The Influence of Stabilizers on Mechanochemical Processes in SBR Rubbers

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ABSTRACT: Mechanochemical processes in commercial and model SBR rubbers containing different stabilizers were investigated. The influence of chemical structure and concentration of stabilizers in the temperature range from 20–170°C and in the presence of air, i.e., under conditions similar to that in industrial processes, were studied. Stabilizers used were diaryl-*p*-phenylene-diamine, alkyl-aryl-*p*-phenylene diamine, polynuclear phenol, aryl-alkyl phenol, and alkyl-alkyl phenol. It was found that mechanochemical processes in SBR rubbers are less developed in the temperature region from 70–130°C, so the influence of stabilizer is less expressive. During increasing temperature (130–170°C) structure and concentration of stabilizers both show a strong influence on type and intensity of mechanochemical processes in SBR rubbers: *p*-phenylene-diamines favor processes of linear degradation, while phenol stabilizers direct them toward branching and crosslinking, which is more expressed in the presence of aryl-substituted phenols than alkyl-substituted phenols. This fact is based on the differences in stability of free stable radicals of *p*-phenylene-diamines, alkyl-substituted phenols and aryl-substituted phenols. The fact that phenol stabilizers are involved in chain degradation as well as in branching and crosslinking processes during rubber processing, can be of high practical importance. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 835–847, 1999

Key words: stabilizers; SBR rubber; chemical structure

INTRODUCTION

Chemical and structural changes of polymers under the influence of mechanical stresses, i.e., mechanochemical processes, are common and very significant in polymer processing and end use.[1–4] These are complex processes involving many reactions that occur by free radical mechanisms. Free radicals are created by dissociation of chain bonds under the parallel influence of mechanical and temperature fields.[5–9] Mechanochemical processes are also important for understanding fatigue, wear, and abrasion processes in rubber products.[10,11]

The first explanation of those processes in rubbers on a purely mechanical basis was provided by Pike and Watson.[12] They proved that mechanical shearing forces destroy chemical C—C bonds and create free macroradicals, capable of reacting with different types of radical acceptors. Further contribution to the research of these processes in SBR rubbers was given by Karmin and Bets.[13] Studying the role of the mechanical action, they ascertained that at lower temperatures (20–30°C)

the processes of linear degradation dominated, while at the temperature of 140°C the mechanochemical process was evident by forming of the crosslinks and branching structure. Slonimskii studied mechanochemical processes in SBR rubbers and their compounds and vulcanizates under various mechanical processing and exploitation conditions.[14,15]

In the case of changing mechanical or temperature rubber processing parameters structure changes may occur, having a negative influence on further behavior in processing and product fatigue and aging.[16]

Keeping in mind that contemporary industrial processes, especially rubber compound mixing, are orientated toward higher speeds, pressures, and temperatures, one should point out that nowadays mechanochemical processes are much more common; however, they are often neglected.

Those trends in processing underline present needs for research on undesirable mechanochemical processes during mixing under real conditions. Factors to be considered in studying these phenomena are multifunctional properties of ingredients in mechanochemical processes, for example, peptizing agents, crosslinking agents, accelerators, and stabilizers.[17,18]

In that sense, stabilizers, having the task to slow down the aging processes in commercial SBR rubbers, can also react with mechanochemically produced macroradials causing structural changes.[19,20]

Dubinskaya, Butyagin, Odincova, Berlin, and Razgon[21–23] examined and compared the reactivity of the primary, secondary, and tertiary amines, as well as phenols and mercaptans with macroradials that were created in frozen solutions of polystyrene, alpha-poly-methyl-styrene and other polymers within the temperature range from −180 to 20°C using ESR spectroscopy. The established order of the amine reactivity decrease was as follows: secondary amines > primary amines > tertiary amines.

As some authors pointed out recently,[24] in the course of the development of antioxidants and mechanisms of antioxidant action, a large amount of literature has accumulated with invaluable information and data. Further studies and detailed information are needed to establish the effect of applied stress on thermo-oxidative stabilities. More time and effort based on the current state of the art in stabilization technology is necessary for better understanding the relations between design of stabilizers and mechanochemical reactions.[24]

The purpose of this article is to study the stabilizer role in mechanochemical processes developed in SBR rubbers during mechanical processing within a wide temperature range and in the presence of air, i.e., under conditions that are close to realistic conditions of the industrial processing of these rubbers.

Special attention has been put on the influence of stabilizer structure (AH) to the behavior of the stable radicals (A$^{\bullet}$) that are produced by neutralization of macroradicals (R$^{\bullet}$) and macroperoxy radicals (ROO$^{\bullet}$) pursuant to the reactions:

$$R^{\bullet} + AH \rightarrow RH + A^{\bullet}$$

$$ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$$

i.e., the influence of the structure of the stable radical (A$^{\bullet}$) on the character and intensity of mechanochemical processes in SBR rubbers during processing.

EXPERIMENTAL

Materials

In this article, commercial SBR rubbers, type YUKA 1500 and YUKA 1502 (FSK Zrenjanin, Yu), obtained by cold emulsion polymerization were used. These two rubber types have chemically identical polymers, but differ in the stabilizer type and concentration. The rubber 1500 contains amine type stabilizer, i.e., N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylene diamine, Vulkanox 4020,[(25a,b)] while the rubber 1502 contains the mixture of alkyl- and aryl-substituted phenols, Stabilizers Y.[(25c,d)] Initial properties and stabilizer content in commercial rubbers are given in Table I.

Apart from the abovementioned commercial rubbers, model rubbers were also used in the experiments. They were prepared starting from latex produced in the same rubber factory. In the laboratory, the following procedure of samples preparations were performed: excess monomer elimination, latex coagulation, rising, grinding, and drying.

In this way, model rubbers contained phenol- and amine-type stabilizers of different structure and concentration. Used stabilizers are the fol-

Table I   Characteristics of Commercial-Grade Rubbers YUKA-1500, YUKA 1502, and Model Rubbers YUKA 1502-No-1 and YUKA 1502-No-2

	Commercial		Model	
Characteristics	YUKA 1500	YUKA 1502	YUKA 1502-No 1	YUKA 1502-No 2
Mooney ML (1 + 4) 100°C	52	52	52	52
Volatile matter content (%)	0.2	0.3	0.25	0.25
Bound styrene (%)	22.8	23.1	23.2	23.2
Salt (%)	0.0	0.1	0.05	0.05
Acid (%)	6.4	6.3	6.3	6.3
Ash (%)	0.05	0.05	0.05	0.05
Extractive matl. cont. (%)	7.2	8.2	7.2	7.7
Lowinox CPL (%)[a]	—	—	0.49	—
Wingstay T (%)[b]	—	—	—	1.18
Bayer Y (%)[c]	—	1.7	—	—
Bayer 4020 (%)[d]	0.41	—	—	—

[a] Lowinox CPL

[b] Wingstay T™

$R_1 R_2 R_3 =$ H, C_4H_9 or C_8H_{17}

[c] Mixture of alkyl and aralkyl-substituted phenols.
[d] N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine.

lowing: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, Vulkanox 4020; mixed diaryl-p-phenylendiamines, Wingstay 200;[25e,f] polynuclear stericaly hindered phenol, Lowinox CPL;[25g,h] mixture of alkyl- and aryl-substituted phenols, Stabilizer Y, butylated octyl phenols, Wingstay T.[25i]

Properties of the model rubbers and content of stabilizer are given in Tables I, II, and III.

Mechanical Processing

Mechanical processing of all rubber samples was performed on a laboratory roll-mill having dimensions of 150 × 300 mm, a clearance of 0.7 mm, and a friction ratio of 1 : 1.2. The speed of the slower roller was 0.4 s^{-1}. The temperature of the roller surface varied from 20 to 170°C, while the duration of the rubber mechanical processing on the rollers was varied within the range from 180 to 900 s. The mass of the processed rubber was 300 g.

Mooney Viscosity Measurements

Monney viscosity of the tested rubbers prior and after mechanical processing was measured by a Mooney viscosimeter produced by Monsanto, according to the standard method: Viscosity and Curing Characteristics of Rubber by Shearing Disc Viscosimeter I.S.O.R. 289.

Determination of the Gel Content in Rubber

The method is based on the sol-fraction dissolving in toluene, and separation from the undissolved gel-fraction by centrifugation. The measured 100 mg of rubber is placed in a 25-mL vessel and

Table II   Characteristics of Model Rubbers YUKA 1502-No3, YUKA 1502-No4, YUKA 1502-No5, YUKA 1502-No6

Characteristics	YUKA 1502-No3	YUKA 1502-No4	YUKA 1502-No5	YUKA 1502-No6
Mooney ML (1 + 4) 100°C	52	53	53	53
Volatile matter content (%)	0.25	0.25	0.25	0.25
Bound styrene (%)	23.2	23.2	23.2	23.2
Salt (%)	0.05	0.05	0.05	0.05
Acid (%)	6.3	6.3	6.3	6.3
Ash (%)	0.05	0.05	0.05	0.05
Extractive matl. cont. (%)	7.8	6.8	8.0	8.0
Lovinox CPL (%)	—	—	—	—
Wingstay T (%)	—	—	—	1.5
Bayer Y (%)	1.25	—	1.5	—
No stabilizer	—	+	—	—

covered with 15 mL of toluene and left for 14 h, shaking it occasionally.

Thereafter, the sample is poured into the centrifuge test tube and processed for about 1 h at 3000 rpm, and then the solution is carefully exhausted by a pipette. The gel residue is then twice again processed in the centrifugal machine with 10 mL of toluene each time, over the 10-min interval. Each time, toluene is removed by a pipette and added to the sol-fraction. That solution is used for determination of the sol-fraction molar mass by viscosity measurement.

The gel residue in the test tube is covered with 10 mL of methanol, and then processed in the centrifugal machine for about 10 min. Methanol is removed by pipette. The gel in the test tube is dried in the vacuum at 90°C, until it reaches constant weight. The gel content is calculated in percentages in relation to the rubber initial mass.

Table III   Characteristics of Model Rubbers YUKA 1502-No7, YUKA 1500-No8, YUKA 1500-No9, and YUKA 1500-No10

Characteristics	YUKA 1502-No7	YUKA 1500-No8	YUKA 1500-No9	YUKA 1500-No10
Mooney ML (1 + 4) 100°C	53	53	53	53
Volatile matter content (%)	0.25	0.25	0.25	0.25
Bound styrene (%)	23.2	23.2	23.2	23.2
Salt (%)	0.05	0.05	0.05	0.05
Acid (%)	6.3	6.3	6.3	6.3
Ash (%)	0.05	0.05	0.05	0.05
Extractive matl. cont. (%)	8.0	7.2	7.4	7.4
Lovinox CPL (%)	1.5	—	—	—
Wingstay 200 (%)*™	—	—	0.6	—
Vulkanox 4020 (%)	—	0.45	—	0.6

[a] Wingstay 200™

R = H or CH$_3$

Figure 1 Dependence of Mooney viscosity on temperature and time of mechanical processing of commercial-grade rubber SBR 1500.

Sol-Fraction Molar Mass Determination

The sol-fraction in toluene is used for determination of the limiting viscosity number so that molar mass of that fraction may be calculated therefrom. Primarily, the sol-fraction is evaporated until dry and its weight measured. Then the toluene solution is prepared, with an initial concentration of about 1%. Measuring of the viscosity of solutions containing different concentrations in toluene is performed in an Ubhelode viscosimeter at 25°C.

To calculate the molar mass from the toluene solution the following equation was used[26]:

Figure 2 Dependence of Mooney viscosity on temperature and time of mechanical processing of commercial-grade rubber SBR 1502.

Table IV Dependence of Mooney Viscosity on Temperature and Time of Mechanical Processing of Commercial-Grade Rubber YUKA 1500

	Mooney Viscosities, ML (1 + 4)				
	Time (s)				
T (°C)	0	120	240	480	960
20	52	45	42	40	38
50	52	47	46	44	42
70	52	48	47	46	43
100	52	49	48	47	46
130	52	49	47	46	44
150	52	49	47	45	43
160	52	47	46	44	42

$$[\eta] = 3.27 \ 10^{-4} M^{0.7}$$

where viscosity is expressed in [dL/g].

Bound styrene was determined according to ASTM |D| 1416.

RESULTS AND DISCUSSION

Experimental results of mechanochemical degradation studies of commercial and model SBR rubbers are presented in Tables IV to XIII, and illustrated in the Figures 1 to 9. For commercial SBR rubbers, YUKA 1500 and YUKA 1502, the results are given in Tables IV and V and Figures 1, 2, and

Table V Dependence of Mooney Viscosity on Temperature and Time of Mechanical Processing of Commercial-Grade Rubber YUKA 1502

	Time (s)				
T (°C)	0	120	240	480	960
20	52	45	43	39	37
50	52	48	46	44	41
70	52	48	46	44	42
100	52	49	48	47	45
130	52	50	49	48	48
150	52	51	51	57	62
160	52	56	63	66	75
170	52	61	72	82	64

Table VI   Dependence of Mooney Viscosity on Temperature and Time of Mechanical Processing of Model Rubber YUKA 1500-No8

T (°C)	Time (s)				
	0	120	240	480	960
20	52	44	42		37
100	52	50	48	44	41
150	52	49	47	44	42

Table VII   Dependence of Mooney Viscosity on Temperature and Time of Mechanical Processing of Model Rubber YUKA 1502-No1

T (°C)	Time (s)				
	0	120	240	480	960
20	52	47	44	41	38
100	52	51	50	49	47
150	52	50	50	52	58

3. Initial properties of the commercial rubbers are given in Table I.

One can observe from Tables IV and V and Figures 1 and 2 a considerable decrease of the Mooney viscosity values with the increase of the time of mechanical processing at constant temperature. This is within the temperature range from 20 to 100°C, and indicates linear degradation of rubber chains. With the temperature decrease the Mooney viscosity decreases more and more rapidly for both commercial rubber types. That negative temperature coefficient is, according to Porter,[19] the basic characteristic of the polymer mechanochemical processes. It is a consequence of the chain scission increase with the temperature decrease, due to the rise of intermolecular cohesive forces.

Macroradicals, formed by mechanocracking, react with the stabilizer incorporated in the rubber and oxygen from the air at the rubber surface. The results are macromolecules of reduced length. It is obvious from the diagrams in Figures 1 and 2 that both types of commercial rubbers react in the same way in the temperature range from 20 to 100°C. But this is not the case when the processing temperature is increased over 130°C.

Figure 3 shows that the commercial rubber types Yuka 1500 and Yuka 1502 behave in a different way at temperatures from 150 to 160°C. For rubber type 1500 the process of linear degradation continues, resulting in macromolecules of reduced length, i.e., the Mooney viscosity decreases. But Mooney viscosity of the rubber type 1502 at the same temperature increases with the rise of the both processing time and temperature. This indicates branching of the macromolecules instead of linear degradation. Because both types of commercial rubbers are of the identical chemical structure (they are obtained by the same pro-

cess), the difference in behavior is produced by the difference of the type and concentration of the stabilizer contained.

To confirm observed phenomena of the stabilizer influence on the mechanochemical processes in SBR rubbers, further testing was performed using model rubbers. Tables VI and VII and Figure 4 illustrate the results for the model rubbers 1500 (No8) and 1502 (No1) containing different stabilizer types of almost the same concentration. The model rubber 1500 (No8) contains 0.45% of the stabilizer *N*-1.3-dimethylbutyl/*N′*-phenyl-*p*-phenylenediamine (see Table III), while the model rubber 1502 (No1) contains 0.49% of the polynuclear phenol stabilizer (see Table I).

Results obtained (see Fig. 4 and Tables VI and VII) confirm that the stabilizer type influences the character of the mechanochemical processes in SBR rubbers. Stabilizers of the amine type produce linear degradation even at higher temperatures. The phenol type stabilizers change the character of the process with the temperature increase, so that linear degradation, which occurs at lower temperatures, turns into the process of macromolecular branching.

The differences in behavior of amine and phenol-type stabilizers in the mechanochemical pro-

Table VIII   Dependence of Mooney Viscosity on the Period of Mechanical Processing of Model Rubbers YUKA 1502-No4, YUKA 1502-No5, and YUKA 1500-No19 at 160°C

Time (s)	1502-No4	1502-No5	1500-No10
0	53	53	53
120	52	58	51
240	51	63	49
480	50	65	47
960	46	68	43

Figure 3 Dependence of Mooney viscosity on temperature and time of mechanical processing of commercial-grade rubbers SBR 1500 and SBR 1502.

cesses are completely in agreement with the general opinion of a higher efficiency of amine-type than phenol-type stabilizers.

The increase of Mooney viscosity implies macromolecular branching in the course of the mechanical processing. The same tendency is present in the model rubber 1502, No5 (1,5% alkyl-aryl phenol) at the temperature increased to 160°C, as shown in Figure 5 and Table VIII. For the model rubber No4 without any stabilizer, the process of linear degradation is characteristic, as well as for the model rubber 1500, No10 (0,6% N-alkyl-N'-phenyl-p-phenylene-diamine). Therefore, it may be concluded that the branching pro-

Figure 4 Dependence of Mooney viscosity on stabilizer type and time of mechanical processing at 150°C of model rubbers SBR 1500-No8 and SBR 1502-No1:(◆) 0.41% N-(1,3-dimethylbutyl)-N'-phenyl-p-phenilene diamine in model SBR 1500-No8; (■) 0.49% polynuclear phenol in model SBR 1502-No1.

Figure 5 Dependence of Mooney viscosity on stabilizer type and time of mechanical processing at 160°C of model rubbers SBR 1502-No4, No5, and SBR 1500-No10: (◆) 0.0 no stabilizer in model SBR 1502-No4; (■) 1.5% alkyl-aryl-phenol in model SBR 1502-No5; (△) 0.6% N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine in model SBR 1500-No10.

cesses are dependent upon the stabilizers of the phenol type.

To establish interrelations between the structure of phenol stabilizers and the character and rate of the mechanochemical processes, the following series of experiments using model rubbers and different phenol stabilizers (different structures) were performed. The results are given in Tables IX, X, XI, and Figures 6 and 7. The properties of the used model rubbers and stabilizers are given in Tables I–III.

It is obvious from the Figures 6 and 7 that, in the case of the phenol-type stabilizers, the phenomenon of branching is dependent upon the stabilizer structure, i.e., upon substituents. Polynuclear phenols cause the biggest changes, and phenols with the most bulky alkyl-substituents (butyl and octyl) the smallest ones.

The diagram, Figure 6 shows that, also with the concentration increase of the same phenol

Table IX Dependence of Mooney Viscosity on Temperature and Time of Mechanical Processing of Model Rubber YUKA 1502-No2

T (°C)	Time (s)				
	0	120	240	480	960
20	52	46	42	40	37
100	52	49	47	46	43
150	52	46	45	45	49

Figure 6 Dependence of Mooney viscosity on phenol stabilizer structure and time of mechanical processing at 150°C of model rubbers SBR 1502-No2 and No3 and commercial rubber SBR 1502: (△) 1.18% alkyl-alkyl-phenol in model SBR 1502-No2; (■) 1.25% alkyl-aryl-phenol in model SBR 1502-No3; (◆) 1.7% alkyl-aryl-phenol in SBR 1502.

type stabilizer, the intensity of the branching process rises.

The results in Table XI and Figure 7 show the change of Mooney viscosity of the model rubber SBR 1502 in the course of mechanical processing at 170°C. These samples have phenol type stabilizers of the same concentration (1.5%) but with different structures. The first stabilizer is polynuclear phenol, the second stabilizer has aryl- and alkyl substituents, while the third one has long alkyl substituents (butyl and octyl). It is obvious that the branching processes at that temperature are faster than at 150 and 160°C (see Figs. 3, 5, and 6). Another important difference is that the Mooney viscosity curves exhibit maxima at that temperature. The viscosity decrease after the maximum value indicates destruction of the previously formed structures. The possible structures apart from branched ones are also crosslinked. Table XI also represents changes in the Mooney viscosity with time of mechanochemical treatment for model rubbers with 0.6% of amine-type stabilizers, but of different structure. It also shows higher efficiency of amine-type stabilizers because (under the same conditions of mechanochemical treatment), linear degradation in 1500-type model rubbers takes part, while in 1502 model rubbers they participate in branching and crosslinking. Table XI also shows absence of the influence of amine-type stabilizer structure on mechanochemical processes in 1500-type rubbers.

Figure 7 Dependence of Mooney viscosity on phenol stabilizer substituent structure and time of mechanical processing of model rubbers SBR 1502-No5, No6, and No7: (■) 1.5% alkyl-alkyl-phenol in model SBR 1502-No6; (◆) 1.5% alkyl-aryl-phenol in model SBR 1502-No5; (△) 1.5% polynuclear phenol in model SBR 1502-No7.

To ascertain the presence of the mentioned crosslinked structures, the gel content of the samples was determined prior and after the rubber mechanical processing. The results are given in Table XII and Figure 8. They show that the gel content increases with the extension of the time of the mechanical processing, and that it reaches the value of 40% within 480 s of the mechanical processing of 1502-type model rubbers with phenol stabilizers. In parallel, Table XII shows no changes in gel content for model 1500 rubbers with 0.6% amine stabilizer under the same treatment.

Molecular weights were determined from viscosity of the sol-fractions for the same samples. The results illustrated in Table XIII and Figure 9 show that the molecular weight of the fractions for the same samples decreases very fast within the first 480 s of the mechanical processing time, for model 1502-type rubbers with phenol stabiliz-

Table X Dependence of Mooney Viscosity on Temperature and Time of Mechanical Processing of Model Rubber YUKA 1502-No3

	Time (s)				
T (°C)	0	120	240	480	960
20	52	44	42	39	37
100	52	49	48	47	45
150	52	51	51	53	59

Table XI   Dependence of Mooney Viscosity on Time of Mechanical Processing of Model Rubbers YUKA 1502-No5, YUKA 1502-No6, YUKA 1502-No7, YUKA 1500-No9, and YUKA 1500-No10 at 170°C

Time (s)	1502-No5	1502-No6	1502-No7	1500-No9	1500-No10
0	53	53	53	53	53
120	56	52	58	48	48
240	66	56	70	46	45
480	68	64	80	44	41
960	55	60	50	39	37

ers. In parallel, Table XIII illustrate the continuous decrease of molar mass of 1500-type rubbers, having 0.6% of amine-type stabilizers during the process.

It follows from presented results that mechanochemical processes of branching and networking take part only in 1502-type rubbers and are connected to phenol-type stabilizers. The intensity of the process increases as well with an increase of time and temperature of the process and stabilizer concentration. Of special influence here is the constitution of phenol-type stabilizers, for example, bulkiness, type, and position of the substituents. But their influence cannot be estimated here in detail for several reasons. The commercial stabilizers used here are not composed exclusively of one isomer, and their structures are not strictly defined and declared. Still, according to results obtained, it is clear that significant branching and networking takes part, mostly in the presence of polynuclear phenols, less for aryl-substituted phenols, and least of all for alkyl-substituted phenols, which is of significant practical importance. The increase of the gel content up to 60% in the course of the model SBR 1502 mechanical processing at 170°C for the maximum processing time (without adding crosslinking agents), implies that crosslinking takes place between the unsaturated bonds of the rubber mac-

romolecules. It can be initiated by radicals of phenol stabilizers, type $AO^\bullet$. The occurrence of the induction period, obvious from Figure 6, proves that the processes of branching and crosslinking is evident only after a certain quantity of the stabilizer of AOH type is reacted, i.e., only after a certain quantity of the $AO^\bullet$ radicals are formed. Transformation of stabilizer molecules AOH into stable radicals $AO^\bullet$ of low energy is in good agreement with the kinetic theory of olefin auto-oxidation proposed by Bolland, Batermen, Gee, and Bloomfield.[27–30] According to them, one among several termination reaction is:

$$ROO^\bullet + AH \rightarrow ROOH + A^\bullet$$

e.g., $$ROO^\bullet + AOH \rightarrow ROOH + AO^\bullet$$

$$AO^\bullet \rightarrow {}^\bullet AO$$

Later, the theory was extended to polyolefin oxidation and stabilization processes.[31–34] But in this contribution, we consider as possible the activity of low energy radicals that occur in mechanochemical branching and crosslinking processes in rubbers under mechanical stress.[35]

Comparing such activities of the phenol stable radicals $AO^\bullet$ to the action of the radical initiators

Table XII   Change in Gel Content Depending on Processing Time of Rubbers YUKA 1502-No5, YUKA 1502-No6, YUKA 1502-No7, YUKA 1500-No9, and YUKA 1500-No10 at 170°C

Time (s)	Gel Content (%)				
	1502-No5	1502-No6	1502-No7	1500-No9	1500-No10
0	4.0	4.0	4.0	4.0	4.0
240	31.0	17.5	33.0	4.0	4.0
480	52.0	41.5	55.0	4.3	4.0
960	60.0	46.0	62.0	4.3	4.0

Figure 8 Dependence in gel content, depending on phenol stabilizer substituent structure and time of mechanical processing of model rubbers SBR 1502-No5, No6, and No7: (■) 1.5% alkyl-alkyl-phenol in model SBR 1502-No6; (◆) 1.5% alkyl-aryl-phenol in model SBR 1502-No5; (△) 1.5% polynuclear phenol in model SBR 1502-No7.

of the polymerization, one can expect them to get linked to the double bond of the rubber macromolecules.

To confirm this, experiments were made (five tests per sample) on commercial rubbers YUKA 1502 and YUKA 1500 at 170°C. The rubbers were chemically analyzed prior and after the mechanical processing. The results of these analyses are given in Table XIV, representing increments of the corresponding characteristics relative to the original values. The table indicates that the content of the extractable stabilizer in the rubber YUKA 1502 is reduced in relation to the rubber YUKA 1500. That may also be proof that the unextracted part of the stabilizer remained bonded in the rubber. The same table also shows that the content of the styrene bonded to the rubber YUKA 1502 is higher after

mechanical processing, but that it is not the case with the rubber YUKA 1500. It means that the bonded stabilizer with its phenyl group provides false data pursuant to this testing method. Apparently the content of the styrene is increased, while, in fact, refractivity is increased by the quantity of the bonded stabilizer.

With the increase of processing temperature the induction periods for the mechanochemical branching and crosslinking processes are considerably shortened. The rate of these processes is augmented not only by the increase of the system heat energy content, but also by the increase of the stress concentration on the unsaturated bonds along macromolecules. Stress concentration is highly influenced by the rigidity and planar structure of voluminous pendant phenyl groups of styrene at low temperatures.

The growth of the concentration of the mechanical stress at the double bonds at higher temperatures can be explained by the fact that intermolecule cohesion forces decrease with the temperature increase diminishing the mechanical stress concentration on styrene segments whose phenyl rings have the highest cohesion energy and are located on the side of the macromolecular chain.

In that way the mechanocracking of the SBR rubber macromolecules, which takes place in the styrene segment range at lower temperatures, becomes strongly reduced. It terminates with the temperature increase, while the mechanical stress is transferred from the styrene group to the unsaturated planar and rigid bonds. Due to the mechanical stress concentration on double bonds, their activation energy is reduced, causing them to be subject to opening followed by branching and crosslinking.

According to Table XIV, stable radicals of amine type do not, but phenol type do, open mechanically stressed double bonds. Boozer and

Table XIII   Change in Molar Mass ($M_{vis.} \cdot 10^{-5}$) of Sol Fraction of Model Rubbers YUKA 1502-No5, YUKA 1502-No6, YUKA 1502-No7, YUKA 1500-No9, and YUKA 1500-No10, Depending on the Period of Mechanical Processing at 170°C

	Molar mass $\cdot 10^{-5}$				
Time (s)	1502-No5	1502-No6	1502-No7	1500-No9	1500-No10
0	3.5	3.5	3.5	3.5	3.5
240	1.5	2.4	1.2	2.9	2.6
480	1.0	1.1	0.9	2.6	2.1
960	0.6	0.8	0.5	1.7	1.7

Figure 9 Dependence change in molar mass ($M_{vis.}$ · 10^{-5}) of sol fractions, depending on phenol stabilizer substituent structure and time of mechanical processing of model rubbers SBR 1502-No5, No6, and No7: (■) 1.5% alkyl-alkyl-phenol in model SBR 1502-No6; (◆) 1.5% alkyl-aryl-phenol in model SBR 1502-No5; (△) 1.5% polynuclear phenol in model SBR 1502-No7.

Hammond,[35,36] considering the efficiency of amine type stabilizers, suggested the following mechanism of electron transfer from nitrogen and formation of the Wurster radical-ion.[36]

On the other hand, from numbers of examples from organic chemistry, it follows that stable radicals with unpaired electrons at the carbon or oxygen atom tend to dimerize, opposite to the

stable radicals having an unpaired electron at the nitrogen atom. In addition, dimerization of stable radicals with an unpaired electron at the oxygen atom has additional specificity. It goes through C—C or C—O bond formation and not through O—O bond formation. Also, it is known that such dimerization is more difficult for *ortho* and *para* substituted radicals. The steric nature of the effects is illustrated by *tert-butyl* substituents, being of highest bulkiness and causing highest constraints.

Summarizing, it should be emphasized that stable radicals of the phenol-type stabilizers can cause branching and crosslinking processes if their access to mechanochemically stressed bonds is not limited by steric hindrances.

CONCLUSIONS

There have been examined mechanochemical processes in commercial SBR rubbers YUKA 1500 and YUKA 1502 with the stabilizers usually used. In addition, to confirm the phenomena observed, model samples based on the same polymer, were specially prepared and examined. In the case of the model rubber type 1500, there were used stabilizers of *p*-phenylendiamine with alkyl and aryl substituents on nitrogen. For the model rubber type 1502, there were used polynuclear phenols, aryl- and alkyl-substituted phenols, and alkyl-, aryl-substituted phenols substituents, and alkyl-alkyl substituents on the phenyl group.

In the presence of the *p*-phenylene-diamine stabilizers, mechanochemical processes that take place within the entire temperature range of interest, i.e., from 20–170°C, have the character of

Table XIV Difference in Chemical Characteristics of Commercial-Grade Rubbers YUKA 1500 and YUKA 1502 after 960 s of Mechanical Processing at 170°C

Properties	YUKA 1500			YUKA 1502		
	Before	After	Difference	Before	After	Difference
Bound Styrene (5%)	23.13	23.0	−0.13	22.94	25.54	2.60
Salt (%)	0.06	0.00	−0.06	0.10	0.00	−0.10
Acid (%)	6.20	5.84	−0.36	5.82	5.30	−0.52
Stabilizer (%)	0.48	0.38	−0.10	1.16	0.79	−0.37
Extractive matl. cont. (%)	6.91	6.67	−0.24	7.26	7.04	−0.22
Stabilizer and extractive matl. (%)	7.39	7.05	−0.34	8.42	7.83	−0.59

linear degradation. In ranges below 100°C these processes have a negative temperature coefficient and, above 100°C, a positive one with minimum changes in the temperature range around 100°C. No dependence of the processes on the stabilizer structure was registered.

Considering stability of the original rubber properties in the course of processing, it follows from the experimental results that the optimum temperature range for the SBR rubbers, processing with stabilizers of the *p*-phenylene diamine type, is around 100°C, i.e., from 70–130°C.

In the presence of phenol stabilizers, mechanochemical processes do not have the same character in the whole testing temperature range, from 20–170°C. They have the characteristic of linear degradation only in the temperature range from 20–130°C, with a negative temperature coefficient below 100°C and positive above 100°C. Minimum changes are observed around 100°C. At the temperatures above 100°C, for all tested samples of the commercial and model rubbers containing phenol stabilizers, comes the rise of Mooney viscosity and the gel content with the increase of time of mechanical processing, meaning that, in that temperature range, the dominant processes are branching and crosslinking.

These processes do not appear in the rubber without any stabilizer (Fig. 5), and are intensified with the increase of the phenol stabilizers concentration (Fig. 6), which means that the phenol stabilizers directly cause branching and crosslinking processes taking place in SBR 1502 in the course of mechanical processing at increased temperatures.

The length of the induction periods, and the rate of the branching and crosslinking processes, depend on the substituents on the phenol stabilizer. The induction periods are longer, the branching and crosslinking processes slower in rubbers with phenol stabilizers having big and bulky alkyl substituents, i.e., phenols whose substituents cause important steric hindrances for the reactions of the phenoxy stable radicals (Figs. 6 and 7).

In general, the stabilizer's secondary activity decreases in the following order i.e., decrease of mechanochemical branching and crosslinking of rubbers caused by phenol stabilizers can be established: polynuclear phenols > aryl-alkyl substituted phenols > alkyl-alkyl–substituted phenols.

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