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Rubbers improved in thermal stability and resistance to microorganisms

Summary — Bis(4-hydroxyphenyl)sulfoxide and brominated bisphenols A, *viz.*, tetrabromobis(4-hydroxyphenyl)propane and tetrabromobis(4-hydroxyphenyl)sulfoxide, were synthesized and used to modify natural rubber, styrene-butadiene rubber, and nitrile-butadiene rubber. Chloroprene rubber, carbon black and clay were used as fillers. The ingredients (Table 2) were mixed in a two-roller mill at 150°C for 15 min. Cured films were prepared and selected mechanical and thermal properties as well as resistance to mineral oils and to microorganisms were examined. Tetrabromobis(4-hydroxyphenyl)sulfoxide and chloroprene rubber imparted enhanced mechanical and thermal insulation properties and also a significant resistance to microorganisms.

Key words: natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, bis(4-hydroxyphenyl)sulfoxide, tetrabromobis(4-hydroxyphenyl)propane, tetrabromobis(4-hydroxyphenyl)sulfoxide, thermal stability, resistance to mineral oils and to microorganisms, thermal conductivity.

The properties of rubber mixes are related to the nature of both the polymer used and the other ingredients of the mix and to the proportions in which they are mixed. The chemical network produced by crosslinks tying up polymer chains, results in substantially improved physical properties and performance characteristics [1].

Fillers or reinforcing agents such as carbon black, clay, and silica are added to rubber to meet material property targets such as tensile strength and abrasion resistance. Carbon black as a reinforcing agent is added to the treadstock in pneumatic tires; amorphous silica is also added to produce white side-walls of the tires [2]. In the next future, colored tires adapted to the color of a car, will be offered.

The marked resistance of neoprene (polychloroprene) to severe conditions such as high temperature, ozone, oil, organic solvents and other chemicals is the main property that makes it valuable for many applications [3].

Synthetic plastics are resistant to microbiological degradation, but naturally occurring polymers can be attacked by microbiological agents such as bacteria and fungi or microbiological agents such as termites, insects and rodents [4, 5]. The extent of the effect of a material on biodegradation of plastics is governed by the interrelations of all the structural groupings providing a given degree of toxicity. Bisphenols are extremely useful in the manufacturing of antiseptic materials [6—8].

The main objective of this work is to prepare rubber with improved mechanical and thermal properties, enhanced oil resistance and improved resistance to microorganisms.

EXPERIMENTAL

Materials

— Natural rubber (NR), a Hevea Malaysian rubber, marketed as SMR cv50, produced by Durham Co., UK;

— Styrene-butadiene rubber (SBR), Cariflex-S1712, produced by Shell Chemicals Co.;

— Nitrile-butadiene rubber (NBR), Perbunan-N, produced by Bayer Co.;

— Chloroprene rubber (CR), Baypren 110, produced by Bayer Co., chlorine content 40%;

— Clay, montmorillonite type (hydrous aluminum silicate), $(OH)_8Al_4SiO_4O_{10}$, particle size 70—120 μ mesh;

— Carbon black, N330-MAF, produced by S.A.E. Co., Alexandria, Egypt, pour density 375 kg/m^3, iodine number 82 g/kg, and sieve residue 0.030%;

— Mineral oil, Esso extra quality multigrade oil 20 W-50 API SF/CC.

Methods

Preparation of bis(4-hydroxyphenyl)sulfoxide

Bisphenol sulfoxide was prepared by condensation of phenol and carbon disulfide containing anhydrous aluminum chloride and thionyl chloride. The method has been described elsewhere [9].

Preparation of brominated bisphenols

Bromine (0.5 mol) was added to a solution of bisphenol A or to the prepared bis(4-hydroxyphenyl) sulfoxide (0.1 mol) in glacial acetic (120 ml) to prepare tetrabromobis(4-hydroxyphenyl)propane or tetrabromobis(4-hydroxyphenyl)sulfoxide, respectively. The method has been described elsewhere [10]. The compounds prepared are characterized in Table 1.

Thermal properties

Thermal conductivity (*k*) was determined according to [14]. Heat resistance was determined at 100 and 150 up to 200°C for 4 h, and evaluated in terms of weight loss percentage [15].

Resistance to mineral oil

Mineral oil resistance was examined for 120 h at 25°C and evaluated in terms of weight change percentage [16].

Resistance to microorganisms

The microorganism test was carried out after [17, 18].

A layer of moistened sawdust (25 mm) was put into a dish, covered to prevent the loss of moisture, and kept at 25±2°C for 1 week. The test samples were buried in the sawdust and incubated at 25±2°C for 4 weeks. Finally, the test samples were washed with cold water and immediately evaluated mechanically at the end of this period by establishing the percentages of decrease in both hardness and tear strength.

Table 1. **Characteristics of compounds prepared**

Bisphenol	Formula	Molecular weight	Melting point, °C	Elemental analysis (calculated, found, %)				
				C	H	O	S	Br
Bis(4-hydroxyphenyl)sulfoxide	$C_{12}H_{10}O_3S$	234.27	116	61.52 61.60	4.30 4.33	20.49 20.25	13.69 13.82	—
Tetrabromobis(4-hydroxyphenyl)-propane	$C_{15}H_{12}O_2Br_4$	543.87	141	33.13 33.36	2.22 2.63	5.88 5.07	—	58.77 58.94
Tetrabromobis(4-hydroxyphenyl)-sulfoxide	$C_{12}H_6O_3SBr_4$	549.85	110	26.21 26.36	1.10 1.21	8.73 8.05	5.83 5.97	58.13 58.41

Formulation of rubber samples

The bisphenols prepared, used at a concentration of 10 parts per 100 parts of rubber (phr), were mixed in a two-roller mill with clay and/or carbon black used as fillers and CR used as a modifier, and added at a concentration of 10—50 phr. Mixing was carried out at 150°C for 15 min. The formulations of NR, SBR and NBR with or without the above-mentioned additives are given in Table 2. Samples of cured films were classified into three groups (I—III) according to the type of the rubber used. Again, each group was classified into ten samples according to the percentage of the modifiers added. Hardness, tear strength, thermal properties, mineral oil resistance of the cured samples and their resistance to microorganisms were tested.

Test and evaluation

Mechanical properties

Shore A hardness was measured in a Zwick durometer in compliance with [11, 12]. Tear strength was determined in compliance with [13].

RESULTS AND DISCUSSION

The service life and performance of a rubber product depend on the nature of the rubber chosen as a basis and the types and proportions of compounding ingredients. Each compound exhibits its own pattern of physical and chemical properties which show selective action against various microorganisms.

In the present work, substituted bisphenols were prepared and mixed at a concentration of 10 parts per 100 parts NR, SBR or NBR. Clay and/or carbon black, as well as CR, were added at appropriate concentrations (Table 2). A goal of the work was to obtain rubber vulcanizates with improved properties.

Mechanical behavior, thermal conductivity, heat stability, and mineral oil resistance were studied in NR, SBR and NBR vulcanizates. Their resistance to microorganisms was also tested.

Hardness and tear strength measurements of films (Table 2) show that:

As compared with unmodified SBR and NBR, the unmodified NR offers the greatest hardness and the highest tear strength. Presumably, NR is sufficiently

Table 2. The formulation and characteristics of samples prepared

Samples		Formulation								Mechanical properties		Thermal properties	Chemical resistance	Resistance to microorganisms	
Group	No.	Rubber		Chloroprene rubber %	Brominated bisphenol-A %	Bisphenol sulfoxide %	Brominated bisphenol sulfoxide %	Clay, %	Carbon black %	Hardness Shore A	Tear strength N/mm	Thermal conductivity coefficient kx10^{-1} cal/sec/cm/°C at 23°C	Mineral oil resistance, weight change % at 25°C for 120 h	Hardness decrease %	Tear strength decrease, %
		type	g												
I	1	NR	100	—	—	—	—	—	—	32	26	0.281	20	18.3	22.4
	2			—	—	—	—	50	—	36	22	0.242	15	17.1	21.6
	3			—	—	—	—	—	50	34	24	0.233	15	16.3	21.1
	4			—	—	—	—	25	25	43	28	0.216	12	15.7	20.8
	5			—	10	—	—	30	10	44	33	0.198	10	13.8	20.2
	6			—	—	10	—	30	10	50	30	0.176	9	13.2	19.5
	7			—	—	—	10	30	10	55	31	0.170	7	12.6	18.4
	8			50	10	—	—	30	10	73	40	0.166	6	10.1	12.5
	9			50	—	10	—	30	10	71	38	0.153	6	9.3	11.3
	10			50	—	—	10	30	10	77	44	0.151	6	8.4	9.6
II	11	SBR	100	—	—	—	—	—	—	25	23	0.266	18	14.6	18.3
	12			—	—	—	—	50	—	31	20	0.278	10	13.5	16.3
	13			—	—	—	—	—	50	28	22	0.210	9	12.6	15.7
	14			—	—	—	—	25	25	36	25	0.203	7	12.1	14.8
	15			—	10	—	—	30	10	41	30	0.188	6	11.6	13.1
	16			—	—	10	—	30	10	43	28	0.178	5	11.1	12.3
	17			—	—	—	10	30	10	46	27	0.166	4	10.7	11.4
	18			50	10	—	—	30	10	57	33	0.156	3	9.3	8.6
	19			50	—	10	—	30	10	53	30	0.151	2.5	7.8	7.1
	20			50	—	—	10	30	10	61	39	0.146	2	6.1	5.4
III	21	NBR	100	—	—	—	—	—	—	20	20	0.264	15	12.9	13.1
	22			—	—	—	—	50	—	26	17	0.231	7	11.2	13.8
	23			—	—	—	—	—	50	23	19	0.210	6	10.5	12.3
	24			—	—	—	—	25	25	31	22	0.191	6	10.3	10.6
	25			—	10	—	—	30	10	33	27	0.173	2	9.2	10.1
	26			—	—	10	—	30	10	36	25	0.168	3	7.4	9.8
	27			—	—	—	10	30	10	39	29	0.159	3	5.8	9.3
	28			50	10	—	—	30	10	48	30	0.151	2	4.3	6.8
	29			50	—	10	—	30	10	46	26	0.148	1	3.6	5.6
	30			50	—	—	10	30	10	58	35	0.143	1	3.1	4.3

stereoregular to exhibit strain-induced crystallization [19]. This effect results in excellent intrinsic hardness, with no need to add reinforcing fillers.

Clay and/or carbon black used as additives give rise to improved hardness and tear strength as compared with the rubber unfilled with these fillers. This improvement can be attributed to the existence of chemical bonds or chemisorptive linkages at the filler-rubber interface [1].

NR, SBR or NBR modified with substituted bisphenols show increased hardness as compared with the unmodified rubbers. The introduction of an aromatic ring structure, into the main chain of the additive has a marked stiffening effect [20, 21]. Incorporation of brominated bisphenol sulfoxide has increased hardness on account of sulfur atom or polar bromine atoms attached to phenyl groups. Chemically networked junctures are formed by insertion of crosslinks between the rubber chains through the vulcanization reaction [1] and the glass transition point of these vulcanizates is raised.

Modification of NR, SBR and NBR with CR, substituted bisphenols and fillers has led to an incremental increase in hardness. In addition to a high chlorine content (40%), the CR chains have a high trans-1,4 structure which is susceptible to strain-induced crystallization [1]. Thus, the rubber containing CR and these ingredients exhibits the best mechanical behavior.

Specific thermal conductivities are listed in Table 2. Practically, thermal conductivity or K-values indicate that:

Unmodified NBR and SBR show low K-values, lower than those of unmodified NR, presumably on account of the polar nitrile groups and the phenyl groups present in NBR and SBR, respectively. These tend to raise the glass transition point and to decrease the K-values [21]. Thus, the NBR and SBR have better thermal insulation properties as compared with NR.

Clay and/or carbon black as additives decrease *K*-values and thus improve thermal insulation properties. Effective intermolecular forces are supposed to increase in the presence of a filler. Carbon black is more effective than clay in improving the thermal insulation properties. The thermal insulation property improves gradually as the amount of the filler is increased in the formulation.

Incorporation of the bisphenols prepared into NR, SBR or NBR has considerably enhanced thermal insulation by sharply decreasing *K*-values in each sample. Incorporation of brominated bisphenol sulfoxide is also expected to improve thermal insulation as compared with bisphenol sulfoxide or brominated bisphenol A added, according to [21].

CR, substituted bisphenols and fillers added to NR, SBR or NBR have improved thermal insulation properties by decreasing the *K*-values as compared with the rubbers unfilled with these ingredients. The rubbers containing these components have shown the best thermal insulation properties.

Heat resistance was studied in terms of the weight loss percentage recorded at different temperatures (*e.g.* 100, 150, and 200°C) in 4 h (Figs. 1—9).

NR has shown the highest weight loss percentages at 100, 150, and 200°C in 4 h (samples 1 in Figs. 1—3) as

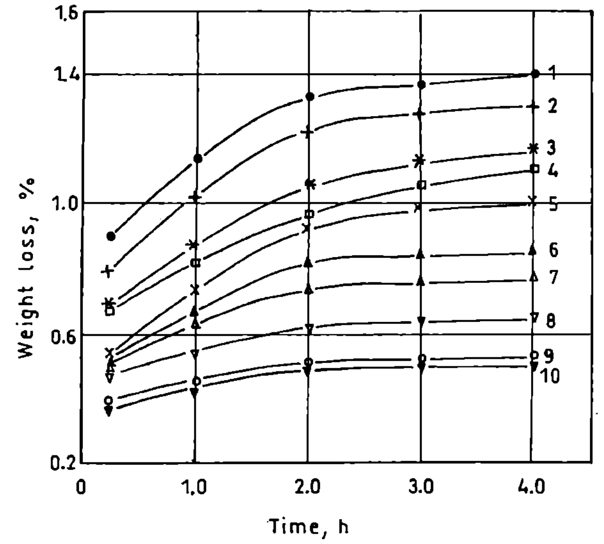

Fig. 1. Weight loss percentage for formulated natural rubber (NR) at 100°C; numbers on curves correspond to Sample numbers (Table 2)

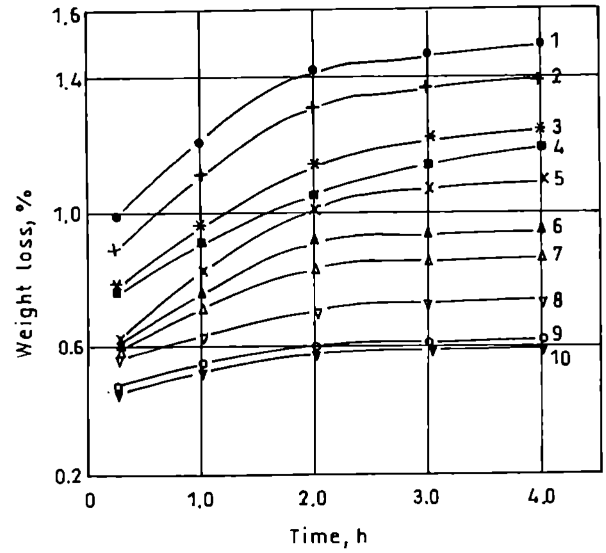

Fig. 2. Weight loss percentages for formulated natural rubber (NR) at 150°C; numbers on curves correspond to Sample numbers (Table 2)

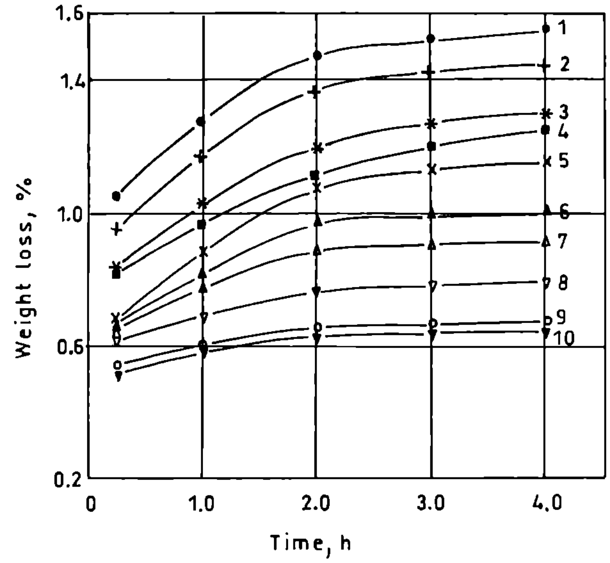

Fig. 3. Weight loss percentages for formulated natural rubber (NR) at 200°C; numbers on curves correspond to Sample numbers (Table 2)

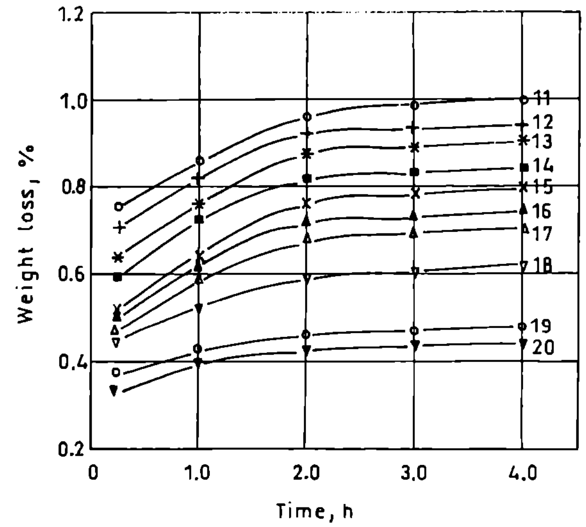

Fig. 4. Weight loss percentages for formulated styrene butadiene rubber (SBR) at 100°C; numbers on curves correspond to Sample numbers (Table 2)

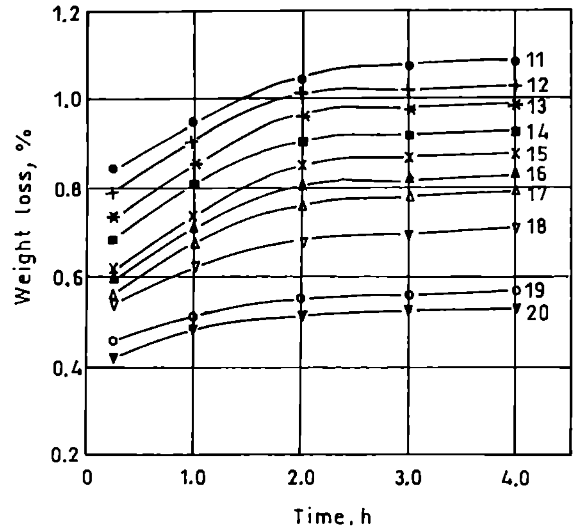

Fig. 5. Weight loss percentages for formulated styrene butadiene rubber (SBR) at 150°C; numbers on curves correspond to Sample numbers (Table 2)

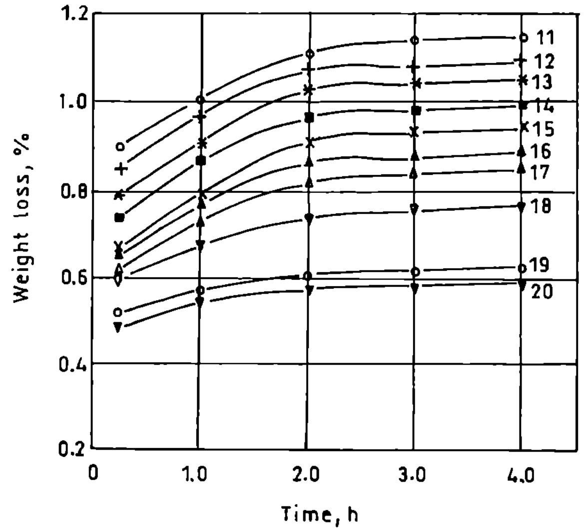

Fig. 6. Weight loss percentages for formulated styrene butadiene rubber (SBR) at 200°C; numbers on curves correspond to Sample numbers (Table 2)

compared with those of SBR and NBR (samples 11 and 21 in Figs. 4—6 and 7—9, respectively). This means that NBR can withstand heat (100, 150, and 200°C) better than do SBR and NR (*e.g.*, they have hot air resistance).

In the presence of a filler, weight loss percentages at 100, 150 and 200°C in 4 h were smaller as compared with unfilled rubbers. Carbon black is particularly effective and generally more suitable than clay. In spite of a common misconception that carbon-containing compounds must have a poor heat resistance [21].

Addition of the bisphenols prepared to NR, SBR or NBR has led to a smaller decrease in the weight loss percentages at 100, 150 and 200°C in 4 h. Brominated bisphenol sulfoxide gave rise to the highest heat stability at 100, 150 and 200°C for 4 h compared with rubbers containing bisphenol sulfoxide or brominated bisphenol A under the same conditions.

CR, substituted bisphenols and fillers incorporated into NR, SBR or NBR produced least weight loss percentages in each rubber at 100, 150 and 200°C in 4 h. The rubbers containing these additives show the best heat resistance at 100, 150 and 200°C (in 4 h).

NR, SBR and NBR vulcanizates were also subjected to the chemical resistance test, by direct immersion in mineral oil at 25°C for 120 h. Their weight change percentages are shown in Table 2.

Incorporation of the bisphenols prepared into rubbers has reduced swelling in mineral oil at 25°C in

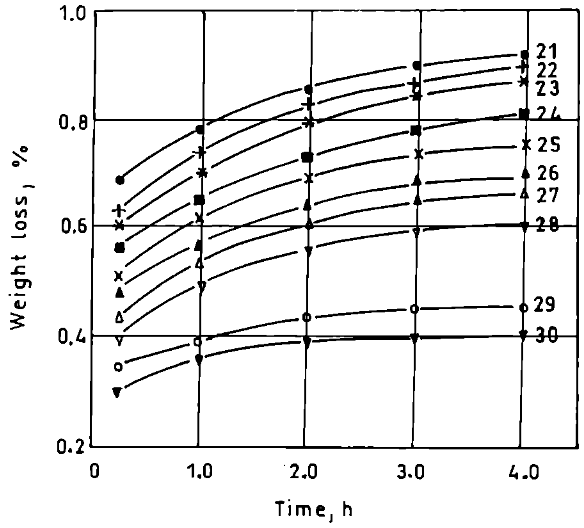

Fig. 7. Weight loss percentages for formulated nitrile butadiene rubber (NBR) at 100°C; numbers on curves correspond to Sample numbers (Table 2)

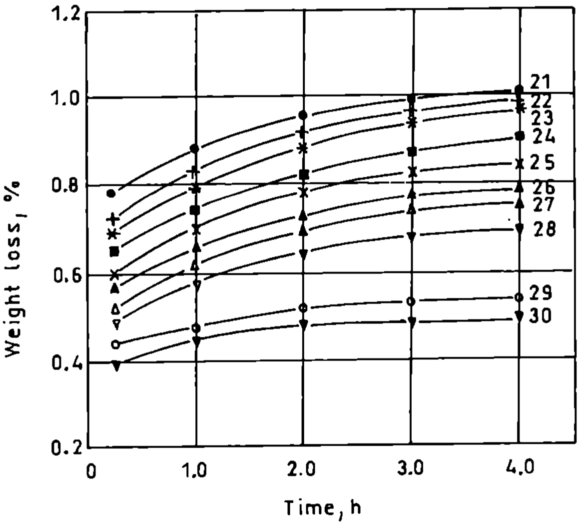

Fig. 8. Weight loss percentages for formulated nitrile butadiene rubber (NBR) at 150°C; numbers on curves correspond to Sample numbers (Table 2)

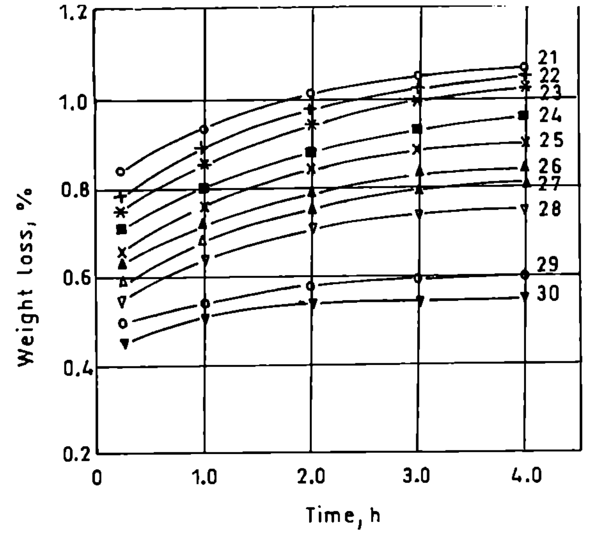

Fig. 9. Weight loss percentages for formulated nitrile butadiene rubber (NBR) at 200°C; numbers on curves correspond to Sample numbers (Table 2)

120 h. Brominated bisphenol sulfoxide gave rise to the least weight change percentages as compared with those modified with bisphenol sulfoxide or brominated bisphenol A.

Incorporation of CR into the rubbers has resulted in the least weight change percentages in mineral oil as compared with rubbers without CR, on account of the electronegative chlorine atom at the 1,4-trans double bond [3]. Thus, the samples containing CR possess excellent stability toward mineral oil at 25°C (120 h).

Swelling of vulcanizates in mineral oils depends not only on the content of a modifier or fillers but also on crosslink density. Hardness and tear strength properties are also functions of crosslink density [1]. The data given in of Table 2 allow to conclude that crosslink density increases with the increase in hardness and tear strength. Thus, the samples having the highest hardness and tear strength values have the highest crosslink density leading to the least weight change percentages in mineral oils at 25°C (120 h).

Resistance to microorganisms was followed in terms of deterioration in mechanical properties of the vulcanizates, *viz.*, hardness and tear strength. The data given in Table 2 indicate that:

Unmodified NBR inhibited the growth of microorganisms more efficiently than did unmodified SBR and NR, as a result of an increasing number of -CH_2- units as well as the presence of nitrile group -CN- in NBR chains. The phenyl group in the main chain of SBR also has a microbiological effect [20]. On the other hand, the biological degradation of NR is facilitated by its linearity [4]. Non-rubber constituents, mainly proteins and carbohydrates, also facilitate the attack of microorganisms.

Addition of the bisphenols prepared to NR, SBR and NBR has resulted in decreased loss percentages in both hardness and tear strength caused by microorganisms. Brominated bisphenol sulfoxide gave rise to the least decrease percentages in both hardness and tear strength caused by microorganisms as compared with those of the samples containing bisphenol sulfoxide or brominated bisphenol A. Two aryl nuclei linked by the -S- bridge are known to produce toxicity and are more resistant to microorganisms than those linked by the propane bridge [9]. Also bromine substituents in the nuclei have an effect on the degree of toxicity of the molecule [22].

Chloro-compounds have been insecticidal to German cockroaches [23]. In this study, CR and substituted bisphenols incorporated into rubbers increased significantly their resistance to microorganisms. This appears to be explicable in terms of the electronegative chlorine atom in CR which is likely to bind with bisphenol derivatives, containing sulfur or bromine atoms or both, whereby the compound becomes electronegatively stronger, and noticeably resistant to microorganisms.

The rubbers containing these modifiers show the least decrease percentages in both hardness and tear strength caused by microorganisms.

CONCLUSION

1. Some mechanical properties of NR, SBR and NBR vulcanizates, such as hardness and tear strength, thermal insulation properties, heat stability, mineral oil resistance and resistance to microorganisms can be improved by addition of some substituted bisphenols.
2. Tetrabromobis(4-hydroxyphenyl)sulfoxide improves these properties of rubbers as compared with those to which bis(4-hydroxyphenyl)sulfoxide or tetrabromobis(4-hydroxyphenyl)propane, was added.
3. Incorporation of CR and tetrabromobis(4-hydroxyphenyl)sulfoxide into NR, SBR and NBR has improved the above-mentioned properties.

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Firma Dow Corning (USA) zaleca **stosowanie nowego środka smarującego do produkcji folii z poliolefin**. Środkiem tym są funkcjonalizowane siloksany o bardzo dużym ciężarze cząsteczkowym, które w procesie wytłaczania szybko skupiają się na powierzchni folii przed jej zakrzepnięciem. W odróżnieniu od silikonowych środków smarujących, zalecane siloksany (dostarczane w postaci przedmieszek) nie migrują po zestaleniu się folii. W celu uzyskania dobrego poślizgu w ustniku, zaleca się stosowanie 1—5% dodatku, ale już 0,1—1% może zapobiec falowaniu strumienia tworzywa opuszczającego ustnik wytłaczarki. Stosowanie środka smarującego umożliwia zmniejszenie obciążenia napędu ślimaka wytłaczarki.

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Firma Borealis oferuje **polipropylen *HL 512 FB* o największym wskaźniku płynięcia** — 1200 g/10 min. Mała lepkość stopionego tworzywa umożliwia wytwarzanie bardzo cienkiego (średnicy < 2 μm) włókna do produkcji włóknin, które dzięki temu mogą być bardziej miękkie i jednorodne. Wytłaczanie polimeru o tak dużej płynności umożliwia oszczędzenie do 40% energii (w stosunku do wytłaczania materiałów dotychczasowych) lub odpowiednie zwiększenie wydajności procesu.

Kunststoffe 1999, **89**, nr 8, 111.

Firma HT Troplast (RFN) opracowała **twardy materiał spieniony *Trolit*.** Otrzymuje się go z tlenowych związków krzemu i glinu, które ulegają sieciowaniu w środowisku wodnym pod wpływem składników alkalicznych przy użyciu specjalnego utwardzacza. Produkt przestrzennie usieciowany ma wytrzymałość tym większą, im większy jest udział glinu w materiale. Z racji składu chemicznego, pianka jest niepalna i nawet podczas długotrwałego ogrzewania nie wydziela toksycznych produktów rozkładu. Wytrzymuje ona temp. 1000°C, może być produkowana w blokach lub formowanych kształtkach, podobnie jak typowe pianki polimerowe. Omawiany materiał piankowy ma wytrzymałość na ściskanie do 1 MPa i dużą przewodność cieplną.

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B. M.