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Colouring Agents for SBR Vulcanizates and Their Effects on Ageing and UV Radiation Resistance

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Summary: Metal free and some metal-perylene polymers as well as some metal phthalocyanine polymers were incorporated into styrene butadiene rubber (SBR) compounds as colouring agents. The ageing and UV resistance of the vulcanizates obtained were studied in terms of their mechanical properties. The results obtained revealed that cobalt perylene and cobalt phthalocyanine polymers showed superior performance in SBR vulcanizates against thermal ageing and UV radiation. The optimum concentration of cobalt phthalocyanine polymer was found to be 1 phr (parts per hundred parts of rubber).

Keywords: ageing; electric properties; mechanical properties; metal perylene polymers; metal phthalocianine polymers; SBR; UV resistance

Introduction

Phthalocyanine polymers and their metal derivatives form an interesting family of compounds with a wide range of properties and applications. Several attempts for preparing high molecular weight phthalocyanine polymers were carried out. The reaction of tetra basic acid derivative e.g. pyromellitic dianhydride with a copper salt, urea and a vanadate or molybdate promoter were reported[1,2]. The uses of phthalocyanine polymers as semiconductors[3–5] in applications such as batteries, solar cells, microlithography, sensors[6]and photoconductors[7,8], and as colorants and UV stabilizers for rubber vulcanizates were also reviewed[9,10]. In previous studies, the synthesis of biphthalocyanine and some modified phthalocyanine pigments has been reported[11,12]. The prepared pigments showed acid and alkali resistance and high thermal stability up to 500 °C. The synthesis of some novel perylene polymers[13,14] (phthalocyanine polymer analogues) has been carried out by the same route via substitution of pyromellitic dianhydride with 3,4,9,10-perylene tetracarboxylic acid dianhydride in the conventional phthalocyanine polymer synthesis[15]. Characterization of the polymeric pigments prepared having Cu, Co and Ni was carried out and their structures were elucidated using chemical analysis (C, H and N) and spectrophotometric measurements (IR, UV visible and XRD) in addition to thermal gravimetric analysis (TGA). The main objective of the present research is to evaluate metal free and some metal perylene polymers as well as metal phthalocyanine polymers as coloring agents, antioxidants and UV stabilizers for SBR.

Experimental

Materials

Styrene butadiene rubber (SBR) of the type 1502, was a product of Bayer, Germany.

Perylene polymers: Metal free perylene polymer (M.F.P.P.), copper perylene polymer (Cu P.P.), cobalt perylene polymer (Co P.P.) and nickel perylene polymer (Ni P.P.), were laboratory prepared. Phthalocyanine polymers: Copper phthalocyanine polymer (Cu Pc. P.) and cobalt phthalocyanine polymer (Co Pc. P.) were laboratory

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prepared. Other compounding ingredients were of commercial grades.

Techniques

Preparation of Metal Phthalocyanine Polymers (M Pc. P.)[13]

Copper and cobalt phthalocyanine polymers were prepared by condensation of pyromellitic dianhydride (43.6 g, 0.2 mol), urea (excess) and metal chloride of copper and/or cobalt (0.05mol) in presence of boric acid catalyst. The fusion was carried out at (200–240) °C with continuous stirring for 4–5 hrs until a highly stable color was formed. The solid mass was cooled, ground and washed several times with boiled distilled water, dilute hydrochloric acid, 1% sodium hydroxide solution, water, methanol and finally acetone and dried at 110 °C for 3 hrs. The greenish-blue dried mass was then ground and subjected to further purification via soxhlet extraction in acetone and sublimation under vacuum at 200 °C (yield >80%).

Preparation of Metal Free Perylene Polymer (M.F.P.P.)[14]

Metal free perylene polymer was prepared by the urea fusion technique in the dry method as follows: A mixture of 3,4,9,10-perylene tetracarboxylic acid dianhydride (7.84 g; 0.02 mol) and urea (excess), in presence of ammonium molybdate as a reaction promoter, were fused together with continuous stirring at (220–240) °C for about 4 hrs until a stable color was formed. The solid mass was cooled, ground, washed several times with boiled distilled water, dilute acid and alkali, distilled water, methanol and acetone. The crude mass was dried at 110 °C for 4 hrs. The pink dried mass was ground and subjected to further purification via soxhlet extraction in acetone for 48 hrs and sublimation under vacuum at 200 °C. (yield >85%).

Preparation of Metal Perylene Polymers (M.P.P.)[14]

Cobalt, nickel and copper perylene polymers were prepared by condensation of 3,4,9,10-perylene tetracarboxylic acid dianhydride (7.84 g, 0.02 mol), urea (excess) and metal chloride of cobalt, nickel and/or copper (0.005 mol) in presence of ammonium molybdate catalyst. The fusion was carried out at (200–240) °C with continuous stirring for 4–5 hrs until a highly stable color was formed. The solid mass was cooled, ground and washed several times with boiled distilled water, dilute hydrochloric acid, 1% sodium hydroxide solution, water, methanol and finally acetone and dried at 110 °C for 4 hrs. The dried mass was then ground and subjected to further purification via soxhlet extraction in acetone and sublimation under vacuum at 200 °C (yield >85%).

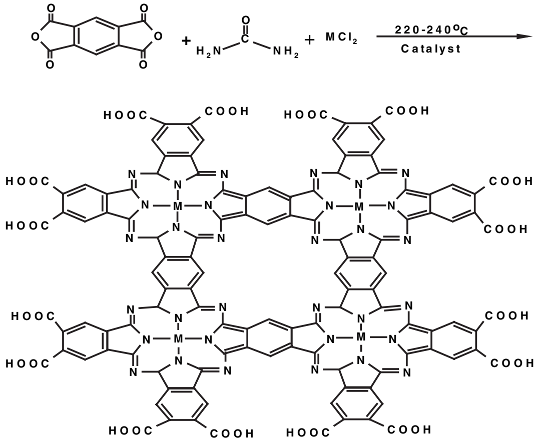
The proposed structures for some metal phthalocyanine polymers as well as metal and metal free perylene polymers are illustrated in scheme 1.

Mixing, Vulcanization and Testing of Rubber

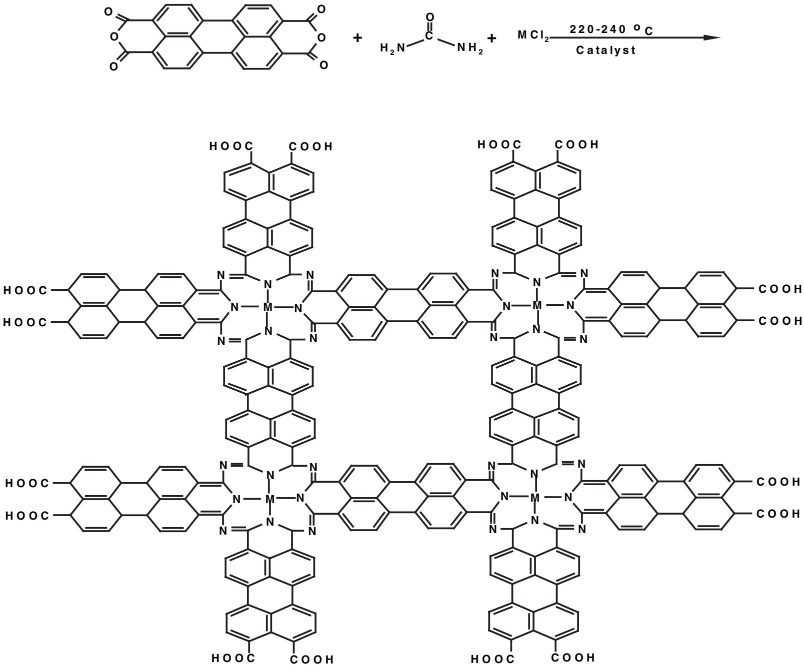
Rubber mixes were prepared on an open two-roll mill of 170 mm diameter and 300 mm working distance, 24 rpm speed of slow roll and 1: 1.4 gear ratio. The rheological characteristics were assessed by using a Monsanto Oscillating Disc Rheometer R−100, at 152 ± 1 °C, according to ASTM D2084-95. The rubber mixes were vulcanized at their optimum cure times (t_{c90}) by the aid of a hydraulic press at the same temperature. The physico-mechanical properties were measured with a Zwick-1425 tensile tester according to ASTM D412-98a. Accelerated thermal ageing was carried out at 90 °C for different periods up to 7 days, according to ASTM D573-88. UV irradiation of the vulcanizates was carried out with the aid of a UV lamp of 240 nm wavelength[10].

Dielectric Measurements

Permittivity (ε'), dielectric loss (ε'') and conductivity (σ) measurements were carried out using LCR meter type AG-411 B (Ando electric Ltd. Japan). A guard ring capacitor of the type NFM/5T Wiss Tech. Werkstatten (WTW) GMBH Germany was used as a measuring cell. The cell



(a) Metal phthalocyanine polymers (M = Cu, Co)



(b) Metal free perylene polymer (M = 2 H)
Metal perylene polymers (M = Cu, Co and Ni)

Scheme 1.

was calibrated by using standard materials. The experimental error in ε′ and ε″ was found to be ±3% and ±5% respectively.

Results and Discussion

Colouring agents namely metal free and some metal perylene polymers (Cu P.P., Co

Table 1.
Formulations, rheometric characteristics and physico-mechanical properties of SBR vulcanizates containing metal free and some metal perylene polymers and metal phthalocyanine polymers.

Coloring agent, phr	S1	S2	S3	S4	S5	S6	S7
M.F.P.P.	0	1	0	0	0	0	0
Cu P.P.	0	0	1	0	0	0	0
Co P.P.	0	0	0	1	0	0	0
Ni P.P.	0	0	0	0	1	0	0
Cu Pc.P.	0	0	0	0	0	1	0
Co Pc.P.	0	0	0	0	0	0	1
Rheometric characteristics, at 152 ± 1 °C							
Maximum torque, dNm.	75	75	76	75	79	79	76
Minimum torque, dNm.	11	10	11	10	10	10	10
Cure time (t_{c90}) min.	20	19	23	19	21	20	20
Scorch time (t_{S2}) min.	6	6	8	6	7.5	7.5	6
Cure rate index, min^{-1}	7.1	7.7	6.7	7.1	7.4	8	7.1
Physico-mechanical properties							
Tensile strength, MPa.	7.1	7.1	7.5	7.1	7.3	6.9	6.6
Elongation at break, %	605	605	620	600	590	525	520

The base recipe contains (phr): SBR 100, zinc oxide 5, stearic acid 1.5, Hi-Sil 40, processing oil 5, N-cyclohexyl 2-benzothiazole sulphenamide (CBS) 1 and sulphur 2.

P.P. and Ni P.P.), as well as some metal phthalocyanine polymers (Cu Pc. P. and Co Pc. P.), were incorporated into SBR compounds; in order to study the effect of the above mentioned compounds upon the thermal ageing and UV radiation resistance. Formulations, rheometric characteristics of the mixes and physico-mechanical properties of the vulcanizates are listed in Table 1. It is noted that the base recipe did not contain any antioxidant, in order to highlight the effect of the colouring agents, added into rubber compounds, upon the thermal ageing and UV resistance of SBR vulcanizates. Probably, the metal free and the metal perylene polymers did not have any adverse effect on either the rheometric characteristics or the physico-mechanical properties of SBR vulcanizates. However, the metal phthalocyanine polymers reduced slightly the physico-mechanical properties of SBR vulcanizates, without affecting the rheometric characteristics. SBR vulcanizates, containing the above mentioned colouring agents, were subjected to shelf ageing for one year, and then exposed to accelerated thermal ageing in an air-circulated electric oven, at 90 °C for periods up to 7 days. Figures 1 and 2 show that all vulcanizates with metal perylene polymers investigated possessed higher tensile strength and elongation at break values throughout the ageing periods than those of the blank vulcanizate containing no colouring agent. Also vulcanizates with Co P. P. showed the highest tensile strength and elongation at break values after thermal ageing.

The SBR vulcanizates were subjected to shelf ageing for one year then exposed to UV radiation for periods up to 16 days. The rubber samples were cut into dumbbell

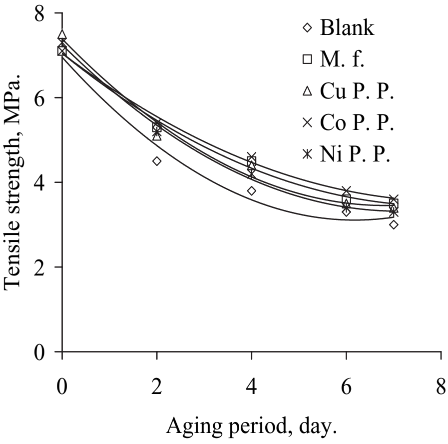


Figure 1.
Tensile strength of SBR vulcanizates with and without different metal and metal free perylene polymers vs aging period at 90 °C.

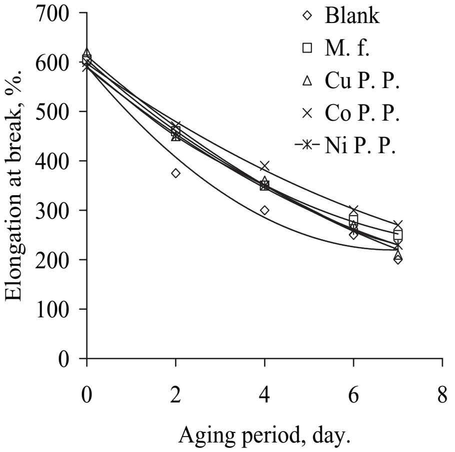


Figure 2.
Elongation at break of SBR vulcanizates with and without different metal and metal free perylene polymers vs aging period at 90 °C.

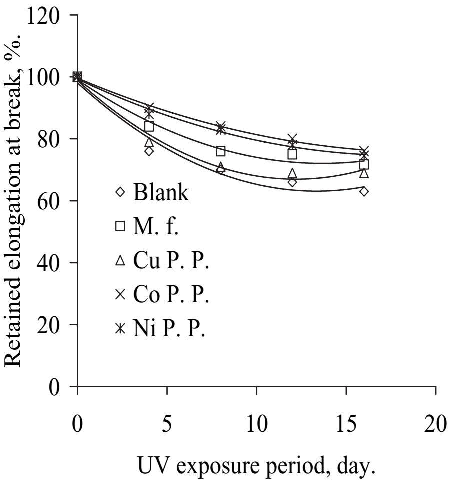


Figure 4.
Retained elongation at break vs UV exposure period, of SBR vulcanizates with and without different metal and metal free perylene polymers.

shape specimens. Then, the dumbbells were exposed to 20% strain during the exposure to UV radiation. Figures 3 and 4 illustrate that the addition of metal free, Cu P.P., Co P.P. and Ni P.P. into rubber compounds improved the retained values, during exposure to UV radiation, of tensile strength and elongation at break of SBR vulcanizates. The vulcanizate containing Co P.P. showed the best performance against UV radiation. The action of metal free and metal perylene polymers as UV absorbers can be attributed to their highly conjugated system that can act as traps for the free radicals created by UV radiation. Figures 5 and 6 show that the SBR vulcanizate containing Co Pc. P. possessed better tensile strength and elongation at break values, after thermal ageing, than the blank and the vulcanizate containing Cu Pc. P. Also, Figures 7 and 8 illustrate that the stability of tensile strength and elongation at break of SBR vulcanizates against UV radiation can be arranged in the following descending order, according to the colouring agent added: Co Pc. P. > Cu Pc. P. > blank.

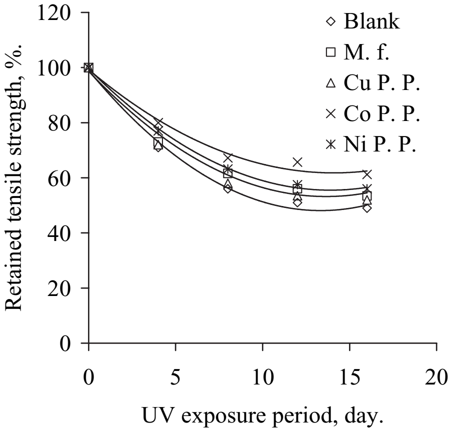


Figure 3.
Retained tensile strength vs UV exposure period, of SBR vulcanizates with and without different metal and metal free perylene polymers.

Co Pc. P. showed higher efficiency as a UV absorber than Cu Pc. P. This we believe arises because of the greater number of free electrons in the d-orbital of Co (II) than that in case of Cu (II). These free electrons can be paired with the free radicals created with UV radiation, and act as free radical scavengers.

Different concentrations of Co Pc. P. were incorporated into SBR mixes; in order to find out the optimum amount of Co Pc. P. that might have superior performance in SBR vulcanizates. The Co Pc. P. amounts, rheometric characteristics and mechanical

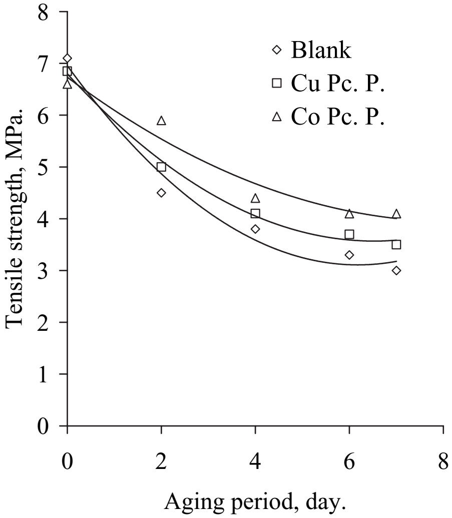


Figure 5.
Tensile strength of SBR vulcanizates with and without metal phthalocyanine polymers vs aging period, at 90 °C.

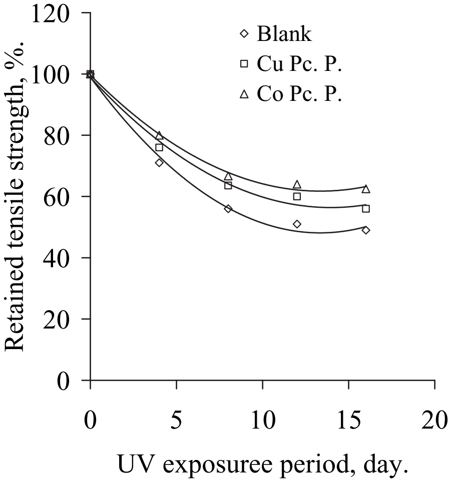


Figure 7.
Retained tensile strength of SBR vulcanizates with and without different metal phthalocyanine polymers vs UV exposure period.

properties of SBR vulcanizates are listed in Table 2. It was found that the maximum torque increased as the Co Pc. P. content increased. However, tensile strength and elongation at break of SBR vulcanizates containing 1, 3 and 5 phr Co Pc. P. were equivalent but less than those values of the blank vulcanizate. SBR vulcanizates with different Co Pc. P. amounts were subjected to shelf ageing for one year, and then exposed to accelerated thermal ageing. All the vulcanizates containing Co Pc. P. showed better tensile strength than the blank vulcanizate (Figure 9) throughout the ageing periods. The vulcanizate containing 1 phr Co Pc. P. showed superior performance to the vulcanizates with 3 and 5 phr Co Pc. P. with respect to the elongation at

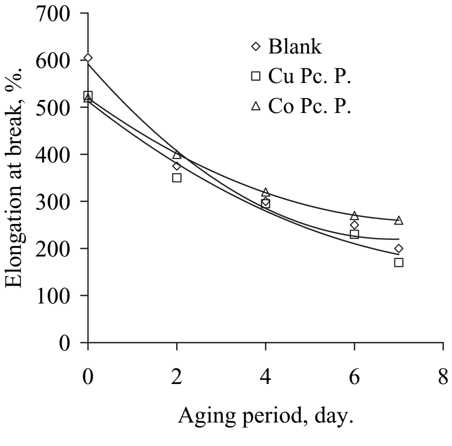


Figure 6.
Elongation at break of SBR vulcanizates with and without metal phthalocyanine polymers vs aging period, at 90 °C.

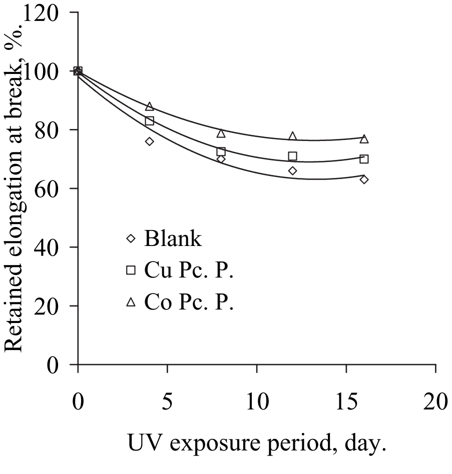


Figure 8.
Retained elongation at break (%) of SBR vulcanizates with and without different metal phthalocyanine polymers vs UV exposure period.

Table 2.
Formulations, rheometric characteristics and physico-mechanical properties of SBR vulcanizates containing different concentrations of cobalt phthalocyanine polymers.

Designation	S1	S7	S8	S9
Co Pc. P., phr	0	1	3	5
Rheometric characteristics, at 152 ± 1 °C				
Maximum torque, dNm.	75	76	78	80
Minimum torque, dNm.	11	10	10	10
Cure time, t_{c90}, min.,	20	20	21	20
Scorch time, t_{S2}, min.,	6	6	5.5	5
Cure rate index, min^{-1}	7.1	7.1	6.5	6.7
Physico-mechanical properties				
Tensile strength, MPa.	7.1	6.6	6.5	6.8
Elongation at break, %	605	520	520	520

The base recipe is the same as indicated in Table 1.

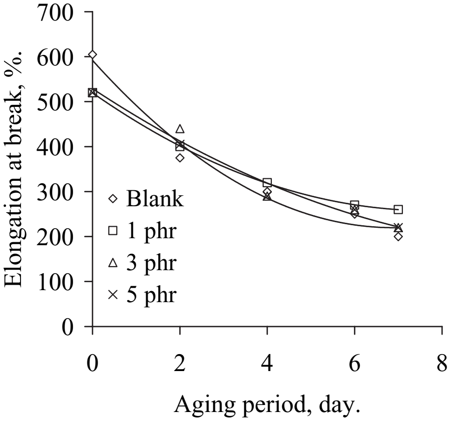


Figure 10.
Elongation at break of SBR vulcanizates with and without different amounts of cobalt phthalocyanine polymer vs aging period at 90 °C.

break during ageing (Figure 10). The SBR vulcanizates under investigation were then subjected to UV radiation. The retained values of tensile strength (Figure 11) and elongation at break (Figure 12) were plotted against the UV exposure time. The vulcanizates with different Co Pc. P. contents possessed better retained values of tensile strength and elongation at break than those of the blank vulcanizate, throughout the exposure to UV. From the thermal ageing and the UV exposure tests, it is obvious that 1 phr Co Pc. P. was good enough to improve the stability of SBR vulcanizates against thermal aging and UV radiation.

Dielectric Properties

Permittivity (ε′) and dielectric loss (ε″) of SBR vulcanizates containing different amounts of Co. Pc. P., after and before shelf ageing for 2 years, were measured over the frequency range from 100 Hz to 100 kHz at 30 °C. It is clear from Figure 13 that ε′ decreased by increasing the

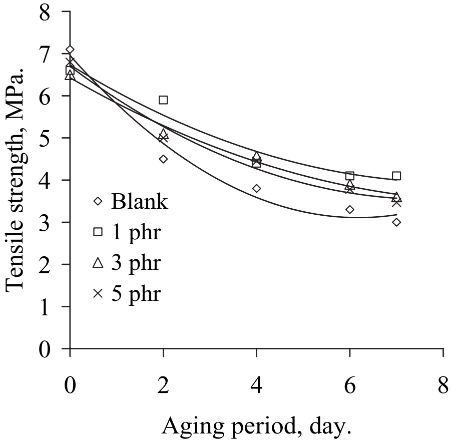


Figure 9.
Tensile strength of SBR vulcanizates with and without different amounts of cobalt phthalocyanine polymer vs aging period at 90 °C.

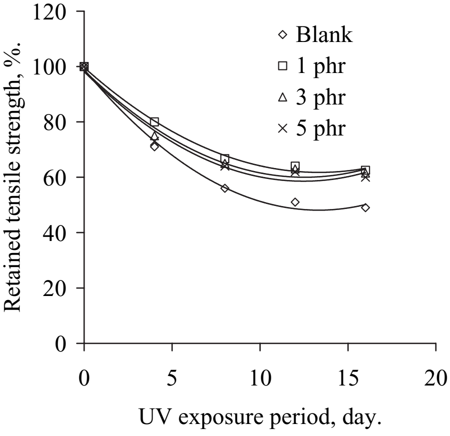


Figure 11.
Retained tensile strength of SBR vulcanizates with and without different amounts of cobalt phthalocyanine polymer vs uv exposure period.

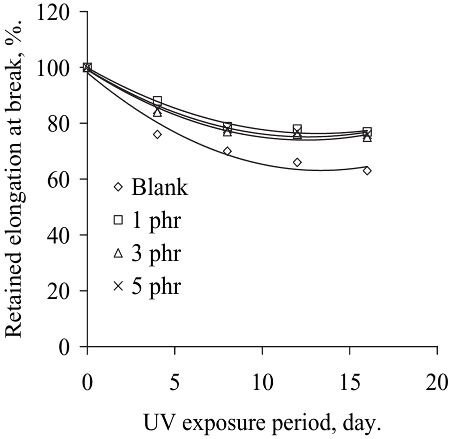


Figure 12.
Retained elongation at break of SBR vulcanizates with and without different amounts of cobalt phthalocyanine polymer vs uv exposre period.

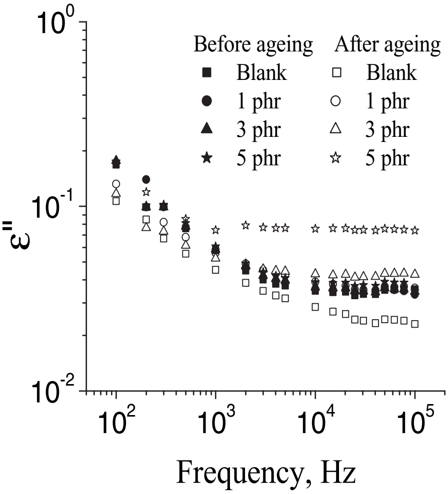


Figure 14.
Dielectric loss (ε″) of SBR vulcanizates with different amounts of Co Pc. P. vs the frequency at 30 °C.

frequency showing an anomalous dispersion, while ε′ increased by increasing Co.Pc.P. content in SBR vulcanizates. This can be attributed to the increase in the number of dipoles which leads to an increase in the orientation polarization[16]. ε′ of the vulcanizates containing 1 and 3 phr Co. Pc. P. was not affected by ageing. However, ε′ of the blank decreased but that of SBR containing 5 phr Co. Pc .P. increased by ageing. As reported in Figure 14, ε″ shows similar trend in behaviour to ε′. Figure 15 reveals that the dc conductivity (σ) is affected slightly with increasing the Co Pc. P. content before ageing, while a pronounced increase from the initially low values is noticed in case of the shelf aged samples. The curves relating ε″ vs log f are broader than Debye curve indicating that more than one relaxation process is present.

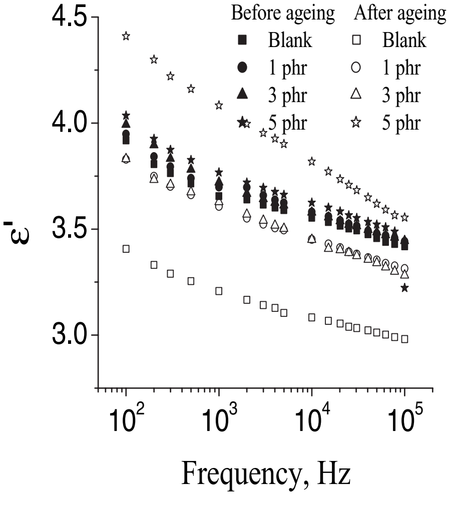


Figure 13.
Permittivity (ε′) of SBR vulcanizates with different amounts of Co Pc. P. vs the frequency at 30 °C.

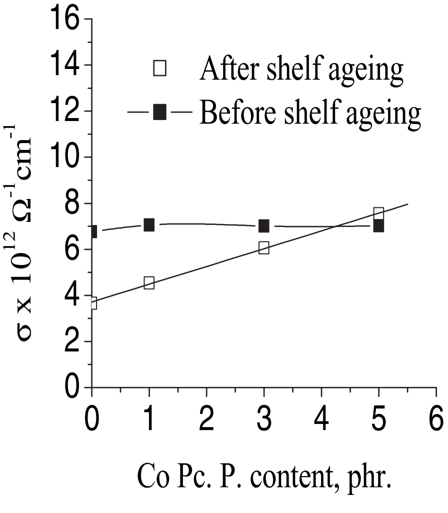


Figure 15.
dc Conductivity (σ) of SBR vulcanizates vs Co Pc. P. content at 30 °C.

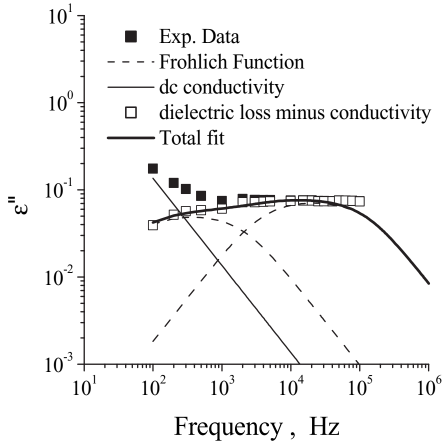


Figure 16.
The absorption curves of SBR vulcanizate with 5 phr Co Pc. P. at 30 °C, after shelf ageing.

Thus the data fitting was performed by a computer program based on all the different spectral functions[17]. The best fitting of the data was done by a superposition of two Fröhlich functions in addition to the conductivity term. Fröhlich function is represented as:

$$\varepsilon''(\omega)_{Fr} = \frac{\varepsilon_s - \varepsilon_\infty}{P}\arctan\left[\frac{\sinh \mathrm{P}/2}{\cosh \ln(\omega\bar{\tau}_{Fr})}\right]$$

P is a parameter describing the width of the distribution of relaxation times and equals $\ln(\tau_1/\tau_2)$. $\bar{\tau}_{Fr}$ is the mean relaxation time and equals $(\tau_1\tau_2)^{1/2}$.ε_s and ε_∞ are the static permittivity and the permittivity at infinite frequency, respectively. An example of the dielectric spectrum and fitting of the data for the SBR vulcanizates containing 5 phr Co.Pc.P., is illustrated graphically in Figure 16. Relaxation parameters obtained according to that fitting are given in Table 3. P is about 3 for the first relaxation time and about 4 for the second. The first absorption region which lies at $f \approx 0.25$ kHz could be attributed to Maxwell–Wagner effect arising from the interfacial polarization caused by the multi constituents of the investigated systems. The difference in ε' and σ values for the constituents of the investigated materials (Table 2) is considered to be the reason for the presence of such effect. The second absorption region with relaxation time in the order of 10^{-6} s, could be attributed to the aggregates[18] which are expected to be formed by the addition of different ingredients to rubber. This relaxation time increased slightly for the vulcanizate containing 5 phr Co. Pc .P. This may be due to an increase in the aggregate size.

Conclusions

1. Cobalt perylene polymer had superior performance, as antioxidant for SBR vulcanizates, to nickel, metal free and copper perylene polymers.
2. Metal free and metal perylene polymers improved the stability of SBR vulcanizates against UV radiation.
3. Cobalt phthalocyanine polymer was superior to copper phthalocyanine polymer because of improving thermal ageing and UV resistance of SBR vulcanizates.
4. One phr was the optimum concentration of cobalt phthalocyanine polymer to be used as antioxidant or as UV stabilizer for SBR vulcanizates.
5. Permittivity and dielectric loss of the SBR vulcanizates with and without different Co Pc. P. amounts decrease as the frequency increases. However, at high

Table 3.
Relaxation parameters of SBR vulcanizates with different Co. Pc.P. amounts.

Sample	Before aging			After aging		
	$\tau_1 \times 10^4$ s	$\tau_2 \times 10^6$ s	$\sigma \times 10^{12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$	$\tau_1 \times 10^4$ s	$\tau_2 \times 10^6$ s	$\sigma \times 10^{12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$
Blank	4.925	4.323	6.76	4.581	3.850	3.66
1 phr	5.295	4.292	7.06	4.581	3.851	4.54
3 phr	5.106	3.851	7.01	4.751	4.784	6.07
5 phr	5.295	4.292	7.02	4.418	7.387	7.54

frequencies a slight change in ε'' was obtained.

6. Permittivity and dielectric loss of the SBR vulcanizates increase with increasing Co Pc. P. content, after shelf ageing.
7. The dc conductivity of SBR vulcanizates increases sharply with increasing the Co Pc. P. content after shelf aging.

In the future, a proper statistical analysis of the collected data will be accurately performed in order to separate the contribution of the measurements errors from the differences in performance shown by the different materials.

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