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Effect of Silica on Mechanical Properties and Degradation of Natural Rubber/Ethylene-Vinylacetate Copolymer Blends

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NR · Ethylene-vinylacetate copolymer · Blend · γ-radiation · Ozone resistance

NR · Ethylen-Vinylacetat-Copolymer · Verschnitt · γ-Strahlung · Ozonbeständigkeit

Blends of NR and ethylene-vinylacetate copolymer (EVA), having different proportions of the components were prepared in an internal mixer and their vulcanizates evaluated for technological properties. The effect of precipitated silica on the properties and degradation of the blends was studied at different loadings. Results indicated that precipitated silica improved tear strength and did not affect tensile strength of the blends having a higher proportion of NR. Silica adversely affected most of the technological properties, except compression set of the EVA rich blends. But, it improved the resistance to degradation by γ-radiation and ozone, of the NR/EVA blends.

Die Wirkung von Kieselsäure auf die mechanischen Eigenschaften und die Ozon- und Strahlenbeständigkeit von Verschnitten aus Naturkautschuk und Ethylen-Vinylacetat-Copolymer

Verschnitte aus NR und Ethylen-Vinylacetat-Copolymer (EVA) mit wechselnden Anteilen der beiden Komponenten wurden in einem Innenmischer hergestellt. Die physikalisch-technologischen Eigenschaften und die Strahlen- un[illegible]beständigkeit der unterschiedliche Mengen gefällter Kieselsäure ent[illegible] den Vulkanisate wurden untersucht. Gefällte Kieselsäure verbessert in Verschnitten mit einem hohen NR-Anteil die Weiterreißfestigkeit, ohne die Reißfestigkeit zu beeinträchtigen, verschlechtert aber in Verschnitten mit einem hohen EVA-Gehalt alle untersuchten Eigenschaften mit Ausnahme des Druckverformungsrests. Die Beständigkeit gegen γ-Strahlung und Ozon wird durch gefällte Kieselsäure erhöht.

1 Introduction

Blending of polymers to achieve diverse technological requirements has become a common practice today. Blends of NR and cis,1-4 polybutadiene rubber (BR), NR and ethylene-propylene diene rubber (EPDM), nitrile rubber (NBR) and poly (vinyl chloride) and that of NR and polypropylene [1–4] are some examples in this line. Selection of elastomers for blending is to be done with utmost care, in order to minimise problems such as phase separation, cure rate mismatch and preferential migration of compounding ingredients to one of the components of the blend, which usually results in very poor mechanical properties for the blend. NR has excellent mechanical properties and good processability. However, its resistance to thermal ageing, hig[illegible]ergy radiation, oxidation and ozonolysis is very poor, due [illegible]e presence of reactive double bonds in the main chain. Properties of ethylene-vinyl acetate copolymer (EVA) depend on its vinylacetate content. If the vinylacetate content is lower, i.e., in the range of 15–30 %, it behaves as a thermoplastic elastomer. This copolymer has a saturated backbone structure and hence exhibits excellent weathering, oxidation and ozone resistance. To some extent, it has thermoplastic processing characteristics, too. Hence, it is expected that useful blends could be developed of NR and EVA if it is possible to combine the good properties of both these elastomers. We have already reported [5] the effects of three different curing systems on the kinetics of vulcanization and mechanical properties of NR/EVA blends. A mixed cure system, consisting of sulphur and dicumyl peroxide, was found to give better technological properties for NR/EVA blends and hence this system was selected for the present work.

All rubber compounds normally contain some filler, either reinforcing or non-reinforcing. Effects of fillers on processability and mechanical properties of elastomers have been thoroughly explored and can be predicted with good accuracy. However, in elastomer blends, the effects of fillers are quite unpredictable, since several factors such as distribution, dispersion and interaction of the filler with the components of the blend may vary widely. In this work, our observations of the effect of precipitated silica on mechanical properties and degradation of NR/EVA blends are presented.

2 Experimental

2.1 Materials used

NR, used for the study was ISNR-5 grade. EVA, having vinyl-acetate content of 18 %, used for this work was Exxon 218 of Exxon Chemical Company, USA. Precipitated silica, Insil VN_3, was supplied by Degussa AG, Fed. Rep. of Germany. All other ingredients such as dicumyl peroxide (DCP) having 40 % active ingredient, sulphur, stearic acid, zinc oxide, accelerators etc. were commercial grade rubber chemicals.

2.2 Preparation and compounding of blends

Blends of NR and EVA were prepared in an internal mixer (Shaw KO Intermix), set at a temperature of 80 °C and speed of 60 rpm. NR was masticated for 2,0 min and then EVA added and blended for another 2,5 min. The blend was sheeted out in a two-roll mill and again blended in the intermix for 1,0 min and finally sheeted out on the mill. Blends containing 0, 20, 40, 50, 60, 80 and 100 % of EVA were prepared and these were designated as A, C, E, F, G, I and J, respectively. Compounds of the blends were prepared as per the formulations given in *Table 1*. For compounding those blends in which the proportion of EVA was 80 % or more, the rolls of the mill were warmed by passing steam, to about 80 °C. Optimum cure times of the blends were determined at 160 °C using Monsanto rheometer 100. Vulcanisates for various tests were prepared in a steam heated hydraulic press set at 160 °C. Test specimens were punched out from the vulcanised sheets for tensile and tear strength tests.

Table 1. **Formulations**

Ingredients	Filler loading phr			
	S_0	S_{15}	S_{30}	S_{45}
Polymer	100	100	100	100
Zinc oxide	5,0	5,0	5,0	5,0
Stearic acid	1,5	1,5	1,5	1.5
MBTS	0,8	0,8	0,8	0.8
Sulphur	2,5	2,5	2,5	2,5
Dicumyl peroxide	4,0	4,0	4 0	4.0
Styrenated phenol	1,5	1,5	1.5	1,5
Precipitated silica (INSIL VN_3)	0,0	15,0	30,0	45.0
Naphthenic oil	0,0	1.5	3,0	4.5
Diethylene glycol	0,0	1,0	1,5	2,0

2.3 Testing of the samples

Properties such as tensile strength, tear strength, hardness, compression set, etc. were determined according to the relevant ASTM/B.S. procedures and abrasion resistance was tested according to DIN 53516 procedure. Ozone resistance of the blends was tested by exposing samples to ozonised air having 50 pphm ozone concentration, at a temperature of 38 °C, in a MAST ozone test chamber. Resistance to high energy radiation was studied by exposing tensile test specimens to γ-rays from a ^{60}Co source and then finding out the percentage retention of tensile strength. The reinforcing activity of silica in the pure components of the blends (Compounds A and J) was determined by finding out the volume fraction of rubber of the unfilled (V_{ro}) and silica filled (V_{rf}) vulcanizates swollen in xylene, according to the method described by *Ellis* and *Welding* [6]. A plot of V_{ro}/V_{rf} against e^{-z} was made and the slopes of the straight lines calculated. z is the weight fraction of filler in the vulcanizate. Higher slope indicated better reinforcing activity [7].

3 Results and discussion

3.1 Effect of silica on tensile and tear strength

Effect of loading of silica on the tensile strength of NR/EVA blends is shown in Figure 1. At 45 phr level, silica adversely affected the tensile strength of the blends. However, loading upto 30 phr did not seriously affect the tensile strength of those *blends which contained a higher proportion of NR. But in* EVA rich blends, silica reduced the tensile strength even at 15 phr loading. From *Figure* 2, it is clear that tear strength increased with increase in proportion of EVA in the blend. Addition of silica increased the tear strength of those blends which had a higher proportion of NR. But in EVA rich blends, tear strength decreased with the addition of silica.

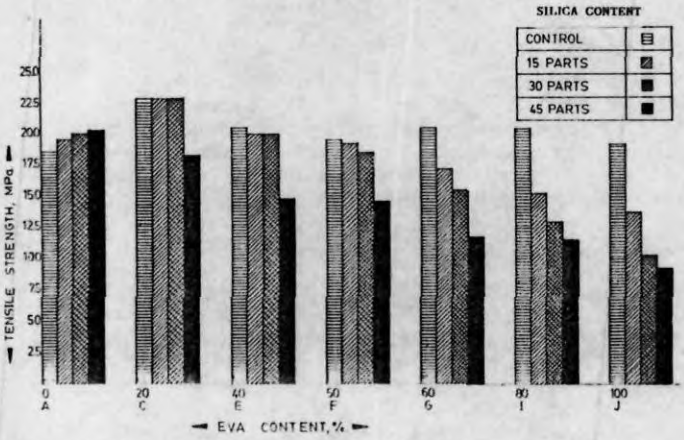

Figure 1. Change of tensile strength with blend ratio and silica content

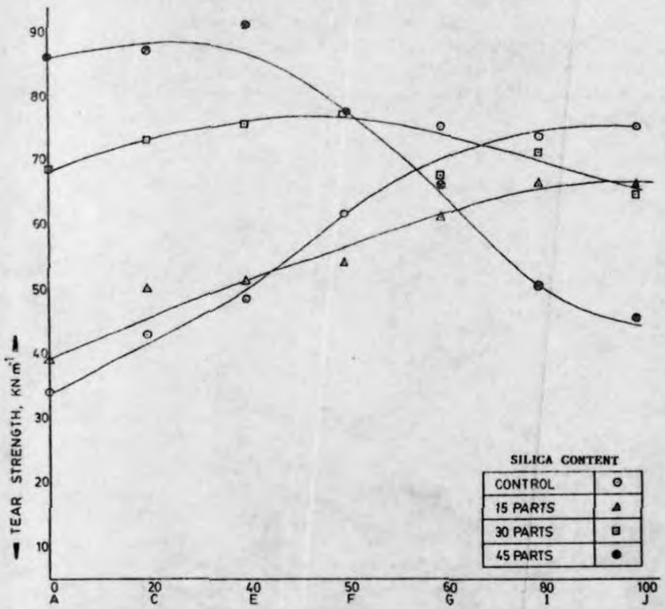

Figure 2. Change of tear strength with blend ratio and silica content

The above observations on tensile and tear strength of silica filled NR/EVA blends can be explained based on the morphology of the blends and distribution of the filler in each phase of the blend. We have already reported that in NR/EVA blends, EVA also formed a continuous phase when its proportion was 40 % or more, due to its lower melt viscosity and that NR remained as dispersed particles when its percentage was 40 or below [8]. It is also well known that silica has better affinity towards polar polymers and preferentially gets distributed into the polar component of the blend [9, 10]. Considering the above, it is possible that silica got distributed preferentially in the EVA phase of those blends in which EVA also formed a continuous phase (blends E to J). Identical slopes of the straight lines obtained by plotting V_{ro}/V_{rf} against e^{-z} (*Figure 3*) for the silica filled EVA and NR compounds, especially in the region of higher silica loading, indicated that reinforcing activity of silica in both the polymers is almost same. But it is already established that strong physico-chemical interactions between filler and polymer can reduce the extent of crystallization of the polymer [11]. Hence, the basic reason for the lower tensile and tear strength of the silica filled EVA and blends containing higher proportion of EVA appears to be due to lower extent of crystallization of the EVA. For NR and NR rich blends, silica improved the tear strength and tensile strength due to reinforcement of the NR phase. However, lower tensile strength of the 45 phr silica loaded blends which contained a higher proportion of NR, remains unexplained.

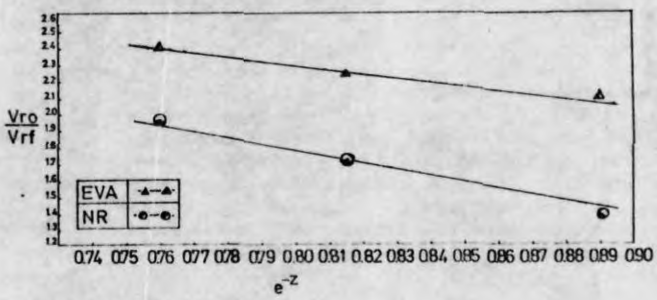

Figure 3. Plots of V_{ro}/V_{rf} against e^{-z}

3.2 Modulus, hardness and abrasion loss

The modulus and the hardness values shown in *Figures 4 and 5* respectively, increased with loading of silica and this effect was more pronounced in blends A to F in which NR remained as a continuous phase. The increased modulus and hardness was due to reduced elasticity of the filled blends. For NR (compound A) abrasion loss reduced with loading of silica due to its reinforcing effect. But in blends as well as in pure EVA (B to I and J) addition of silica increased abrasion loss (*Figure 6*). This observation again pointed out the fact that the expected property increase due to reinforcement of the EVA phase was offset by the reverse effect caused by the decrease in the extent of crystallization of the EVA phase. This is further supported by the compression set behaviour of the silica filled NR/EVA blends.

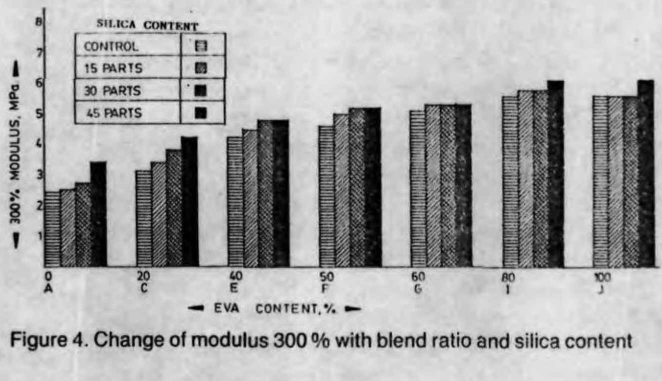

Figure 4. Change of modulus 300 % with blend ratio and silica content

3.3 Effect on compression set

Figure 7 shows the compression set behaviour of silica filled NR/EVA blends. Compression set of NR (compound A) in-

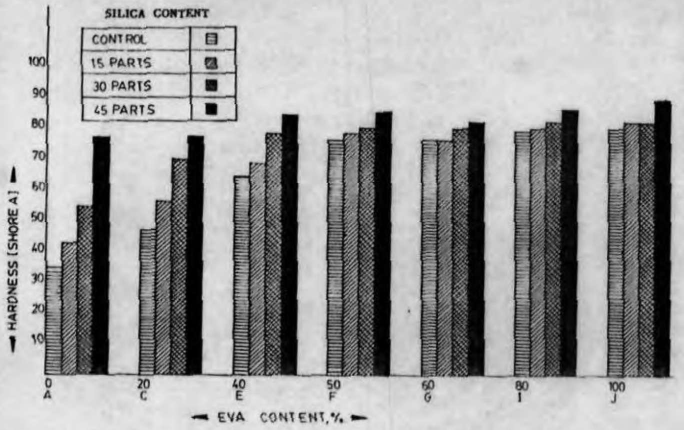

Figure 5. Change of hardness (Shore A) with blend ratio and silica content

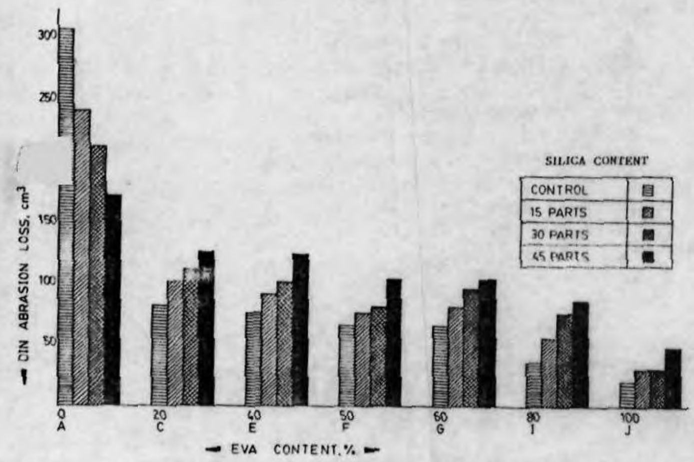

Figure 6. Change of DIN abrasion loss with blend ratio and silica content

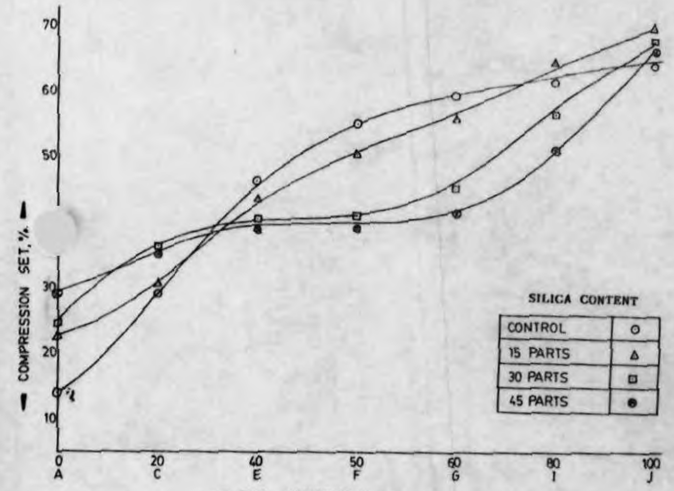

Figure 7. Change of compression set with blend ratio and silica content

creased with loading of silica filler, which is typical for compounds containing high reinforcing filler. However, this tendency was reversed from blend E onwards in which EVA also showed phase continuity. In these cases, compression set was lower for the blends when filler loading was increased. For crystallizing elastomers, it is reported that compression set values decreased when the crystallizing tendency was reduced [12–14]. In the present case also, strong physico-chemical interaction between EVA and silica might have adversely affected the extent of crystallization of the EVA phase, which resulted in lower compression set values of the blends, as the filler loading was increased.

3.4 Effect on radiation resistance

Retention of tensile strength of silica filled NR/EVA blends, after exposing the test samples to 20 Mrad of γ-radiation, from a ^{60}Co source, is presented in *Figure 8*. As the EVA content increased, resistance to degradation by γ-radiation also increased as evidenced by higher retention of tensile strength. This effect was found to be more pronounced in blends E to I in which EVA formed a continuous phase. Silica enhanced the resistance to degradation by radiation and this effect increased with loading of silica. During irradiation by γ-rays two types of reactions take place, i.e., degradation and crosslinking of the polymer chains. When the former reaction predominates, the strength of the material is decreased. Precipitated silica is found to favour the second type of reaction, as shown by better tensile retention of silica filled NR, EVA and their blends.

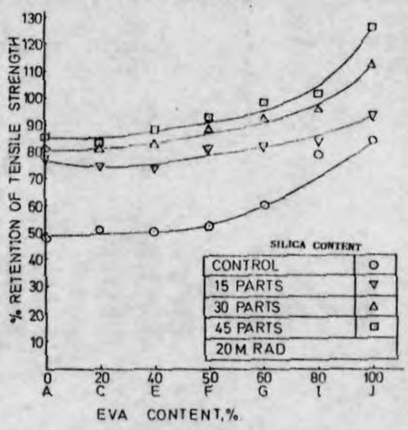

Figure 8. Change of retention of tensile strength with blend ratio and silica content

3.5 Effect on ozone resistance

Figure 9 is the photograph of samples exposed to ozonised air for 8 h (top) and 85 h (bottom) respectively. In the unfilled blend (C_3So) small cracks were initiated after 8 h of exposure. This sample developed deep cracks as seen in the photograph after

Figure 9. Photograph of blend C (80:20, NR:EVA) having different silica content after 8 h and 85 h of exposure to ozonised air

85 h of exposure. On the other hand, samples C_3S_{15}, C_3S_{30} and C_3S_{45} which contained 15, 30 and 45 phr precipitated silica respectively, did not develop any crack during this period. Addition of silica increased the modulus of the blend and reduced its elongation. Hence, the stress required to produce the critical strain, necessary for the ozone attack to take place, might be much higher in silica filled blends.

4 Conclusions

In NR/EVA blends, precipitated silica improved the tear strength and did not affect the tensile strength when the proportion of NR in the blend was higher. Addition of silica adversely affected the technological properties, except compression set, of the blends having a higher proportion of EVA. Silica imparted resistance to degradation by γ-radiation and ozone, for NR/EVA blends.

References

[1] C. S. L. Baker and I. R. Wallace, J. Nat. Rubber Res. **1** (1/1986).
[2] N. M. Mathew, K. T. Thomas and E. Philipose, Indian J. Nat. Rubber Res. **1** (1/1988) 8.
[3] C. Y. Almond, Rubber Chem. Technol. **35** (1962) 716.
[4] D. J. Elliott, Kautsch. Gummi, Kunstst. **39** (1986) 621.
[5] A. T. Koshy, B. Kuriakose and S. Thomas, Indian J. Nat. Rubber Res. **3** (2/1990) 7.
[6] B. Ellis and G. N. Welding, Rubber Chem. Technol. **37** (1964) 563.
[7] R. Mukhopadhyay and S. K. De, Rubber Chem. Technol. **52** (1979) 263.
[8] A. T. Koshy, B. Kuriakose and S. Thomas, Polym. Degrad. Stab. (in press).
[9] A.Leehtenboehmer, H. G. Moneypenny and F. Mersch, Brit. Polym. J. **22** (1990) 265.
[10] P. J. Corish and B. D. W. Powell, Rubber Chem. Technol. **47** (1974) 482.
[11] S. Thomas, Int. J. Polym. Mater **12** (1987) 1.
[12] A. Stevenson, Kautsch. Gummi, Kunstst. **37** (1984) 105.
[13] L. R. Barker, NR Technol. **18** (1/1987) 13.
[14] K. M. George, P. V. Pillai and N.M. Mathew, Indian J. Nat. Rubber Res. **4** (1/1991) (in press).

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Hinweise · Notes

Im VDI-Handbuch Reinhaltung der Luft sind in den Monaten Juni bis August folgende VDI-Richtlinien erschienen:

VDI 2114 – Emissionsminderung. Thermische Abfallbehandlung. Verbrennung von Hausmüll und hausmüllähnlichen Abfällen. Juni 1992. Ersetzt den Entwurf vom März 1989.
VDI 3926 Blatt 1 Prüfung von Filtermedien. Juni 1992. Entwurf
VDI 3928 – Abgasreinigung durch Chemisorption. Juni 1992. Ersetzt den Entwurf vom März 1990.
VDI 4300 Blatt 1 Messen von Innenraumluftverunreinigungen. Allgemeine Aspekte der Meßstrategie. Juni 1992. Entwurf.
VDI 2580 – Emissionsminderung. Anlagen zur Herstellung von Industrierußen (Carbon Black). Juli 1992. Ersetzt den Entwurf vom August 1984.
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