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Thermal Ageing of Thermoplastic Elastomeric Natural Rubber-Low Density Polyethylene Blends

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ABSTRACT

The effect of amount and type of antioxidants on the mechanical properties in the 65/35 NR/LDPE blend was investigated using thermal aging both unstressed and under tensile elongation. The ageing of a family of thermoplastic elastomers from blends of natural rubber and low density polyethylene was studied using thermal treatments at 60°C for 3 days, and 70°C for 5 days. Thermal ageing of the blends of two polymers caused the tensile properties to deteriorate, especially at longer times or higher temperatures of ageing. When an antioxidant for rubber or heat or light stabilizer for polyethylene was added, thermo-oxidative stability was increased. Mechanical properties also indicated changes due to ageing. Samples were prepared with dicumyl peroxide crosslinking agent. The antioxidants used were (i) N, N'-diphenyl-1,4-phenylenediamine; DPPD, (ii) Tetrakis[methylene(3,5-di-tert-butyl hydroxyhydrocinnamate)]methane; Irganox, and (iii) Tris(2,4-di-tert-butylphenyl) phosphate; Irgafos. All of the antioxidants produced considerable improvement in the thermal-resistance. The most effective one was the combination of Irganox and Irgafos even though the continuous phase in these blends was low-density polyethylene.

Key words: natural rubber, low-density polyethylene, thermal ageing

INTRODUCTION

Blending of two or more existing polymers or copolymers is nowadays a widely accepted method in order to respond to the demand of new materials. Blending of two polymers usually gives better properties than those of a single polymer.

The emergence of thermoplastic elastomers (TPEs) is one of the important developments in the field of polymer science and technology in recent years. TPEs are a new class of materials which combine the properties of vulcanized rubbers with the ease of processability of thermoplastics. TPEs based on rubber-plastic blends have potential for many applications in engineering and consumer goods (Walker, 1979 and Holed *et al*., 1996). The outdoor applications such as automotive window seals and footwear are necessary to develop satisfactory stabilization systems to ensure prolonged life. Stabilizers are required to protect the compounds from thermal degradation (at the elevated temperatures used in processing) and photo-degradation caused by the ultraviolet irradiation (UV) in sunlight (Adam *et al*., 1991 and Cataldo, 2001). Although some stabilizers have a wide application and can be used with many different polymers, some additives act as a stabilizer with one polymer and as a pro-degradant for another. Therefore, when choosing

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a stabilizing system for a polymer blend, it is necessary to know the effect of the stabilizer on both polymeric components. Similarly, any possible pro-degradant action of any other additives must be considered (Bhowmick *et al.*, 2002 and Sulekha *et al.*, 2004).

Ideally a stabilizer will have a beneficial effect on both component polymers but in many cases it will be present to protect one of the components only. In this case it is unfortunate that it will usually become distributed into both polymeric components during compounding and subsequent fabrication. This is a common problem for all polymer blends, not for the thermoplastic elastomers.

As rubber and plastics are generally stabilized with different types of additives. These thermoplastic elastomeric compositions consist of continuous plastics matrix and dispersed rubber domains, it is worth while to investigate which type of antioxidants would be most efficient in protecting these materials. The effect of commercial antioxidants on the thermal degradation behavior of a family of TPE based on natural rubber/low-density polyethylene blends was reported. There are several antioxidants that provide the good protection against oxidation extending outdoor lifetime.

The object of this experiment was to study the effect of amount and type of antioxidants on the mechanical properties in the 65/35 NR/LDPE blen under thermal ageing.

MATERIALS AND METHODS

Materials

Natural rubber (NR) supplied by Sengmui, Thailand had molecular mass 780×10^3 g/mol, intrinsic viscosity (benzene 30°C m^3/kg [η] = 0.44) and Wallance plasticity 59.0. The low density polyethylene (LDPE) supplied by Thai Petrochemical Industrial had Melt Flow Index (MFI) 40 g/10min. Dicumyl peroxide (DCP) as a crosslinking agent was supplied by Aldrich, Germany. Pigment (green) was supplied by Lucky Four, Thailand. Compounds based on the homopolymers but containing DCP were prepared to compare the effect of DCP on the individual components of the blends. The antioxidants selected for investigations were:

1. DPPD; N, N'-diphenyl-1,4-phenylenediamine, an antioxidant for rubber, supplied by Aldrich, germany.
2. Irganox; Tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane, a high molecular weight phenolic antioxidant (1178 $gmol^{-1}$) as a thermal (processing) stabilizer for plastics, supplied by Ciba Specialty Chemicals, Switzerland.
3. Irgafos; Tris (2,4-di-tert-butylphenyl), a phosphate stabilizer for protection against discoloration and change of physical properties caused by excessive heat exposure for plastics, supplied by Ciba Specialty Chemicals, Switzerland.

Mixing and vulcanization procedures

The blends of natural rubber and low density polyethylene with compositions were given in Table 1. The blends were prepared in a Brabender Plasticorder by melt mixing the plastic and the rubber at 130°C at rotor speed of 60 rpm (Cam Blade) for approximately 7 minutes. The polyethylene was melted first and the rubber was then added and blended. The antioxidants and pigment were mixed at this stage. The curative DCP was added at a level of 0.7 part per hundred of resin (phr) and the mixing continued until the torque increased by 3-4 units. The compounds based on the homopolymers containing DCP (NR/DCP) were also prepared. The mixes were sheeted with the two-roll mill and kept at room temperature for a day.

To vulcanize the blend, the mixes were compressive molded using a hydraulic hot press at 170°C, under pressure 17 MPa. The

Table 1 Compositions of the rubber-polyethylene blends.

Sample Code	NR:LDPE (phr)	DCP (phr)	DPPD (phr)	Irganox (phr)	Irgafos (phr)
N100C	100:00	0.7	-	-	-
N65C	65:35	0.7	-	-	-
$65N_1$	65:35	0.7	0.5	-	-
$65N_2$	65:35	0.7	0.75	-	-
$65N_3$	65:35	0.7	1	-	-
$65I_1$	65:35	0.7	-	0.5	-
$65I_2$	65:35	0.7	-	0.75	-
$65I_3$	65:35	0.7	-	1	-
$65N_1I$	65:35	0.7	0.25	0.75	-
$65N_2I$	65:35	0.7	0.5	0.5	-
$65N_3I$	65:35	0.7	0.75	0.25	-
$65I_1F_1$	65:35	0.7	-	0.5	0.1
$65I_1F_2$	65:35	0.7	-	0.5	0.25
$65I_1F_3$	65:35	0.7	-	0.5	0.5

Note All blends contain 0.5 phr of pigment

vulcanization times were calculated from a decomposition half-life of DCP. In the present study, at the cure temperature of 170°C, the decomposition half-life of DCP was approximately 1.7 min. Consequently, the cure time of about 12 min was used to achieve approximately 99.2 % cure.

Ageing

Accelerated thermal ageing tests were followed in the present investigation. It was well known that natural rubber without any stabilizer degraded to a liquid at high temperature or long ageing times. The thermal ageing experiment was performed in a closed oven using various times and temperatures; 60° for 3 days, and 70°C for 5 days. The aged samples were allowed to rest at room temperature for 30 min and the physical properties were then measured.

Mechanical properties testing

Tensile testing

The vulcanized samples were cut into tensile specimens using the punching machine. The cutting die punched the sample into dumbbell-shape (Figure 1). Testing was carried out on a universal testing machine (Instron model 5569) in accordance with ASTM D412-92

The testing crosshead speed of 500 mm/min was used with a full scale load cell at 1 kN. At least 5 specimens were used for each measurement. The following tensile properties were measured: 100% modulus, 300% modulus, tensile strength and elongation at break.

Calculation

Moduli were calculated from the equation,

$$\sigma = F/A \qquad (1)$$

where σ = stress (MPa)
F = observed force (N)
A = cross-sectional area of unstretched specimen (mm^2)

1. 100 % modulus = stress at 100% elongation
2. 300 % modulus = stress at 300% elongation
3. Tensile strength = stress at rupture of specimen

4. The percentage of elongation at break

The percentage of elongation at break was calculated from the equation

$$\text{Percentage of elongation} = (l-l_o)/l_o \times 100 \quad (2)$$

where l = observed distance between the grips extensometer on the stretched specimen (mm)

l_o = original distance between the extensometer (mm)

Hardness

The hardness of the specimen was measured using Shore A hardness tester (Wallace). The 6 mm thick specimen was placed on a test platform. The indenter was held in a vertical position to provide indentations at least 12 mm from any edge of the specimen. Five measurements were made at different positions on the test piece at least 6 mm apart. An average of the five measurements was taken as the hardness value of the test sample.

Abrasion

The 12 mm thick specimens about were detected the density by Densimeter. The weight of the specimens was measured before and after the test friction by DIN abrasion (ZWICK). The equation for loss volume is as follows:

$$\text{Loss volume} = m_1 - m_2 / D \quad (3)$$

where m_1 = weight of the specimen before testing

m_2 = weight of the specimen after testing

D = density of the specimen

Compression set

The original thickness of the specimens was measured. The test specimens were placed between the plates of the compression device with the spacers on each side, allowing sufficient clearance for the bulging of the rubber when compressed (Figure 2).

The specimens were held at 70°C for 22 hr, then, rested on a poor thermally conducting surface, such as wood, for further 30 min before making the measurement of the final thickness.

The calculation of compression set as follow:

$$C_B = [(t_o - t_i) / (t_o - t_n)] \times 100 \quad (4)$$

where: C_B = compression set expressed as percentage of the original deflection

t_o = original thickness of specimen

t_i = final thickness of specimen

t_n = thickness of the spacer bar used (4.5 mm)

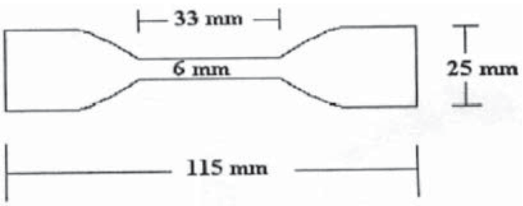

Figure 1 Tensile test specimens.

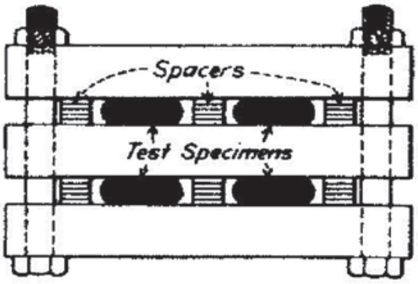

Figure 2 Device for compression set test under constant deflection.

RESULTS AND DISCUSSION

Mechanical properties

The results of the tensile tests on the conditioned samples containing different amounts and types of antioxidants were shown in Figures 3 and 4, respectively. The effect of DPPD content on the tensile properties of the 65/35 NR/LDPE blend was shown in the Figure 3. It was noticed that the stress-strain curves decreased as the DPPD increased. The blend with 0.5 phr of DPPD ($65N_1$) showed the highest values of tensile strength and elongation at break, which can be explained that the higher levels of antioxidant may retard the cure and reduce the efficiency of peroxide. However, the use of DPPD as an antioxidant was not appropriate for the 65/35 NR/LDPE blend because lots of bubbles existed on the sample including the change of the color from green to dusky green similar to those found in the case of 70/30 NR/LDPE blend (Bhowmick *et al*., 2001).

Figure 3 showed the effect of Irganox content on the tensile properties of the 65/35 NR/LDPE blend. It was observed that the blend with the lowest amount of Irganox (0.5phr, $65I_1$) showed the highest value of tensile and elongation at break. It was then obviously confirmed that the tensile properties of blends depended strongly on the concentration of Irganox. Comparing to a combination of DPPD and Irganox (Figure 4), the tensile properties was decreasing with increasing DPPD content in the blend. This is accordance with what Bhowmick et al. observed in studying the effect of stabilizers in photodegradation of 70/30 NR/LDPE (Bhowmick et al., 2001).

Figure 4 showed the plot of stress versus strain for the 65/35 NR/LDPE blend with and without additives, i.e., DPPD and Irganox. It can be seen that the tensile strength of the blends decreased with the addition of antioxidants. Obviously, the blend with 1 phr of DPPD ($65N_3$) showed the lowest value of tensile strength, which

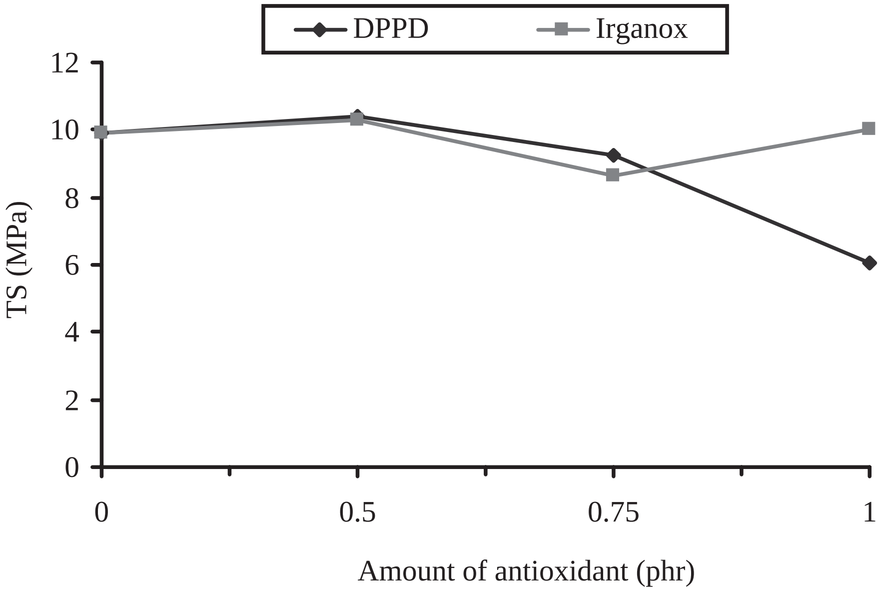

Figure 3 Tensile strength versus the amount of antioxidant in the 65/35 NR/LDPE blend with various types of antioxidant.

could be owing to too many bubbles inside the sample as discussed previously. But, the elongation at break value of the blend increased with increasing the amount of Irganox. It should be noted that the type of antioxidant had strong effect on the tensile properties of the 65/35 NR/LDPE blend.

As a result, it is of interest to say that the performance of tensile properties depended strongly on the amount and type of antioxidant in which all blends with N,N¢-diphenyl-1,4-phenylenediamine ($65N_1$, $65N_2$, $65N_3$, $65N_1I$, $65N_2I$, and $65N_3I$) presented low tensile strength and elongation at break due to too many bubbles on the sample. Hence, Irganox was considered to be a suitable antioxidant for the 65/35 NR/LDPE blend. This is accordance with what Bhowmick *et al*. observed in studying the effect of etabilizer inphotodegradation of 70/130 NR/LDPE (Bohowmck *et al.*, 2001)

Table 2 depicted the mechanical properties i.e., hardness, compression set, and abrasion of the blend with various amounts and types of antioxidant. It was found that the mechanical properties decreased with increasing antioxidant loading. Thus, the concentration of antioxidant had strongly effect on the efficiency of peroxide as a curing agent in a blend of NR with LDPE. However, the antioxidant was required to protect the blend from UV, natural sunlight and thermal degradation. So, the suitable type and amount of antioxidant considered from the mechanical properties and the appearance on the sample was Irganox with the lowest loading (0.5phr.) into the blends. Hence, the 65/35 NR/LDPE blend with 0.5 phr Irganox will be fixed to further study in the next section.

It should be noted here that one of the outstanding properties of N100C (pure NR), shown in Table 2, was its high tensile strength due to strain-induced crystallization. Therefore, the tensile strength of natural rubber can not be detectable, whereas that of all blends can be improved as given in Table 2. Moreover, it can be seen that the pure natural rubber had low value of compression set, indicating that the rubber will

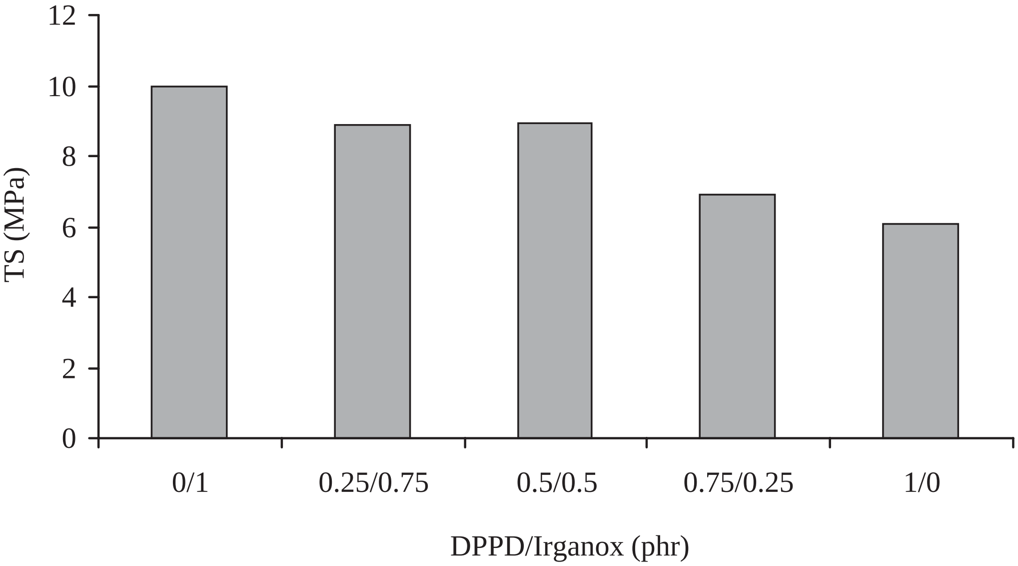

Figure 4 Tensile strength versus the antioxidant combination of DPPD and Irganox in the 65/35 NR/LDPE blend.

Table 2 Mechanical properties of various types and amounts of the 65/35 NR/LDPE blend.

Sample Code	Wt% NR	DPPD (phr)	Irganox (phr)	Stress at max load (MPa)	Elongation at break (%)	100% modulus (MPa)	300% modulus	Hardness (shore A)	Compression set (%)	Loss volum (cm^3)
N100C	100	-	-	-	-	-	-	29.16	8.27	-
N65C	65	-	-	9.92	595.30	1.88	3.28	66.52	45.30	0.22
$65N_1$	65	0.50	-	10.43	718.22	1.74	2.08	63.13	52.50	0.28
$65N_2$	65	0.75	-	9.23	670.66	1.60	2.76	62.68	52.95	0.28
$65N_3$	65	1	-	6.06	589.20	1.84	2.94	62.05	55.08	0.29
$65I_1$	65	-	0.50	10.32	621.32	1.83	3.22	63.98	51.51	0.23
$65I_2$	65	-	0.75	8.62	595.74	1.74	3.01	63.05	50.63	0.24
$65I_3$	65	-	1	10.00	624.98	1.77	3.01	62.85	47.93	0.25
$65N_1I$	65	0.25	0.75	8.89	608.90	1.67	2.93	62.25	44.68	0.25
$65N_2I$	65	0.50	0.50	8.94	619.78	1.56	2.84	60.77	38.58	0.31
$65N_3I$	65	0.75	0.25	6.91	563.00	1.55	2.80	56.45	44.54	0.29

quickly regain its original shape after being deformed, while poor hardness. However the addition of 35wt% LDPE with various amounts and types of antioxidant showed the opposite trend.

Effect of Irgafos on mechanical properties and thermal resistance (Fixed 0.5 phr Irgafos)

As well known, Irganox phenolic antioxidants function as oxygen-centered radical scavengers to provide processing and long-term thermal stability. Irgafos phosphites function as hydroperoxide decomposers to provide processing stability and color control as depicted in Figure 5.

The blends with fixed Irganox content (0.5 phr) were prepared with various amounts of Irgafos (0.1, 0.25, and 0.5 phr). In order to study the effect of Irgafos on the mechanical properties and thermal resistance in the blend of 65/35 NR/LDPE, tensile properties, hardness, compression set, and abrasion were determined and compared with the blend without Irgafos ($65I_1$). Mechanical testing under both unaged and thermal ageing was undertaken.

Unageing

After melt mixing, it was found that all blends with various amounts of Irgafos including the one without Irgafos ($65I_1$) showed the same appearance that was lack of tackiness, color green and no bubble on the sample. Table 3 illustrated the relative mechanical properties of the 65/35 NR/LDPE blend with various amounts of Irgafos. In polymer blends with Irgafos, their mechanical properties, i.e., hardness, modulus, and compression set were better than the blend without Irgafos ($65I_1$). In other words, Irgafos was believed to be capable of improving the mechanical properties in the 65/35 NR/LDPE

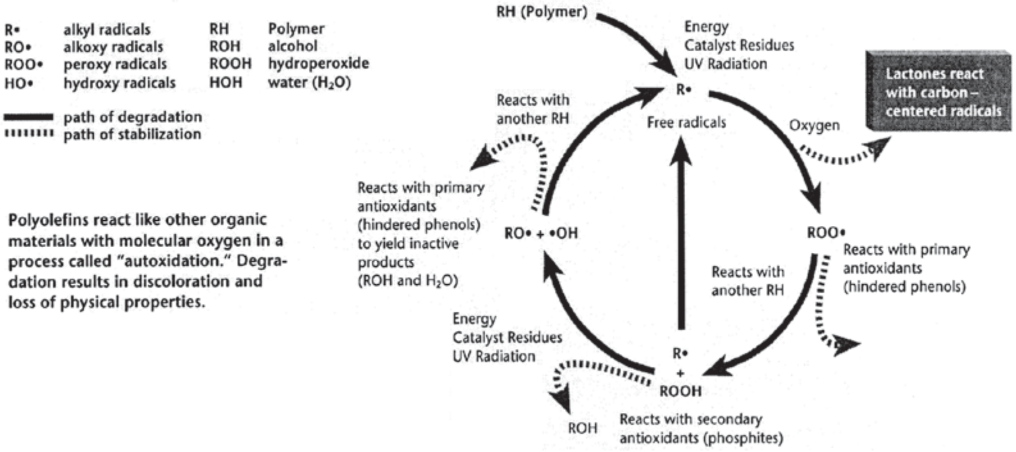

Figure 5 Schematic of auto-oxidation. (http//www.cibasc.com)

Table 3 Mechanical properties of various amount of Irgafos in 65/35 NR/LDPE blend.

Sample Code	Irgafos (phr) (MPa)	Stress at max load (%)	Elongation at break (MPa)	100% modulus (MPa)	300% modulus	Hardness (shore A)	Compression set (%)	Loss volume (cm^3)
65I1	-	10.32	621.32	1.83	3.22	63.98	51.51	0.23
65I1F1	0.1	9.12	524.78	2.02	3.74	67.56	45.55	0.22
65I1F2	0.25	9.64	575.53	1.91	3.38	68.64	48.66	0.23
65I1F3	0.5	8.26	554.62	1.82	3.24	67.82	47.06	0.23

blend with 0.5 phr Irganox. However, the concentration of Irgafos had no significant affect on their mechanical properties.

Thermal ageing

For outdoor applications, the prolonged exposure (air, sunlight, rain, etc.) resulting in the change in elastomer molecule, cannot be avoided. These changes were accelerated by oxidation from ozone and oxygen in the atmosphere, ultraviolet rays, temperature variations, and other environmental factors. Nevertheless, the effect of thermo-oxidative degradation on mechanical properties was determined in this study by varying temperatures and times; 60°C for 3 days and 70° C for 5 days.

The effect of Irgafos content on mechanical and tensile properties in the 65/35 NR/LDPE blend with and without ageing was given in Table 4 and Figure 6, respectively. It was found that the tensile properties of the blends decreased gradually with increasing the period of ageing time and temperature, possibly due to the degradation of the polymers, which also led to the reduction in the 100%, and 300% modulus, similar trend was observed in the case of 70/30 NR/LDPE blend (Bhowmick *et al.*, 2002). The hardness of the aged blends was higher than that of the unaged. This may be attributed to the crosslink density which increased due to the thermal ageing, indicating the post-vulcanization reaction during ageing (Bhowmick *et al.*, 2002). However, it was confirmed by the increase of rebounding value after thermal ageing.

Figure 6 depicted the effect of Irgafos content on the tensile properties in the blends after thermal ageing. It was discovered that the amount of Irgafos acting as a secondary antioxidant showed no significant effect on the thermo-oxidative stability of the blends. Because the thermal degradation was prevented by primary antioxidant, not secondary antioxidant. However, it was expected to be capable of protecting the

Table 4 Effect of Irgafos content on mechanical properties in 65/35 NR/LDPE blend with and without ageing.

Sample Code	Irganox (phr)	Temp (°C)	Temp (°C)	Stress at max load (MPa)	Elongation at break (%)	100% modulus (MPa)	300% modulus (MPa)	Hardness (shore A)	Compression set (%)	Loss volume (cm^3)
$65I_1F_1$	0.1	-	-	9.12	524.78	2.02	3.74	67.56	45.55	0.22
		60	3	8.49	547.14	1.88	3.38	68.43	-	-
		70	5	8.66	561.92	2.13	3.44	71.74	33.09	0.23
$65I_1F_2$	0.25	-	-	9.64	575.53	1.91	3.38	68.64	48.66	0.23
		60	3	9.66	532.84	1.98	3.85	68.60	-	-
		70	5	9.45	563.64	2.13	3.67	70.74	32.73	0.22
$65I_1F_3$	0.5	-	-	8.26	554.62	1.82	3.24	67.82	47.06	0.23
		60	3	9.00	551.85	1.92	3.46	68.74	-	-
		70	5	9.49	573.42	2.11	3.54	72.20	30.89	0.18

Note All blends contain 0.5 phr of Irganox

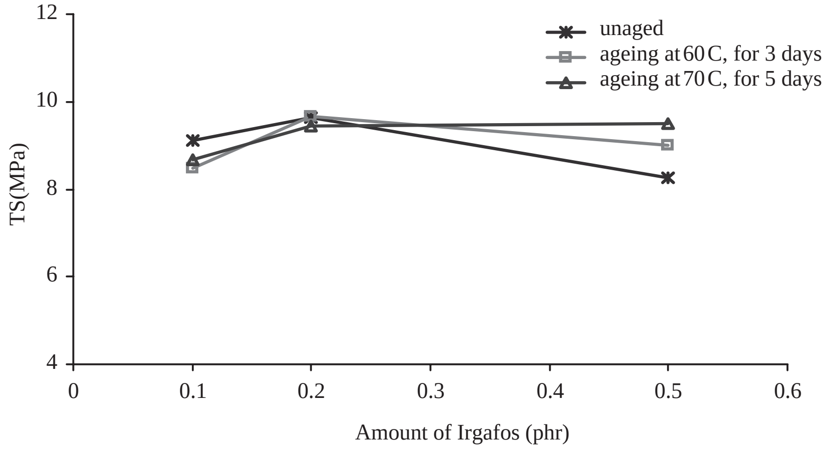

Figure 6 Plot of tensile strength versus the amount of antioxidant in the 65/35 NR/LDPE blend with and without ageing.

blends from UV, heat and sunlight. As seen in Table 4 the values of composition set in the blends with Irgafos reduced compared with those without Irgafos. That is to say Irgafos was quite necessary for the blend of NR and LDPE in order to improve the rebound of the blends in both unaged and thermal aged blends.

CONCLUSIONS

The effect of amount and type of antioxidants on the mechanical properties in the 65/35 NR/LDPE blend was investigated. It was found that the type of antioxidants had strongly effect on the efficiency of mechanical properties. That is, the mechanical properties of the blends decreased with increasing the amount of DPPD. The blends containing only Irganox showed the similar trend. Furthermore, the improvement of the mechanical properties and thermal resistance can be obtained in the blend with the combination of Irganox and Irgafos.

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