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Effect of Maleic Anhydride on the Physico-mechanical properties of NR/PE blends

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Blending of two or more polymers is used as a new technique to produce new materials with new properties at low production cost and investment. Rubber / Rubber blends are well known in tire industry. In the last few decade rubber and plastic blending attract the interest of many researchers and technologists.

In the present work NR and LLDPE was blended in presence of maleic anhydride MAH on a Brabender premixer at different conditions and namely temperature and time. The blends obtained were cured with sulpher and peroxide curing systems. Peroxide can crosslink both NR and LLDPE, while sulpher system crosslinks only the rubber phase in the blend. The data obtained showed that the addition of MAH greatly improved the physico-mechanical properties of NR/LLDPE blends. The surface morphology of the blends under investigation was studied by SEM. The results reveal the enhancement of blend compatibility in the presence of MAH.

Keywords: Blends, Sulpher/accelerator system, Peroxide-curing system, Maleic anhydride.

Introduction:

In the last few decades polymer blends have attracted the attention of many investigators world wide, since blending technology has become a practical tool for new materials production. The blends can be tailored with new useful and desirable properties. It was reported that large number of diene rubbers and polyolefines blends find the largest number of applications[1-3]. Rubber/Olefine blends can be cured by organic peroxides or by radiation [4,5] .

A review of rubber blends was published by Roland[6]. Kumar et al[7] produced thermoplastic elastomers (TPEs) composed of low-density polyethylene (LDPE), gum rubber and ground tire rubber (GTR), with enhanced elastic recovery and elongation at break values.

Abdel-Bary et al[8] studied the effect of some curatives on the properties of EPDM/PE blends. They reveal that the presence of EPDM/PE blends in their crosslinked state only by dicumyl peroxide (DCUP) affects the mechanical properties of the blends. The tensile strength at room temperature strongly increases with increasing the weight fraction of PE.

In another work[9] the authors studied the rheological and mechanical characteristics of NBR/CR blends crosslinked by two different curing systems. They found that the rheological and mechanical properties of the vulcanized blends depend on the vulcanizing system. In addition the dynamic compliance of NBR/CR blends over wide ranges of frequency and temperature reveal that NBR/CR blends are incompatible.

Jana and Nanda found that the blend of silicone rubber and low-density polyethylene is incompatible and can be compatible by using different ethylene copolymers to improve physical properties and thermal stability, decrease the size of the phase domains and influence dynamic properties[10] .

The present work aims at the study the physico-mechanical characteristics of NR/LLDPE blends crosslinked with sulpher/ accelerator and peroxide systems in the presence of MAH. Also to investigate the effect of blending and crosslinking on the degree of crystallinity of LLDPE.

Materials and Experimental Techniques :

Materials:

- Natural rubber (NR), of the type SMR-20, density = 0.913, Mooney viscosity ML (1 + 4) at 100^{o}C = 60-90, and glass transition temperature Tg =-75^{o}C, kindly obtained from Transport and Engineering, Company (TRENCO), Alexandria.
- Linear low density polyethylene (LLDPE), obtained from SABIC,SA, with density 0.916 g/cm^{3}.
- Sulpher element (S), pale yellow, sp . Gr. (2.04-2.06).
- N-cyclohexyl-2-benzothiazole sulphenamide (CBS), pale grey, non hygroscopic powder, melting point (95- 100^{o}C) and sp gr. 1.27.
- Dicumyl proxide (DCP), pure grade, melting point (39-41^{o}C) Mwt= 270.37g/mol, Aldrich product.
- Maleic anhydride, pure grade, Mwt= 98.06 g/mol melting point (54-56^{o}C), Aldrich product.

Blend preparation:

The blends were prepared by melt mixing of the components in the brabender plasti-corder (C.W, Bra, instrument, INC) at various temperatures, times and blend ratios. The cross linking agents were added to the mix on a laboratory two-roll mill of outside diameter=470 mm and working distance=300 mm, speed of the slow roll= 24 rpm and friction ratio of 1.4:1. The blend was removed and subsequently compressed at about 150^{o}C for 7 min. into thin sheets of thickness about 2mm from which test specimens were prepared.

Experimental Techniques:

- Tensile and elongation at yield and break: This were determined according to ASTM D 412-98a using Zwick tensile testing machine (model- 1425).
- X- ray diffraction patterns were performed at room temperature using Philips XRD apparatus type 1390, Cu target and Fe-filler (λ= 1.542 A^{o}). The x-ray tube was operated at 30 KV and 30 mA. Samples were packed in alumina holder. The diffraction angle 2θ was scanned at a rate of one degree per minute.
- Scanning Electron Microscopy (SEM)was carried out using the electron microscope model JSM-T 20 JEOL scanning microscope, Japan. For scanning the surface of the blend. The samples were

mounted on a standard specimen stub, coated with a very thin layer of gold.

Results and Discussions:

NR was blended with LLDPE by the ratio (50:50) in the brabender premixer at different temperatures (140, 150, 155, 160 & 165^{o}C) for different mixing times (5, 8, 10 & 20 min.) at 60 r.p.m. to determine the optimum mixing conditions. The physico-mechanical properties of the prepared blend samples were determined and listed in Table (1 & 2). From the data obtained, it is clear that the mixing at 155^{o}C for 10 min. can be considered as the optimum conditions for preparation of NR/LLDPE blends, which gives the most promising physico-mechanical characteristics. At such condition the most homogeneous blend of NR/LLDPE can be obtained. The decrease in tensile strength for sample mixed at 165 ^{0}C can be attributed to oxidative rupture of NR chains, when subjected to higher temperature and shear during mixing. Further, different blend ratios of NR and LLDPE were prepared at 155^{o}C for 10 min. The physico- mechanical properties were determined and the results are given in Table (3). One can see from the obtained data, that the physico-mechanical properties (tensile strength and elongation) decreases as the concentration of NR increases in the blend. This can be explained on the basis that NR is not subjected to the vulcanization process. Therefore, any composition rich in NR will produce elastomeric material, which exhibits lower tensile strength properties.

Table (1): The physico-mechanical properties of the blend 50:50 NR/LLDPE at 60 rpm and 7 min, at different temps.

Temp., ^{o}C	σ_B, MPa	σ_R, MPa	ε_β, %	ε_R, %
145	7.3	5.02	265	270
150	7.55	5.2	300	325
155	7.69	5.75	332	340
160	7.4	5.11	299	305
165	6.34	3.74	243	250

σ_B: Stress at yield; MPa, σ_R: Stress at rupture; MPa, ε_β: Strain at yield; %, ε_R: Strain at rupture; %.

Table (2): The physico-mechanical properties of the blend 50:50 NR/LLDPE at 60 rpm and 155^{o}C for different times.

Time,min.	σ_B, MPa	σ_R, MPa	ε_β, %	ε_R, %
5	4.5	3.86	312	316
8	7.6	5.8	330	338
10	8.7	7.98	368	373

15	6.27	5.6	274	295
20	6.11	4.3	239	246

Table (3): The physico-mechanical properties of the blend NR/LLDPE at 60 rpm, 155°C, 10 min. for different blend ratios.

Blend ratios NR/LLDPE	σ_B, MPa	σ_R, MPa	ε_β, %	ε_R, %
0/100	27.2	26.7	835	850
10/90	22.4	22.15	756	800
20/80	14.8	14.1	730	650
30/70	12.9	11.8	580	600
40/60	11.4	10.5	485	500
50:50	8.5	7.5	340	330
60/40	6.7	6.4	520	550
80/20	2.5	2.01	360	400
90/10	1.9	1.83	320	400

Curing of the NR/LLDPE blends:

The blend NR/LLDPE with the blend ratios 20/80 and 50:50 were selected to be crosslinked with different crosslinking agents and namely with peroxide and sulphur/accelerator systems.

The physico-mechanical properties were determined and the results are given in Tables (4) and (5). Table (4) contains data for crosslinked NR/LLDPE blends i.e. vulcanized with different concentrations of S/CBS. From these data, one can see that the tensile strength of the blend samples increases with the increase in the curing system concentration. On the other hand the elongation at break of the vulcanized rubber was decreased due to the crosslinking of NR gum in the blend . As the crosslinking process started and the NR chains were connected with each other via chemical bonds, the elongation was decreased and then leveled off, while the tensile strength was increased. This is based on the fact that S/CBS system crosslinks only the NR phase in the blend. This is clearly seen from the data in table (4) for the NR/LLDPE blend 50:50, where the NR content was increased and LLDPE decreased.

It is worthy to notice that high concentration of S and CBS gives the high tensile strength and elongation at break values. Since most S and CBS distributed also in LLDPE[8], but without creating crosslinks in LLDPE phase.

On the other hand peroxide has been used for crosslinking the selected blends. It was noticed that the tensile strength and elongation at break values were improved with the increase of peroxide content and have higher values compared with S/CBS system (Table 5). This can be attributed to the fact that peroxide can crosslink both NR and LLDPE phases, but S/CBS system crosslink only the NR phase in the blend as mentioned before.

It has been also noticed that the tensile strength of 20:80 blend ratio is higher than that for 50:50 blend ratio. The only way to explain this behavior may be attributed to ability of peroxide to crosslink LLDPE more than NR[8] .

Table (4): The physico-mechanical properties of the blends vulcanized NR/LLDPE with S/CBS.

Vulcanizate system	Blend ratio NR/LLDPE	σ_R, MPa	ε_R, %
Without S/CBS	20/80	14.1	650
With S/CBS			
0.5/ 1		15.8	344
0.7/ 1.2		17.9	400
0.9/ 1.5		19.3	486
Without S/CBS	50:50	7.5	330
With S/CBS			
0.6/ 1		12.62	320
0.8/1.25		13.41	550
1/ 1.75		18.5	600

Table (5): The physico-mechanical properties of the NR/LLDPE Blends cured with peroxide.

Vulcanizate system	Blend ratio NR/LLDPE	σ_R, MPa	ε_R, %
Without peroxide	20/80	14.1	650
With peroxide (phr)			
2		22.06	770

3		25.6	800
4		26.5	820
Without peroxide	50:50	7.5	330
With peroxide (phr)			
2		18.79	629
3		21.32	677
4		22.94	690

The effect of maleic anhydride (MAH) on the NR/LLDPE blends:

To improve the compatibility of NR/LLDPE blends, maleic anhydride was introduced in the blends during mixing . The (MAH) reacts with LLDPE and modify its to be ready homogenized with NR. In this case maleated LLDPEis formed.

The physico-mechanical properties were determined and the results are given in Table (6). The data obtained reveal that the improvement of the physico-mechanical properties is due to the enhancement of the compatibility of the blends under investigation[10].

Table (6): The physico-mechanical properties of the blend ratio 20/80 and 50:50 NR/LLDPE with 4phr MAH.

Blend ratios	**NR/LLDPE**	**σ_B, MPa**	**σ_R, MPa**	**ε_β, %**	**ε_R, %**
Crosslinking agent, (phr)					
Peroxide (4phr)	(20/80)	29.8	28.5	850	875
	(50:50)	26.66	26.5	695	700

(S/CBS)(0.9/1.5phr)	(20/80)	22.56	21.6	710	730
(S/CBS)(1/1.75phr)	(50:50)	20.67	20.1	720	740

X –ray diffraction:

Fig.(1) represent the intensity (I) against the blend 20/80 of NR/LLDPE without using crosslinking agent, with S/CBS, with peroxide and blend with (MAH), respectively. From these (Intinisities) one can determine the degree of crystal linty using the following equation[11]

Degree of crystal linty = 1/ I x 100

which is represented in Table (7), the degree of crystallization of the blend containg (MAH) is (59%) which indicate that (MAH) reacts with the main components of the blend and consequently, enhance the compatibility of the blend [12,13,14], which reflect itself on the blend crystal linty .

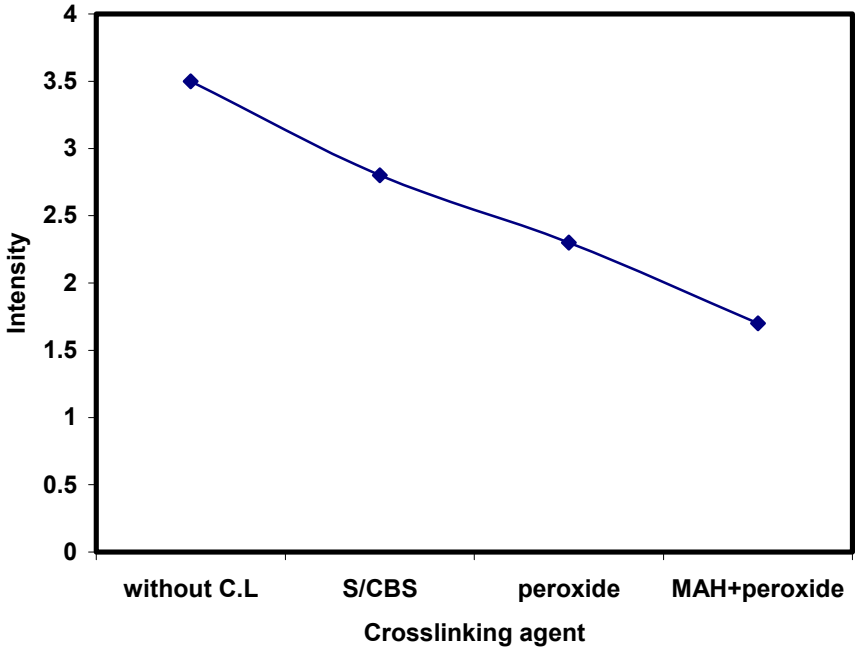

Fig.(1): The relation between the intensity and the C.L agent in the blend of NR/LLDPE 20/80

Table (7): Degree of crystallinity of blend 20/80 NR/LLDA without, with crosslinking agent and with MAH.

C.L agent	Without	S/CBS 0.9/1.5 phr	Peroxide 4 phr	MAH/Peroxide 4/ 4 phr
Degree crystallinity, %	28.5	36	43.5	59

Scanning Electron Microscopy (SEM):

Figure 2 (a, b, c) show the SEM photomicrographs at 1000 X of the blend 20/80 of NR/LLDPE, without crosslinking agent, with peroxide and with (MAH) respectively. From these spectrographs, it is clear that the blends which contain (MAH) in Fig. (2.c) shows the finner morphology compared to the other spectrographs. This indicates the good homogenization of the blend component with the addition of (MAH)

consequently, it is recommended to add (MAH) to the blend (NR/LLDPE).

Conclusion:

1. The physico-mechanical properties of the blend NR/LLDPE depend on the mixing conditions. The most suitable conditions for blending was found to be 155^{o}C for 10 min at 60 rpm.
2. The peroxide curing system improved the physico-mechanical properties, when compared with sulphur curing system.
3. The use of maleic anhydride improves the physico-mechanical properties and plays the role of blend modifier.

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a

b

c

Fig.(2): SEM micrographs of NR/LLDPE (20/80), Mag.1000

- **a- without crosslinking agent**
- **b- with peroxide 4 phr**
- **c- with MAH/ peroxide, 4/4 phr**