Journal of Natural Sciences Research
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.4, No.24, 2014

The Study of the Development of Natural Rubber Blends using Different Types of Polymers and Fillers on the Mechanical and Chemical Properties of the Vulcanizates

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Abstract

The mechanical properties, natural rubber (NR) blends were studied in various ratio; 100:0, 85:15, 70:30 and55:45.Two different types of filler were tested: carbon black and carbon Nano. It was found that, the increasing carbon black and carbon Nano compositions improve the tensile strength of the NR/PE,NR/PS blends. It was found that the incorporation of(PE , PS) in the blend compositions leads to the decrease in degree of swelling, Mechanical properties of the vulcanizates were examined. As expected, when the (PE, PS) were increased, The range of ratios evaluated are NR(70) /PE (30) , NR(85) /PS (15) blends resulted in better tensile properties.The effect of chemical and oil resistance on rubber blends were studied.

Keywords :-natural rubberblend , Fillers, mechanical properties tensile strength, Modulus

INTRODUCTION

Blending of polymers provides an efficient way of developing new materials with tailored properties, and thus has received much attention from academia and industry. By blending different polymers, several properties can be improved, while retaining some of the original properties. However, the desire of polymer scientists and engineers to produce improved products by blending a particular pair of polymers is often frustrated by their low compatibility. The incompatibility between polymer pairs and their consequently poor phase morphology are responsible for the poor mechanical properties of most polymer blends. As a result, there is a strong need to enhance compatibility, and the compatibilization of polymer blends by the addition of block or graft copolymer has become an important feature of polymer science and technology [1]. The complete miscibility of polymers requires that the free energy of the mixing be negative, which implies an exothermic mixing or large entropy of mixing [2]. Therefore, most blends of elastomers are immiscible because mixing is endothermic and the entropic contribution is small due to the high molecular weights. Fortunately, miscibility is not a requirement for most rubber applications However, adhesion between the polymer phases is necessary. In this scenario vulcanization of elastomers containing different phases (blends) is an important. rubber with different state of cure than in the bulk. Furthermore, completely miscible elastomers have a single narrow glass transition temperature when they are in the cured state[3]. Partial compatible blends may shown two glass transition temperatures *Tg* different than those of the components, the NR/PE and NR/PS systems is an example[4]. Thermoplastic elastomers (TPEs) are polymeric materials, which combine the excellent process ability of the thermoplastic materials at high temperatures and a wide range of physical properties of elastomers at service temperature [5]. TPE grades are often characterized by their hardness. Olefinic thermoplastic vulcanizes (O-TPVs) are one of a class of TPE. These materials are composed of vulcanized rubber component in a thermoplastic olefinic matrix. O-TPVs have a continuous thermoplastic phase and a discontinuous vulcanized rubber phase. OTPVs are dynamically vulcanized during a melt-mixing process in which vulcanization of rubber polymer takes place. O-TPVs's principal uses are automotive applications, appliance uses building/constructions, , prominent electrical uses, business machines and uses in healthcare application [6-7]. Natural rubber (NR) has good resilience, high tensile strength, low compression set, resistance to wear and tear and good electrical properties. range of application. Thermoplastic due to its intrinsic properties such as translucent, good chemical resistance, tough, good fatigue resistance, integral hinge property, good heat resistance. It does not present stress-cracking problems and offers excellent electrical at higher temperatures. These include a lower density, higher softening point and higher rigidity and hardness. Easy incorporation of high loadings of fillers and reinforcing agents, and ability to produce blends with other polymers including rubbers makes Thermoplastic versatile [8-9]. Fillers are incorporated into polymer matrix mainly to achieve improvement of service properties or to reduce the material cost. The results indicated that the tensile strength increase with increasing carbon black [10]. This study was basically aimed to investigate the effects of various filler and thermoplastic loadings on the mechanical properties of natural rubber blends, in this paper, we have studied the use blends from natural rubber with thermoplastic (PE,PS) have received considerable attention. Tensile strength ,modulus ,elongation ,hardness and compression resistance have been improved using filler. Mixing of the thermoplastic is an important variable in order to minimize the NR domains and also to control the filler distribution in the natural rubber phase.

EXPERIMENTAL

Materials:-

Natural Rubber (SMR20),Polystyrene, polyethylene(Sabic.Co)/K.S.A, Supper abrasion furnace (SAFN110)(Thai carbon product Co,Ltd)/Thailand and Carbon Nano(APS:<80nm,PH:6-7, Ash:<0.5% ,purity :99.9%)(NanoShel)/Americano. was used as filler , Zinc Oxide and Stearic Acid was used as Activators, 2,2`-Dibenzothiazyl Disulphide (MBTS), Tetra methyl thiuramdisulphide (TMTD) was used as Accelerators/(Flexsys Co. Ltd) / Thailand, Sulfur was used as Vulcanizing agent, N-(1,3-Dimethylbutyl)-N`-phenyl-P-phenylenediamine(6PPD) was used as Antioxidants/Antiozonant Commercial (Chemmin Co. Ltd.) / Thailand,Aromatic Oil was used as Process Oils (Gulf CO) /U. A. E .

Physico-mechanical properties of the test samples:-

Tensile strength and modulus (M100) properties were measured on dumbbell-shaped sample using a tensile testing machine from (LARYEE Co)/ China.with a load cell of 20 kN and a cross-head speed of 200 mm/min at room temperature The sample dimensions were accordance to ASTM D-412 .

Hardness and Compression. Set:-

The hardness of vulcanizates was measured using a Shore A durometer according to ASTM D-2240and the readings was taken after 3 seconds indentation. All tests were carried out at room temperature (25±2 C^0). Compression set was measured according to ISO 1653 at ambient temperature.

Gel Content and Swelling Index.

Gel contents were determined by Soxhlet extraction technique using acetone as solvent. The samples were extracted for 32 h and dried in air and in vacuum oven at 70°C until constant weight. The gel content was calculated as follows:

$$\text{Gel content (\%)} = \frac{\text{weight after extraction}}{\text{weight before extraction}} \times 100$$

Swelling of the test samples:-

The experiments were carried out according to ASTM D-471. The swelling was performed by immersing the specimens in air-tight, metal-capped test bottles filled with acetone, which kept at a constant temperature of 25±2 C^0 . The samples were periodically removed from the test bottles. This procedure was continued until equilibrium swelling was attained. The equilibrium swelling (solvent uptake) was expressed as weight percent of the original sample weight according to the following equation:-

$$\text{Equilibrium Swelling \%} =[(W-W_0) / W_0]* 100$$

where W_0 is the initial un swollen mass and W is the mass after equilibrium swelling.

Curing (Vulcanization):-

The rubber mixes were compression-molded at 150±2 C^0,at 20 min using an electrically-heated hydraulic press (HITOP RUBBER CO.) Model (XLB300X300X2) to their optimum cure times derived from rheological measure me.

Differential Scanning Calorimetry:-

DSC measurements were analyzed on (DSC 131 Evo, SETARAM, (France)). Around10 mg of samples was placed in aluminum cups that were subsequently crimped hermetically. The sample and reference, which consisted of an empty aluminum cup similarly crimped, were heated to 250 C^0. The DSC curves were obtained as heat flow versus temperature plots by heating from room temperature to 250 ^{0}C at a rate of 10 ^{0}C/min under N_2atmosphere.

SAMPLE PREPARATION

Each NR type was first incorporated into the neat polymers by means of an internal mixer (Record E3000). The rotor speed was adjusted to 50 rpm and the mixing time set at 10 min.The mixing temperature was70 C^0 for rubber materials and 180 C^0 and 190 C^0 for those containing PE and PS In the next step, Binary systems consisting of NR, thermoplastic. Rubber was allowed to melt with PE and PS (weight proportion 85/15,70/30 and 55/45) in the kneader for 4 min at 180 $C^0$and 190 C^0repectively , then NR was added and mixed for (6) min. For rubber compounding , Mixing was performed according to ASTM D-3182 on a two-roll mill : rolls dimensions are: Outside diameter 150 mm, working distance 300 mm, speed of the slow roll 24 rpm and gear ratio 1.4 Compounds recipes are summarized in Tables (1,2,3and4) .A typical mixing specification is shown in the next steps, Rubber is passed through rolls twice without banding, at a mill roll opening of 0.2 cm at 70°C for (3 minutes, Add Stearic Acid for (3 minutes), Add other ingredients, add the zinc oxide (5 minutes)., carbon black and add process oil for (10 minutes) , Add antioxidants/ antiozonants for (4 minutes), Add the accelerator (TMTD) and (MBTS) for (4 minute), Add Sulfur to the master batch stock for (4 minute) Cooling the batch to room temperature. Total time is about(30 minutes). The blend was then molded at150 C^0 for 20 min in an electrically heated hydraulic press to prepare specimens of2 mm thickness for physical measurements, After molding, the mix was cooled under pressure (200 bar) to room temperature

Ingredients	Recipes 1 phr	Recipes 2 phr	Recipes 3 phr	Recipes 4 phr	Recipes 5 phr	Recipes 6 phr
NR	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
6PPD	1	1	1	1	1	1
Carbon black (SAFN110)	10	20	30	40	50	60
Process Oils	5	5	5	5	5	5
(MBTS)	1	1	1	1	1	1
(TMTD)	0.1	0.1	0.1	0.1	0.1	0.1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

Table (1):-Composition of rubber compounds prepared with various carbon black (SAF)

Ingredients	Recipes 1 phr	Recipes 2 phr	Recipes 3 phr	Recipes 4 phr	Recipes 5 phr	Recipes 6 phr
NR	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
6PPD	1	1	1	1	1	1
Carbon black Nano	1	2	3	4	5	6
Process Oils	5	5	5	5	5	5
(MBTS)	1	1	1	1	1	1
(TMTD)	0.1	0.1	0.1	0.1	0.1	0.1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

Table (2):-Composition of rubber compounds prepared with various carbon (Nano)

Ingredients	Recipes 1 phr	Recipes 2 phr	Recipes 3 phr	Recipes 4 phr	Recipes 5 phr	Recipes 6 phr
NR	85	70	55	85	70	55
PE	15	30	45	-	-	-
PS	-	-	-	15	30	45
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
6PPD	1	1	1	1	1	1
Carbon black (SAFN110)	50	50	50	50	50	50
Process Oils	5	5	5	5	5	5
(MBTS)	1	1	1	1	1	1
(TMTD)	0.1	0.1	0.1	0.1	0.1	0.1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

Table (3):-Compound formulation used in NR/PE,NR/PS at constant carbon black (SAF)

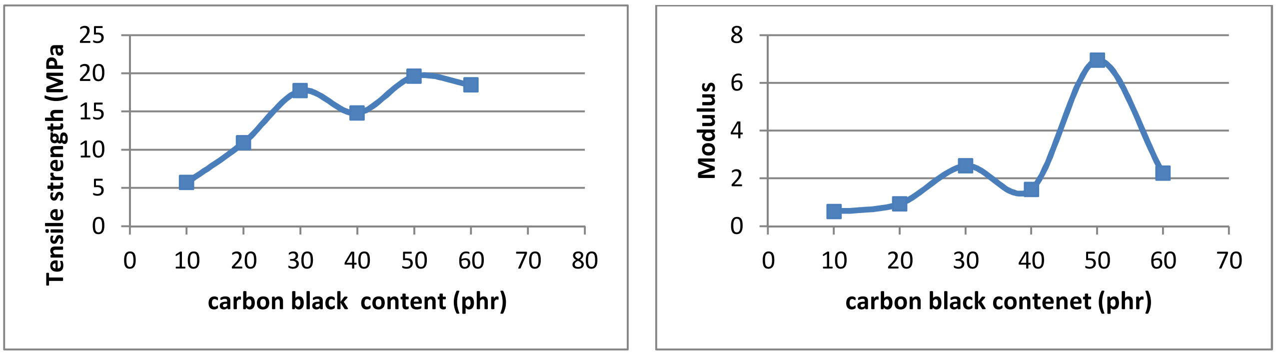
Ingredients	**Recipes 1 phr**	**Recipes 2 phr**	**Recipes 3 phr**	**Recipes 4 phr**	**Recipes 5 phr**	**Recipes 6 phr**
NR	85	70	55	85	70	55
PE	15	30	45	-	-	-
PS	-	-	-	15	30	55
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
6PPD	1	1	1	1	1	1
Carbon black Nano	5	5	5	5	5	5
Process Oils	5	5	5	5	5	5
(MBTS)	1	1	1	1	1	1
(TMTD)	0.1	0.1	0.1	0.1	0.1	0.1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

Table (4):- Compound formulation used in NR/PE,NR/PS at constant carbon (Nano)

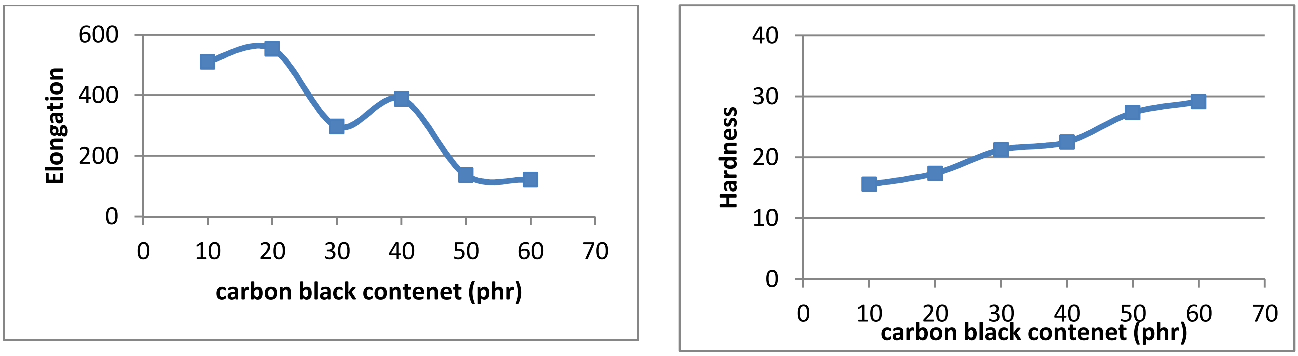
RESULTS AND DISCUSSION:-

Effect of carbon black(SAF) loading on physic-mechanical properties of the NR blends:-

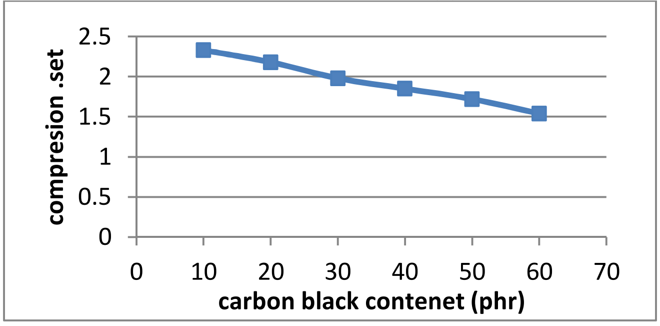
Carbon black particles are firmly fused together in rubber, and the smallest discrete entity existing in rubber is always the aggregate. By virtue of their irregular morphology, the aggregates are bulky, and occupy an effective volume considerably larger than that of carbon black itself. These voids are capable of absorbing polymer and partially shielding it from stress when the rubber matrix is deformed. In Figure (1)with the same loading ratio, carbon black shaving higher specific surface area were accompanied with the larger tensile strength value. Tensile strength is mainly related to the stress distribution within rubber and the effective increase in the rupture path. Strong carbon black-polymer interaction is important **to** maximize micro- dispersion, which is essential to achieving the highest possible level of tensile strength for a given carbon black[12].It can be seen that the tensile strength increase with increasing carbon black content. This observation is due to the carbon black (N110) is reinforcing filler which has good surface activity, chemical properties and non-uniform of porous surface which contribute to maximum interphase interaction between polymer chain and filler [13] . Generally, tensile strength increase is a result ofthe additional reinforcement of the polymer phase. The degree of reinforcement depends on the extent of polymer and filler interaction. The interactive forces increase with carbon black concentration and so does the degree of reinforcement. Carbon black is also believed to influence the thermally induced interaction between the natural rubber and thermoplastic(PE,PS)phases [16]. As carbon content increases, the rubber – filler interactions increase which cause the increase of hardness, tensile strength and modulus at 100% elongation (M100) due to greater polymer matrix-filler particles interaction . The decrease in compression is due to the compression of the chains mobility resulting from the physical cross-links introduced by the filler [11].the effect of filler loading on elongation-at-break. It indicates that elongation-at break (%) decreases gradually with increasing filler loading. The reduction of elongation-at-break is due to stiffening of the polymer matrix by the filler. Further increase in filler loading causes the molecular mobility decrease due to extensive formation of physical bond between the filler particles and the polymer chain that between the filler particles and the polymer chain that stiffen the matrix the increase in filler loading leads the matrix progressively becoming reinforced and hence lowering elongation-at-break at any filler loading greater than 20%.For 60 phr carbon black , the lowest tensile strength observed is due to large mean agglomerate particles size of carbon black and weak interaction between filler and polymer matrix These observations indicate that the mean agglomerate particles size play an important role in affecting the mechanical properties rubber compound[16].



a. Tensile strength **(b) Modulus**



(c) Elongation **(d) Hardness**

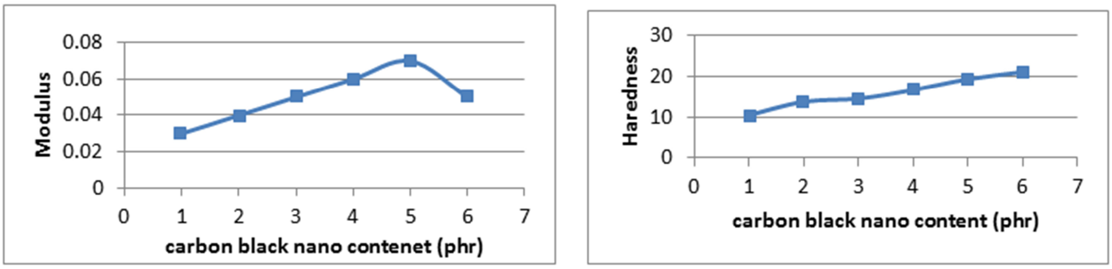


(e) Compression

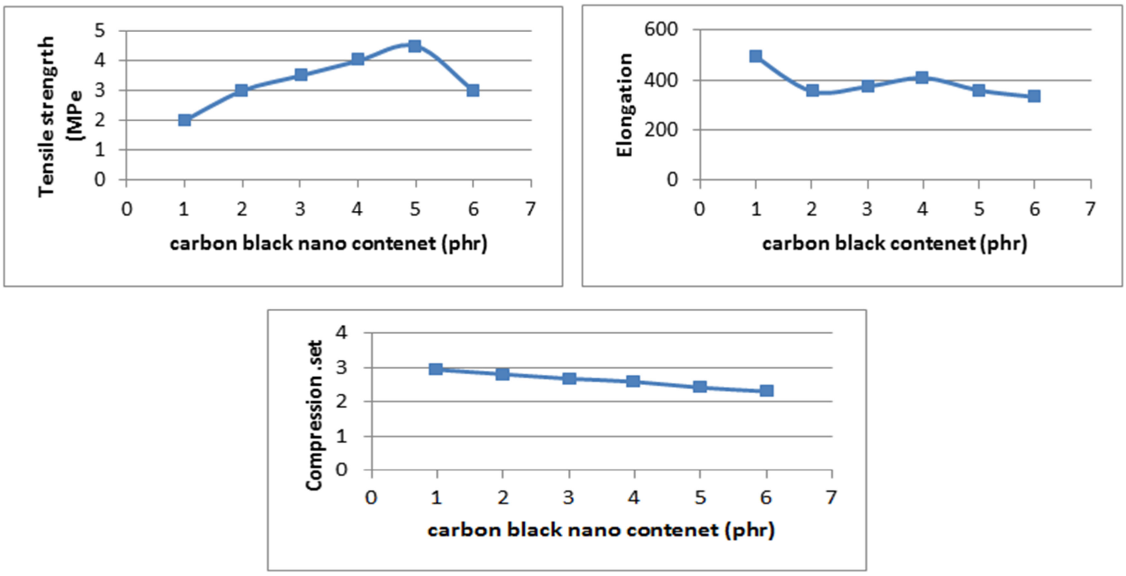
Figure 1: The effect of carbon black (SAF) loading on the mechanical properties of rubber compounding

Effect of carbon black(Nano) loading on physic-mechanical properties of the rubber compounding :-

Figure 2: It is well known that the incorporation of Nano fillers such as carbon black Nano in a polymeric matrix can markedly promote improvements in mechanical and chemical properties of Nano rubber compounds[19] .shows the stepwise increasing trend of tensile strength ,modulus and hardness of Nano blending with increasing content of carbon Nano. It shows that the carbon Nano endowed rubber compounds excellent mechanical properties. The tensile strength ,modulus ,and hardness of Nano compounds based on 5.0 per loading increased respectively, which indicated the super-reinforcement of carbon Nano. When the, carbon Nano content was higher than 5.0 phr, the slower improvement rate of the mechanical properties was due to the poor dispersion of Carbon Nano, as the partial multi-layered carbon Nano would enhance the strength little. The formation of carbon Nano aggregates reduces the interfacial area between the polymer and carbon Nano layers, which leads to lower mechanical properties[20]. As carbon content increases, the rubber – filler interactions increase which cause the increase of hardness, tensile strength and modulus at 100% elongation (M100) due to greater polymer matrix-filler particles interaction . The decrease in compression is due to the compression of the chains mobility resulting from the physical cross-links introduced by the filler [11].



(a) Tensile strength (b) Modulus

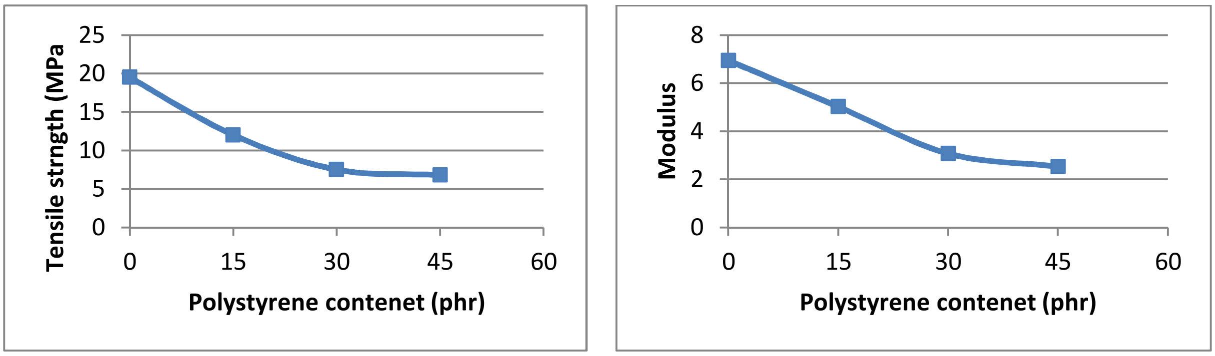


(e) Compression

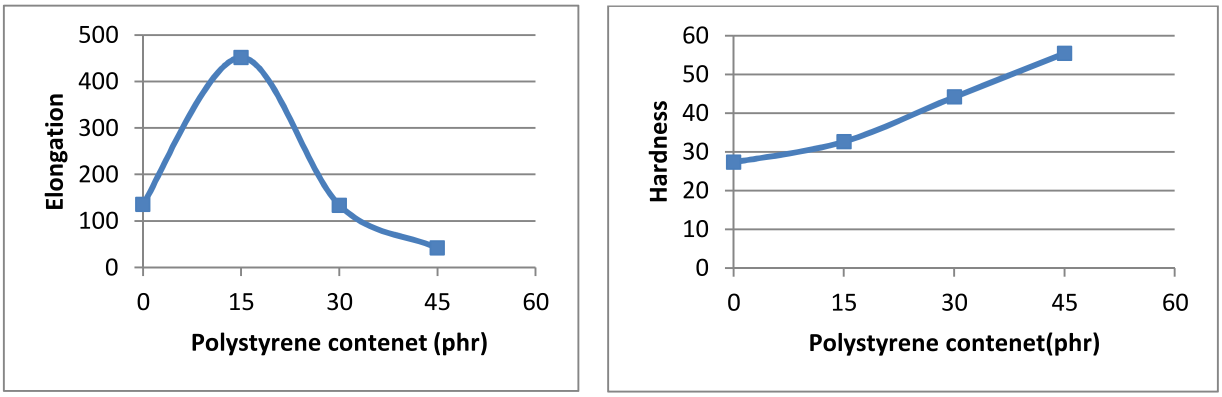
Figure 2: The of effect carbon black (Nano) content on the mechanical properties of NR compounding

Effect of thermoplastic Blending on physic-mechanical properties of Natural rubber compounding:-

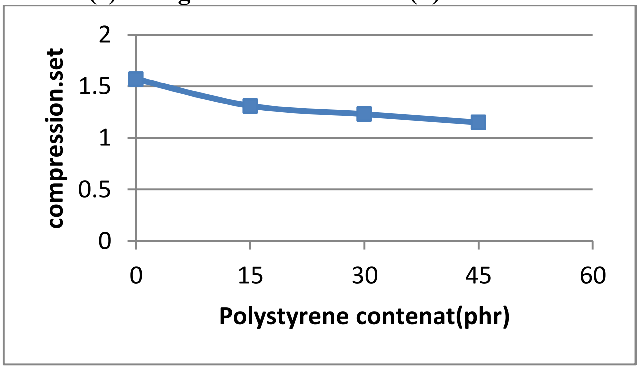
The interfacial adhesion between NR and thermoplastic matrix is a main factor for controlling the NR into thermoplastic results in lowering of mechanical properties of blends because of poor interfacial adhesion between NR and thermoplastic matrix as well as lack of reactive sites on surface of NR , the interfacial adhesion between NR and thermoplastic matrix is poor due to cross-linked structure of NR which blocks molecular. The most thermoplastic matrixes used in blending of NR with (PS) and (PE) . Mechanical properties of blends based on NR and thermoplastic depend on nature of NR, content of NR, polymer matrix type, interfacial adhesion between NR and thermoplastic matrix [14]. Tensile strength and modulus at 100% elongation (M100) of NR/PE and NR/PS blends are summarized in Figures (3,4) .Tensile strength and modulus at 100% elongation (M100) increase with the increase of rubber loading from 55% to 85% was observed, this is due to the increment of rubber loading. Rubber is known to be soft and elastic. Therefore blends with high rubber loading are softer and have higher elasticity compare to those which had lower rubber loading. For both NR/PE and NR/PS blends, blend ratio at 70/30 for NR/PE gave the best tensile strength, and blend ratio at 85/15 for NR/PS gave the best tensile properties. The grafted PE and PS contributed to the stiffness and strength of NR/PE and NR/PS blends looking at the total volume of rubber/thermoplastic ratio between NR/PE and NR/PS: 55/45 blends from, the blends are having higher amount of thermoplastic; i.e. PE and PS from NR. At lower rubber amount, the blend is expected to be stiffer and stronger. This is in agreement with the results observed; i.e. NR/PE and NR/PS: 55/45 blends are stiffer and stronger than NR/PE and NR/PS 85/15 blend[15]. It can be seen that tensile strength of NR/PE 55/45 and NR/PS blends exhibited increases in tensile strength with increasing NR content in the blends until it reaches the maximum of pure PE and PS . Elongation at break also shows a similar behavior i.e. the value increases as PF and PS content is higher [18].Increase in hardness in rubber blend due the increment of thermoplastic (PE,PS) loading, The addition of NR into (PE,PS) resulted in lowering compression set because of is due to the restriction of the chains mobility resulting from the physical cross-links introduced by the thermoplastic[11,18] .



(a) Tensile strength (b) Modulus

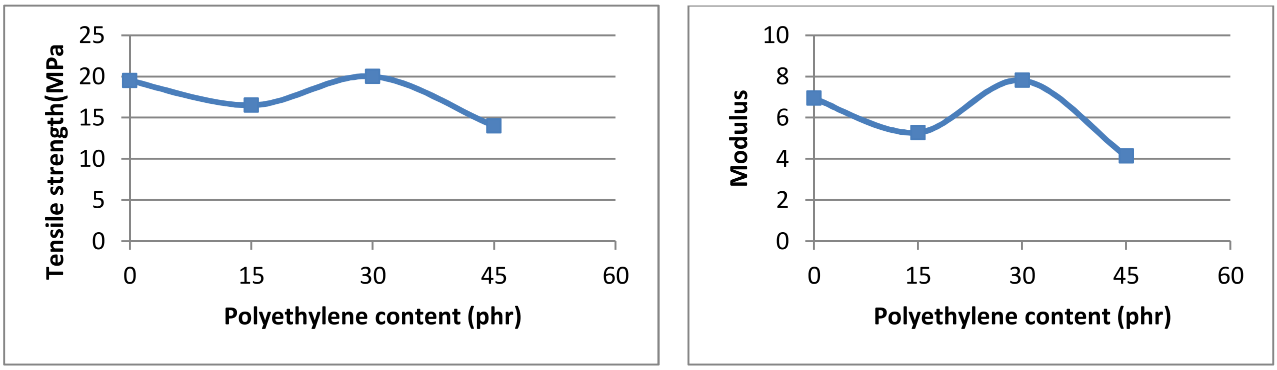


(c) Elongation (d) Hardness

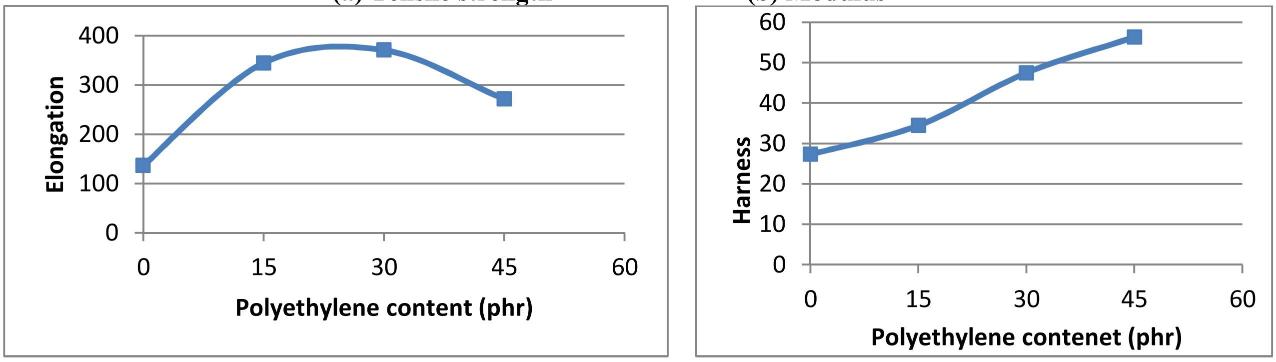


(e)Compression

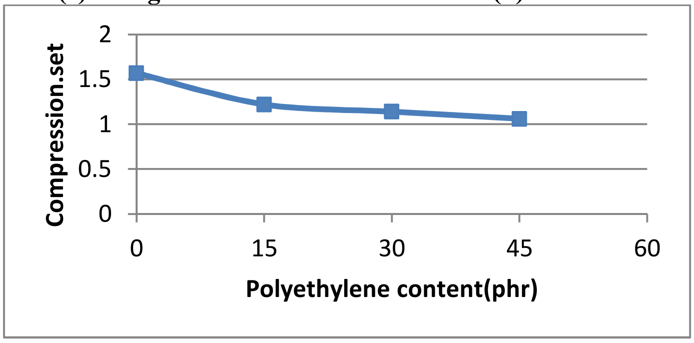
Figure 3: The effect of t Polystyrene content on the mechanical properties of NR compounding



(a) Tensile strength (b) Modulus



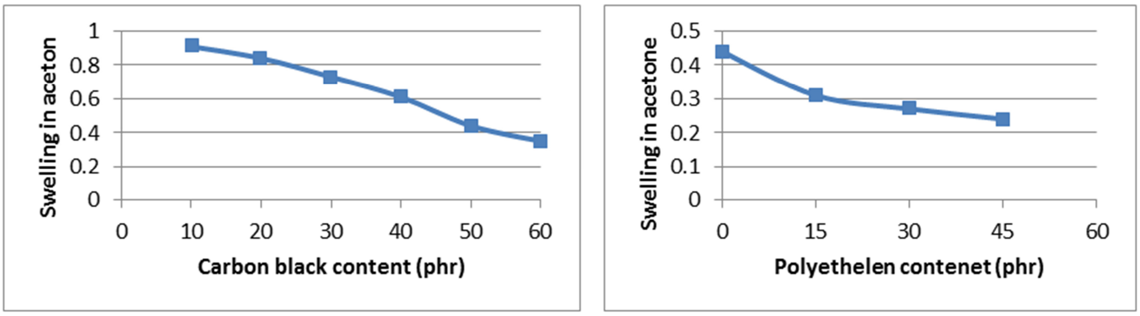
(c) Elongation (d) Hardness



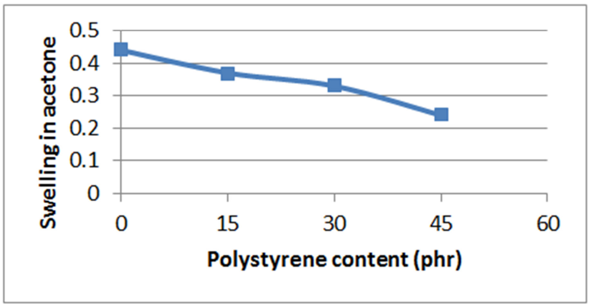
(e)Compression

Figure 4: The effect Polyethylene content on the mechanical properties of NR compounding Effects of carbon black loading on swelling behavior:-

The solvent uptake decreases linearly with increasing carbon black loading and the effect ismore pronounced with the highly swelling solvent (Acetone) which possess the highest slopes (as observed in figures (5,6):- This is again because of the introduction of physical cross-links which restrict the swelling of the rubber. Maximum swelling occurs with acetone because of the rubber blend have solubility parameter value close to the solubility parameter of this solvent [11]. It is believed that strong interaction occurs between the rubber and plastic phases and the matrix-filler interphase. decrease in swelling with filler loading is due to the formation of a network structure pronounced by the filler. Reactions involving radical- radical recombination and macro-radical additions across the double bonds are expected to enhance in the presence of fillers. Swelling index can be used as anindicator for the formation of cross-links in the blends. Swelling index decreases with increasing filler loading which indicates an increase in the cross-link density[16].

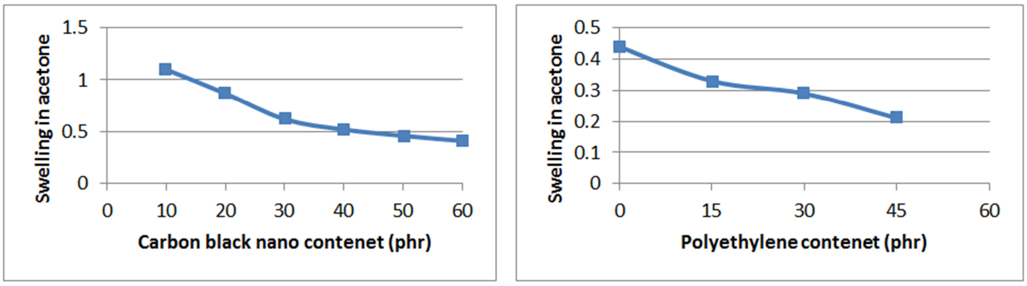


(a). : swelling of NR **(b) : swelling of NR/PE**

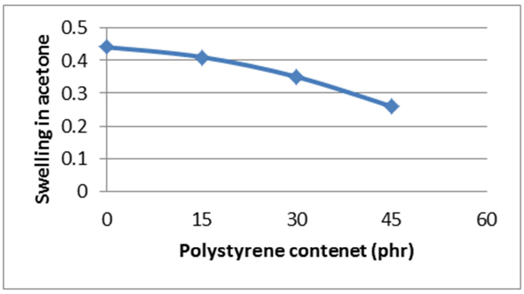


(b) : swelling of NR/ PS

Figure 5: The effect of swelling on the mechanical properties of NR , NR/PE and NR/PS blending in presence of carbon black



(a). : swelling of NR **(b) : swelling of NR/PE**



(b) : swelling of NR/PS

Figure 6: The effect of swelling on the mechanical properties of NR , NR/PE and NR/PS blending in presence of carbon Nano

Chemical resistance to acid:-

It is very important that polymeric materials should not interact with the medium during service. Evidently this can be achieved by using strongly polar polymers in non-polar media, or non-polar polymers in polar media. An important characteristic of polymers (plastic or rubber), is their stability to attack by various aggressive media, such as mineral acids, this is of great practical importance[21]. Blends of NR by two types of thermoplastic (PE,PS) and their blends show good L resistance to acid, base, at temperature up to 70 C°. They are exceptionally resistance to diffusion. We have made more concentration on testing resistance for acid and base. .

These test were carried out in two ways:

a. for 96 hrs at 70 C^{0}
b. for 96 hrs at room temperature

The first route is followed for concentrated 50% and 70% from Sulfuric and nitric acid. The second rout is considered on using (70% KOH).

tables(5,6.7 and 8) indicates the resistance of the main rubber blending to acid and state the temperature to which these data apply As can be seen the resistance of vulcanizates to chemicals, is good and products have found particular applications where there is contact with acids such as Sulfuric and nitric acid. The tableswhich gives the weight increase or decrease of different vulcaniztes percentages show in change in weight for vulcanizates dipped in concentrated Sulfuric and nitric acid at 70 C° for 96 hours does not change over 4.9%. This value corresponds to excellent chemical resistance[22]. Since maximum chemical resistance for specialty rubber is allowed to 1% change in weight according to their resistance to Sulfuric and nitric acid, the tested rubber materials can be arranged in the following order:

NR/PS(55/45) phr>NR/PE (55/45)phr>NR/PS (70/30) phr>NR/PE (70/30)phr>
NR/PS(85/15) phr>NR/PE(85/15) phr

Chemical resistance to base:-

Samples from NR/PE ,NR/PS were subjected to 70% potassium hydroxide for 96 hours at 70 C° and room temperature. Results are given in tables(5,6.7 and 8) : A well-known fact is that carbon bonds with O2, S, N2 are readily cleaved by acids, Basis and other corrosive materials compared with carbon-carbon bonds, since most of these corrosive materials are ionic and / or highly polar in nature. Since rubber chains are mostly built up from homochain carbon skeleton, it is easy to identify their stability against normal common chemicals According to chemical resistance obtained in the presence of different rubbers and blends, the chemical resistance order can be written as follows[22]:-

NR/PE(55/45) phr>NR/ PS (55/45)phr>NR/PE (70/30) phr>NR/PS (70/30)phr>
NR/PE(85/15) phr>NR/ PS(85/15) ph

Chemical resistance to oil:-

In many cases mechanicals rubber products, particularly dynamic seals operate in contact with oil and greases Depending on the composition of rubber and lubricants changes may be observed in the mass and dimension of finished rubber articles which comes in contact with oils and lubricants. Another problem which is serious for thin components but which may be insignificant with thick components is oil resistance Hydrocarbon oils are absorbed to a greater or lesser extent by all rubbers, but those which are oil resistant absorb a relatively small amount. A non-oil resistant rubber may absorb up to twice its own volume of oil at equilibrium but the time taken to reach equilibrium depends on the viscosity of the oil and on the distance of the center of the rubber from the surface in contact with oil. The total volume of the swollen rubber is equal to the sum of the volume of rubber plus the volume of the oil absorbed. The equilibrium amount of oil absorbed is determined by the nature of the oil and rubber as well as the degree of crosslinking and filler loading. From tables (5,6.7and 8)the same vulcanizates were tested at room temperature and at 70^{o}C for the same time period (4 days). Analyzing the data in both tables it was found that weight increases with the rise in temperature. The range of increment in weight at 70^{o}C to weight at R.T., this is by fair means a good stability for vulcanizates obtained[23].

Recipes (pphr)	**Temperature ^{o}C**	**Change in weight of tested sample % in**					
		H_2SO_4 70%	**H_2SO_4 50%**	**HNO_3 50%**	**HNO_3 70%**	**KOH 70%**	**Oil**
15	RT	-0.17	-0.19	-0.16	-0.15	+0.38	+0.31
	^{o}C	-0.16	-0.18	-0.17	-0.14	+0.39	+0.32
30	RT	+0. 22	+0. 24	-0.19	-0.17	+0.34	+0.30
	^{o}C	+0. 24	+0. 25	-0.18	-0.16	+0.32	+0.28
45	RT	+0. 26	+0. 28	+0.24	+0.23	+0.26	+0.21
	^{o}C	+0. 28	+0. 30	+0.26	+0.25	+0.23	+0.23

Table(5):Effect of acids, bases, oils on NR/ Polyethylene properties (SAF) filler

Recipes (pphr)	**Temperature ^{o}C**	**Change in weight of tested sample % in**					
		H_2SO_4 70%	**H_2SO_4 50%**	**HNO_3 50%**	**HNO_3 70%**	**KOH 70%**	**Oil**
15	RT	-0.15	-0.18	-0.15	-0.13	+0.46	+0.35
	^{o}C	-0.16	-0.17	-0.16	-0.15	+0.48	+0.34
30	RT	+0. 21	+0. 23	-0.18	-0.17	+0.35	+0.31
	^{o}C	+0. 23	+0. 27	-0.19	-0.17	+0.33	+0.32
45	RT	+0. 25	+0. 28	+0.22	+0.21	+0.28	+1.25
	^{o}C	+0. 26	+0. 32	+0.25	+0.24	+0.27	+0.23

Table (6):Effect of acids, bases, oils on NR/ Polyethyleneproperties(NANO) filler

Recipes (pphr)	**Temperature ^{o}C**	**Change in weight of tested sample % in**					
		H_2SO_4 70%	**H_2SO_4 50%**	**HNO_3 50%**	**HNO_3 70%**	**KOH 70%**	**Oil**
15	RT	-0.13	-0.17	-0.13	-0.12	+0.47	+0.36
	^{o}C	-0.14	-0.16	-0.15	-0.13	+0.45	+0.34
30	RT	+0. 21	+0. 23	-0.19	-0.16	+0.37	+0.31
	^{o}C	+0. 22	+0. 25	-0.17	-0.15	+0.32	+0.32
45	RT	+0. 25	+0. 27	+0.22	+0.21	+0.27	+0.27
	^{o}C	+0. 27	+0. 29	+0.28	+0.27	+0.28	+0.28

Table (7) :Effect of acids, bases, oils on NR/ Polystyrene properties(SAF) filler

Recipes (pphr)	**Temperature ^{o}C**	**Change in weight of tested sample % in**					
		H_2SO_4 70%	**H_2SO_4 50%**	**$HNO_3$50%**	**HNO_3 70%**	**KOH 70%**	**Oil**
15	RT	-0.10	-0.15	-0.14	-0.13	+0.61	+0.38
	^{o}C	-0.12	-0.16	-0.13	-0.12	+0.53	+0.36
30	RT	+0. 21	+0. 21	-0.19	-0.15	+0.42	+0.33
	^{o}C	+0. 21	+0. 23	-0.18	-0.16	+0.47	+0.34
45	RT	+0. 22	+0. 23	+0.22	+0.24	+0.33	+0.25
	^{o}C	+0. 21	+0. 22	+0.21	+0.25	+0.35	+0.24

Table (8):Effect of acids, bases, oils on NR/ Polystyreneproperties(Nano) filler

Differential scanning calorimetry(DSC) :-

DSC measures the amount of energy absorbed or released by a sample as it is heated, cooled or held at a constant temperature. It is achieved by placing two temperature probes in the furnace and simultaneously measuring the temperature of the sample and furnace temperature while heating the sample at a constant rate. This technique is used for polymer and pharmaceutical applications. The DSC will be resulted in a heat input against temperature curve. Glass transition temperature, crystallization point, melting point etc can be determined from the DSC curve.

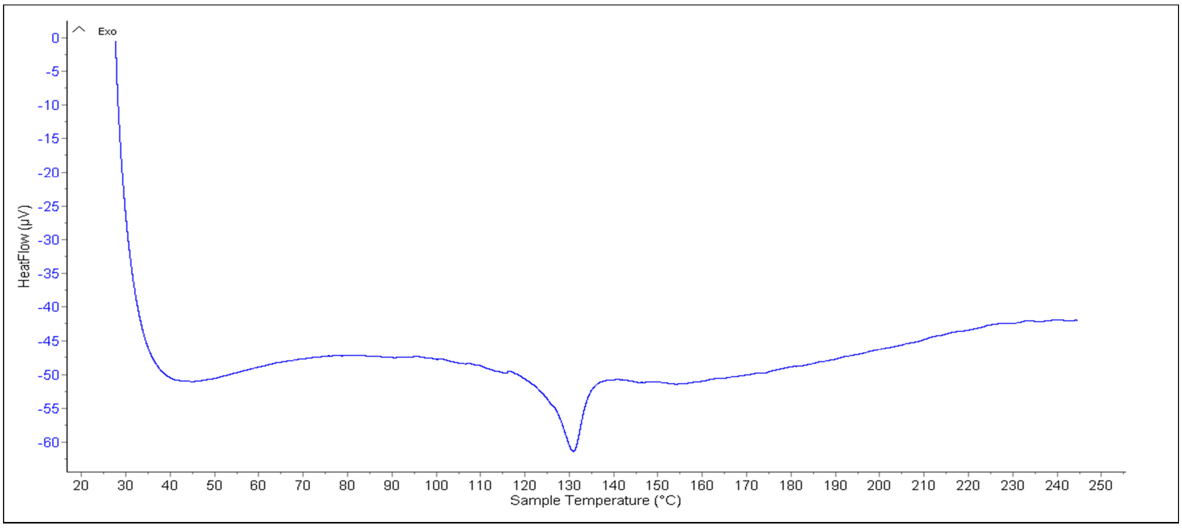


Figure7: DSC curve for NR/PE

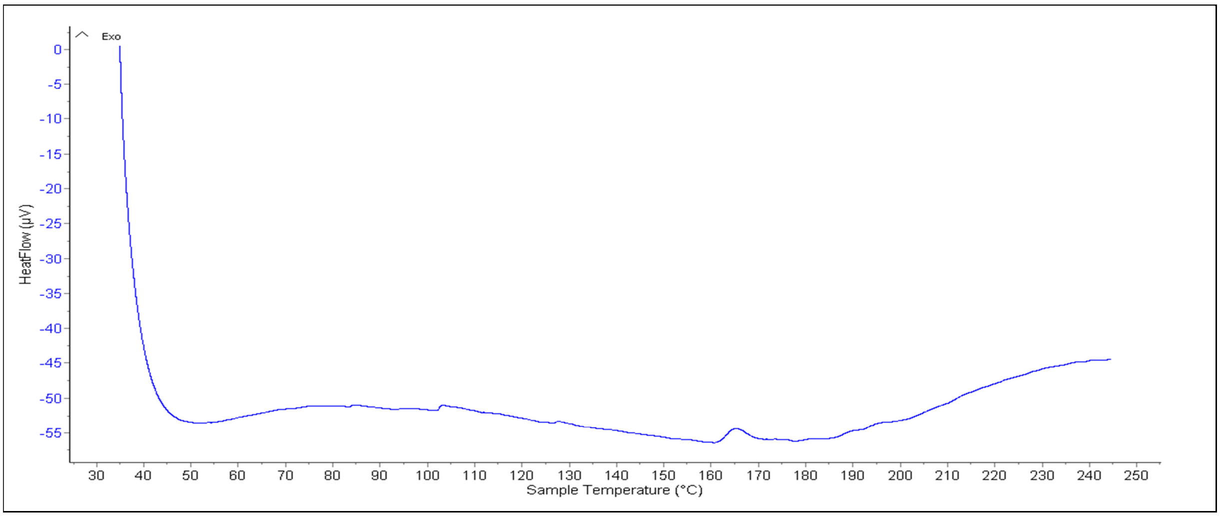


Figure 8: DSC curve for NR/PS

Figure (7,8) :- shows the DSC curve of sample prepared with NR/PE ,85/15phr and NR/PS 85/15phr. From the graph, it can be understand that, the glass transition occurs at a temperature of 38^{0}C NR/PE and 42^{0}C NR/PS. It was indicated by the increase in heat flow. It is the glass transition temperature where the sample starts withdrawing heat at increased rate. Then it reaches its melting point, where it melts completely. Then the heat absorption reduces. And continues till its degradation starts. Here we can see the melting point as 235^{0}C NR/PE and 163^{0}C NR/PS. DSC for the rest of the sample also was done[24].

sample	Tm	Tg	Tc
NR/PE	235 ^{0}C	38^{0}C	130^{0}C
NR/PS	163 ^{0}C	42 ^{0}C	103 0C

Table (9). The glass transition, melting temperature and crystallization temperature obtained from DSC.

The effect of aging on the mechanical properties of rubber compounds:-

NR and their blends with PE, PS were subjected to thermal ageing at 80°C for various time periods up to 6 days. The mechanical properties were measured and the retained values were calculated and are given in Tables (12,13,14 and 15) . These data showed that the binary blends have slight increase in tensile strength, modulus and decrease elongation values (NR/PE,NR/PS) blends . The ageing resistance of the rubber blends are due to the presence of PE,PS in NR blends .The effect of aging on the mechanical properties of rubber compounds containing different loading of filler is illustrated in tables (10,11) .It can be seen that rubber compounds containing different loading of filler show decrease in tensile strength and modulus valuesafter 6 days at 80°C.This may be due to the rapture in forms of chemical sorption and physical entrapment of free molecules and cross linking of free molecules to the filler –rubber complex on aging and deactivation of the already cross linked by filler . The hardness increased highly on aging this maybe on aging, be a consequence of polymer penetrating of the internal void space of the structure aggre ; there as a result of high local carbon black concentration , molecules are adsorbed more efficiently than on the exterior surface , leading to higher bound rubber and increased reinforcing action. The elongation value increased slight on aging. The may be explained by the cross-linked that formed after (6) days[25].

Carbon black (SAF) phr	Tensile strength	Modulus	Elongation	Hardness
10	5	0.44	518.4	27
20	8	0.53	542.2	33
30	9	1.43	309.8	35
40	11	1.23	392.4	42
50	12	4.75	152.8	46
60	10	1.14	129.9	51

Table (10):Effect of aging on NR reinforcement by carbon black(ASF)

Carbon black (Nano)phr	Tensile strength	Modulus	Elongation	Hardness
1	1	0.01	495.1	16
2	1.5	0.02	364.6	22
3	2	0.03	385.3	25
4	3	0.05	412.8	31
5	3.5	0.06	363.2	34
6	2.6	0.03	337.2	39

Table (11):Effect of aging on NR reinforcement by carbon black(Nano)

Polyethylene phr	Tensile strength	Modulus	Elongation	Hardness
15	19	5.34	252.4	41
30	24	8.21	150.5	53
45	17	4.27	112.2	67

Table (12):Effect of aging on NR/PE blending reinforcement by carbon black (SAF)

Polyethylene phr	Tensile strength	Modulus	Elongation	Hardness
15	6.5	0.03	273.6	39
30	14	0.07	320.3	48
45	16	0.03	247.9	52

Table (13):Effect of aging on NR/PE blending reinforcement by carbon black(Nano)

Polystyrene phr	Tensile strength	Modulus	Elongation	Hardness
15	13	0.04	364.7	46
30	9	0.07	98.2	52
45	7.5	0.23	23.2	60

Table (14):Effect of aging on NR/PS blending reinforcement by carbon black (SAF)

Polystyrene phr	Tensile strength	Modulus	Elongation	Hardness
15	4	0.03	278.7	37
30	5	0.05	198.4	42
45	6	0.4	112.3	49

Table (15):Effect of aging onNR/PE blending reinforcement by carbon black(Nano)

CONCLUSIONS

From this study, the following conclusions can be drawn the increasing filler compositions improve the properties of the natural rubber. The tensile strength, modulus and hardness, increased with increasing filler loading while elongation at break and compression set decreased. The solvent uptake decreased linearly with increasing filler loading and the effect was more noticeable in the highly swelling solvents.The study has investigated the effect of thermoplastic (PE,PS) on natural rubber properties, NR 70phr/PE30phr based binary blends resulted to the best loading according to the tensile properties, while NR 85phr/ PS 15phr based binary blends resulted to the best loading according to the tensile properties.Excellent chemical resistance can be obtained by using NR/PE,PS blends.

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