

Properties of Thermoplastic Elastomers Vulcanizates curing by Polymethylol Resin (Resole)

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Abstract

The vulcanization of Natural rubber with different loading of polymethylol resin (Resole) was studied to know the role of resole as curing agent. It was found that the vulcanization of natural rubber with resole showed higher tensile strength, Modulus and Hardness were seen with (10 phr) loading of resole, while an adverse effect observed only with a high loading at (15 phr). Thermoplastic elastomers (TPE) blends based on NR/PE, NR/PS, NR/PP and NR/PVC blends in various ratio; 100:0, 70:30, 85:15, 85:15 and 85:15 respectively were prepared. The mechanical properties of natural rubber (NR) blends were studied. It was found that the incorporation of (PP, PVC, PE and PS) in the blend compositions leads to the decrease in degree of swelling. As expected, when the (PP, PVC, PE, PS) ratios were increased in the blends resulted in better tensile properties. The effect of chemical and oil resistance on rubber blends were studied. The thermal properties of vulcanized thermoplastic elastomers blends were studied by the differential scanning calorimetry (DSC) revealed that thermoplastic/Natural rubber blends are thermodynamically miscible. Aging of rubber compounds were studied also.

Key words:-Natural rubber blend, Fillers, Resole, mechanical properties, Polymethylol resin. Thermoplastic elastomers

1.INTRODUCTION

Generally the crosslinked of rubber compounds is by sulfur vulcanization [1-3], peroxide curing[4], or resole curing[5]. The vulcanization by sulfur is the most common S-S and C-S bonds made by sulfur curing are quite unstable. Therefore, the sulfur curing at elevated temperature weakens the mechanical properties of rubber because of reversion. Vulcanization using phenolic resin (resole) creates more stability for C-C bonds than S-S and C-S bonds. So, a resole-cured rubber vulcanizate has a high reversion resistance at elevated temperatures. Chroman mechanism is suggesting the crosslinking between unsaturated elastomers and phenolic resole resin, rooted in the study of low molecular weight model compounds [6-10]. A phenolic resole is changed to an o-methylene Quinone intermediate by dehydration at high temperatures [11-12]. Double bonds of olefins suffer intermediate reacts and forms chroman structures by a 1, 4-cycloaddition. A significant role of polymer blends has played in the last few decades in revolutionizing polymer technology, causing essential and helpful applications. A mixture of two or more polymers dissimilar in structure is expressed as 'polymer blend' or copolymers providing enhance to materials with vary of properties, not carried by any of the constituents. There are many reasons for choosing blends include: achievement of particular item performance, by enhancing the industrial properties of the original polymers, by adjusting the processing characteristics and decreasing the cost [13-17]. Thermoplastic elastomers are polymeric materials with the processing behavior of thermoplastic but having the mechanical properties and elastic recovery similar to vulcanized rubbers. Thermoplastic elastomer (TPE) is a new family in the field of polymer blending. Currently thermoplastic vulcanized (TPVs) are growing in very fast manner segment of the elastomer market and take up an essential position in the family of TPEs because of their huge possible. On the other hand, there are a number of unclear technological troubles, which are caused by a shortage of correct understanding of the TPVs. TPV production process and the relationship between the structure and properties of the TPVs are still in the development stage [18-19]. Thermoplastic elastomers from blends of poly butadiene rubber (BR) and polyethylene (PE) find applications in wire and cables, oil seals, hoses, automotive, household articles footwear, military and other molded articles by virtue of their easy process ability, excellent oil resistance and good mechanical properties. New application of polymer blend in the field of transfer actions of

various organic solvents and gases through polymers is of big technological importance and it takes an essential role in a diversity of barrier applications [20-22].

In this research, the curing agent consists of polymethylol resin (Resole), the loading amount of resole used were (2.5, 5, 7.5, 10, 12.5 and 15 phr). A resole as curing agent in the curing of natural rubber was studied. Aging and its effect on the mechanical properties also was studied. The preparation of NR(85) /PP (15), NR(70) /PE (30), NR(85) /PS (15), NR(85) /PVC (15), thermoplastic elastomer blends using different percent of resole as a vulcanizing agent in the presence of zinc oxide and magnesia.

2. EXPERIMENTAL

Materials

Natural Rubber (SMR20), Polystyrene, Polypropylene and Polyvinylchloride polyethylene (Sabic.Co)/K.S.A, Supper abrasion furnace (SAFN110) (Thailand carbon product Co, Ltd), Zinc Oxide and Magnesia was used as Activators, (Flexsys Co. Ltd) / Thailand, Polymethylol resin (Resole) 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 test

Dumbbell-shaped specimen using a tensile testing machine from (LARYEE Co) / China were used to measure the tensile strength and elastic modulus (M100) . With a load cell of 20 KN and a cross-head speed of 200 mm/min at room temperature . The dimensions of sample were designed according to ASTM D-412.

Hardness test

All hardness tests were carried out at room temperature ($25 \pm 2 \text{ C}^0$). And the hardness values of vulcanizates samples were measured using a Shore Adurometer according to ASTM D-2240 and the readings was four readings and taken after 3 seconds of indentation.

Compression test

Compression set was measured according to ISO 1653 at ambient temperature.

Gel Content

Soxlet extraction technique using for determined the gel contents using acetone as solvent. The samples were extracted for 32 h and dried in air and in vacuum oven at 70 C^0 until reach to constant weight. The gel content was calculated as follows:

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

Swelling test

The testing was carried out according to ASTM D-471. The swelling test completed by immersing the specimens in air-tight, metal-capped test bottles filled with acetone, which kept at a constant temperature of $25 \pm 2 \text{ C}^0$. The samples were periodically removed from the test bottles. This process was continued until stability in swelling was achieved. 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 swollen mass and W is the mass after equilibrium swelling.

Curing (Vulcanization)

The rubber mixes were compression-molded at $195 \pm 2 \text{ C}^0$, at 50 min using an electrically-heated hydraulic press (HITOP RUBBER CO.) Model (XLB300X300X2) to their best cure times derived from rheological measurement.

Differential Scanning Calorimetry

DSC measurements were analyzed on (DSC 131 Evo, SETARAM, (France)). Around 10 mg of samples was sited in cups of aluminum and then 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 gained as heat flow

versus temperature plots by heating from room temperature to 250 °C at a rate of 10 °C/min under N₂atmosphere.

3.SAMPLE PREPARATION

Primary NR was incorporated into the neat polymers by uses of an internal mixer (Record E3000). With aspeed of rotor was set at 50 rpm and the mixing time was 10 minute. The mixing temperature was70 C⁰ for rubber materials and 180 C⁰,195 C⁰ , 75 C⁰and 190 C⁰ for those containing PE,PP,PVC and PS In the next step, Binary systems consisting of NR, thermoplastic. Rubber was allowed to melt with PE,PP,PVCand PS (weight proportion 85/15,70/30and 55/45) in the kneader for 4 min at 180 C⁰and 190 C⁰,70 C⁰,210C⁰repectively , then NR was added and mixed for (6) min. For rubber compounding , Mixing was carried out according to ASTM D-3182 usea tworoll mill,dimensions of rolls 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) .A typical mixing specification is shown in the next steps, Rubber is passed through rolls two times without banding, at a mill roll opening of 0.2 cm at 70°C for (3 minutes),then we add Magnesia for (3 minutes), , add the zinc oxide (5 minutes)., add carbon black and add process oil for (10 minutes) , add antioxidants/ antiozonants for (4 minutes), add polymethylol resin (resole) to the master batch stock for (4 minute) Cooling the batch to room temperature. Total time is about(30 minutes). The blend was then casted at195 C⁰ for 50 min in an electrically heated hydraulic compress to get readysampleswith thickness =2 mm, subsequent to molding, cooled the blend was less than pressure (200 bar) to room temperature.

Table (1): COMPOSITION OF RUBBER COMPOUNDS PREPARED IN PRECENCE OF CARBON BLAK(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
Magnesia	4	4	4	4	4	4
6PPD	1	1	1	1	1	1
Carbon black (SAFN110)	50	50	50	50	50	50
Aromatic oil	5	5	5	5	5	5
Resole	2.5	5	7.5	10	12.5	15

TABLE (2) : THERMOPLASTIC/NATURAL RUBBER BLENDS FORMALATIONS

Ingredients	Recipes 1 phr	Recipes 2 phr	Recipes 3 phr	Recipes 4 phr
NR	70	85	85	85
PE	30	-	-	-
PS	-	15	-	-
pp	-	-	15	-
pvc	-	-	-	15
Zinc oxide	5	5	5	5
Magnesia	4	4	4	4
6PPD	1	1	1	1
Carbon black (SAFN110)	50	50	50	50
Aromatic oil	5	5	5	5
Resole	10	10	10	10

RESULTS AND DISCUSSION4.

Effect of resole loading on physic-mechanical properties of the natural rubber compounds

Table (3): listed the changes in the mechanical properties of vulcanizates with resole loading. Examination of the data in table explains large difference in several properties. Especially, tensile strength and hardness (Shore A) values are a maximum for high resole content compounds. This may be associated with the temperature, resin acidity, structure, free phenol, formaldehyde contents, and the resin moisture content. Because of reactive molecules when heating tend to concentrate, during methylol groups reaction, to stable methylene links causes the creation of three-dimensional network of resin, which act together with rubber network. For the elongation is greatly reduced with resole loading increasing. All mechanical properties that measured in the presence of resole at 10 phr of. An increase in resole loading higher than 10 phr decreased the mechanical properties values of thermoplastic elastomers compounds. The losing of the main-chain modification may be associated to the causes [23].

TABLE (3) MECHANICAL PROPERTIES OF THE RUBBER COMPOUNDS WITH DIFFERENT LOADINGS OF RESOL

phr	Tensile strength MPa	Modulus at 100%	Elongation%	Hardness	Compression
2.5	4.5	3	164.8	28.23	3.54
5	6.5	4	178.5	31.56	2.98
7.5	10	5	203.3	35.34	2.70
10	15.5	6	132.7	42.34	2.32
12.5	5.5	5	187.8	47.34	2.10
15	5	5.4	104.3	49.56	2.02

Effect of Thermoplastic Blending on physic-mechanical properties of Natural rubber compounds

A chief factor for controlling the NR into thermoplastic is the interfacial adhesion between NR and thermoplastic matrix, as a result inferior of mechanical properties of blends for the reason that weakness in 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), (PE), (PP) and (PVC). Mechanical properties of blends related to NR and thermoplastic, depend on nature of NR, content of NR, polymer matrix type, interfacial adhesion between NR and thermoplastic matrix [24]. Tensile strength, modulus of elasticity and elongation 100% at break of NR/PE, NR/PP, NR/PE and NR/PVC blends are summarized in Figures (1). Observed from figure there are good increasing in the tensile strength, elastic modulus and elongation at break with the increase of rubber loading from 55% to 85%, this is due to the increment of rubber loading. Rubber is known to be soft and elastic. So blends with higher rubber loading and have higher elasticity and softer compare to blends which had lower rubber loading. For both NR/PE, NR/PP, NR/PE and NR/PVC blends, blend ratio at 70/30 for NR/PE gave the best tensile strength, and blend ratio at 85/15 for NR/PP, NR/PE and NR/PVC gave the best tensile properties. The grafted PE and PS contributed to the stiffness and strength of NR/PE, NR/PP, NR/PE and NR/PVC blends looking at the total volume of rubber/thermoplastic ratio between NR/PE, NR/PP, NR/PS and NR/PVC: 70/30, 85/15 blends from, the blends are having higher amount of thermoplastic; i.e. PE, PP, PVC 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, NR/PP, NR/PE and NR/PVC: 70/30, 85/15 blends are stiffer and stronger than NR/PE, NR/PP, NR/PE and NR/PVC 85/15 blend [25]. It can be noted that tensile strength of NR/PE 55/45 and NR/PP, NR/PE and NR/PVC blends showed enhances in tensile strength with increasing the content of NR in the blends until it reaches the maximum of pure PE, PP, PVC and PS. similar behavior was also showed by elongation at break a i.e. the value increases as PE and PS content is higher [26]. Increase in hardness in rubber blend due the

increment of thermoplastic (PE,PS,PP,PVC) loading, The addition of NR into (PE,PS,PP,PVC) resulted in lowering compression set because of the limitation of the mobility of chains ensuing from the physical cross-links initiated by the thermoplastic^[26].

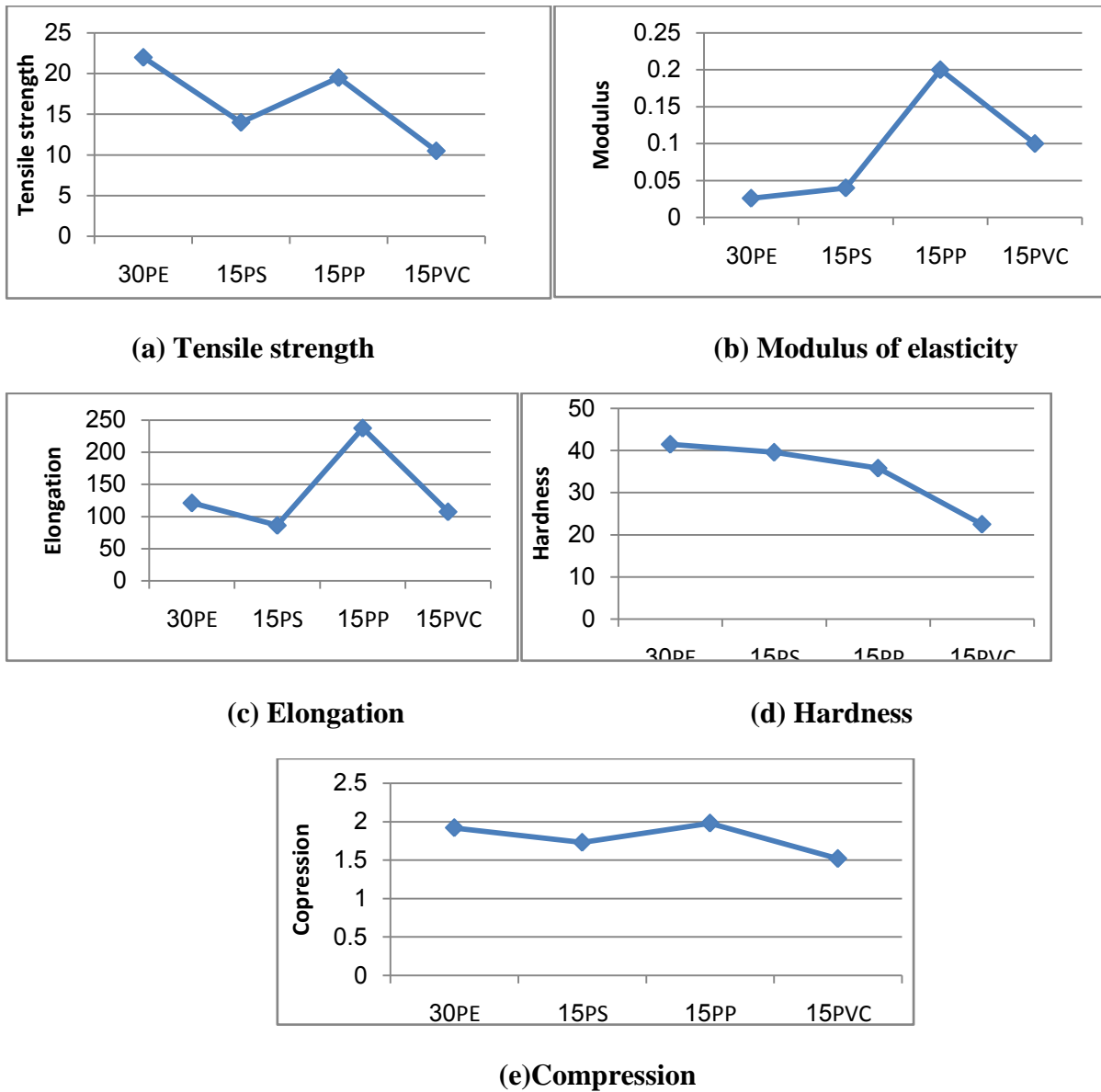
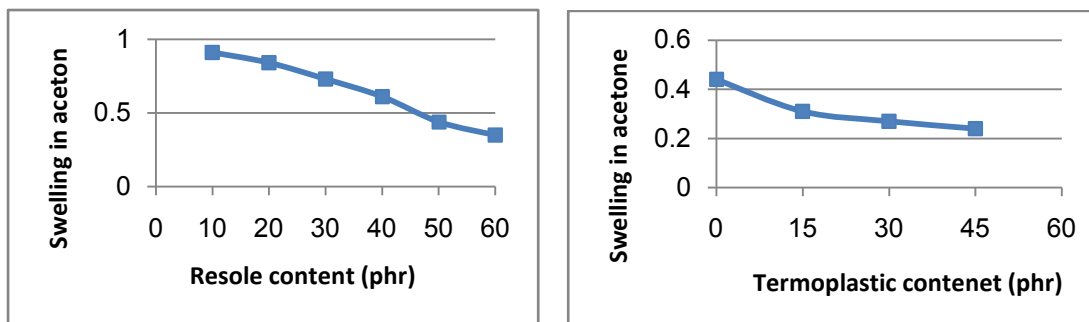


Figure (1): The effect of thermoplastic content on the mechanical properties of NR compounds

Effects of resole loading on swelling behavior

With increasing resole loading the solvent uptake decreases linearly and the effect is more distinct with the highly swelling solvent (Acetone) which possesses the highest slopes (as observed in figures (2)). For a second time that may be because of the beginning of physical cross-links which limited the rubber from swelling. Highest swelling happens with acetone because of the solubility parameter of rubber blend have value close to the solubility parameter of this solvent^[27]. It is assumed that tough contact happens between the rubber and plastic phases, the matrix-filler interphase diminish in swelling with resole loading may be because the configuration of a network arrangement marked by the resole. Swelling index can be used as helping blends in the formation of cross-links. Swelling index decreases with increasing resole loading which indicates an increase in the cross-link density^[26].



(a) : swelling of NR

(b) : swelling of NR/Thermoplastic

Figure (2): The effect of swelling on the mechanical properties of NR compounds and NR/Thermoplastic blends in presence of Resole

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,PP,PVC) 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 tests were carried out in two ways:

- a. for 96 hrs. at 70 C⁰
- b. for 96 hrs. at room temperature

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

Tables(4) 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 table which gives the weight increase or decrease of different vulcanizates percentages shows 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^[28]. 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:

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(4) .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^[28].

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

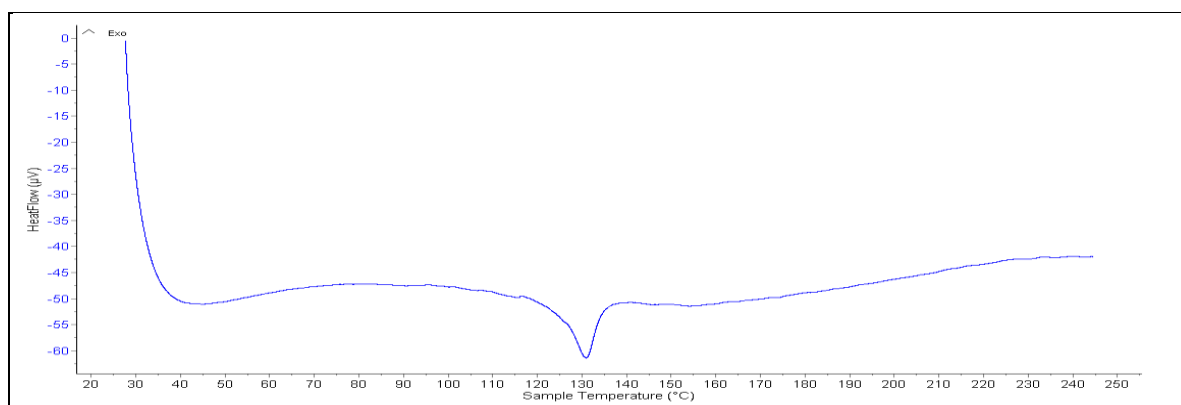
equilibrium but the time taken to reach equilibrium depends on the viscosity of the oil and on the distance of the center of the rubber from the surface in contact with oil. The total volume of the swollen rubber is equal to the sum of the volume of rubber plus the volume of the oil absorbed. The equilibrium 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 (4) the same vulcanizates were tested at room temperature and at 70°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°C to weight at R.T., this is by fair means a good stability for vulcanizates obtained^[29].

TABLE (4) EFFECT OF ACIDA, BASE AND OIL ON NR/ THERMOPLASTIC PROPERTIES

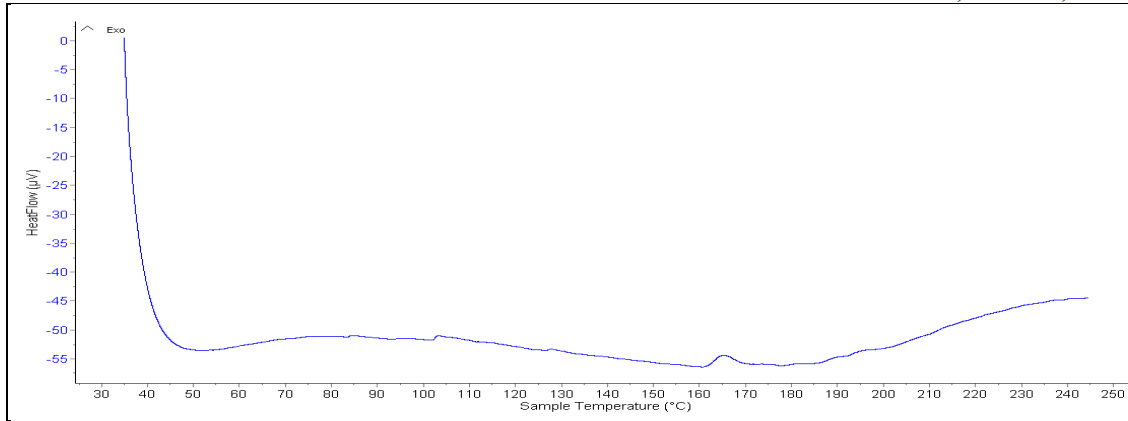
Recipes (phr)	Temperature °C	Change in weight of tested sample % in					
		H ₂ SO ₄ 70%	H ₂ SO ₄ 50%	HNO ₃ 50%	HNO ₃ 70%	KOH 70%	Oil
NR/PS	RT	+0.27	+0.24	+0.21	+0.24	+0.32	+0.28
	°C70	+0.26	+0.123	+0.23	+0.26	+0.35	+0.29
NR/PP	RT	+0.24	+0.21	+0.21	+0.23	+0.35	+0.30
	°C70	+0.26	+0.23	+0.23	+0.25	+0.31	+0.25
NRLPE	RT	+0.26	+0.22	+0.24	+0.23	+0.28	+0.23
	°C70	+0.28	+0.25	+0.27	+0.25	+0.25	+0.30
PVC	RT	+0.23	+0.21	+0.21	+0.22	+0.33	+0.37
	°C70	+0.25	+0.24	+0.23	+0.24	+0.39	+0.41

Differential scanning calorimetry(DSC)

When samples are heated, cooled or held at a constant temperature, the total absorption or release of energy is measured by DSC. It is completed by using two temperature probes where replacing them in the furnace with a sample, which is heated at a constant rate and at the same time measuring the temperature of the sample and furnace. This method is employed for polymer and pharmaceutical applications. The DSC will be resulted in a heat input against temperature curve. It can be determined from the DSC curve many properties such as glass transition temperature, crystallization point, melting point.



Figure(3): DSC curve for NR/PE



Figure(4) : DSC curve for NR/PS

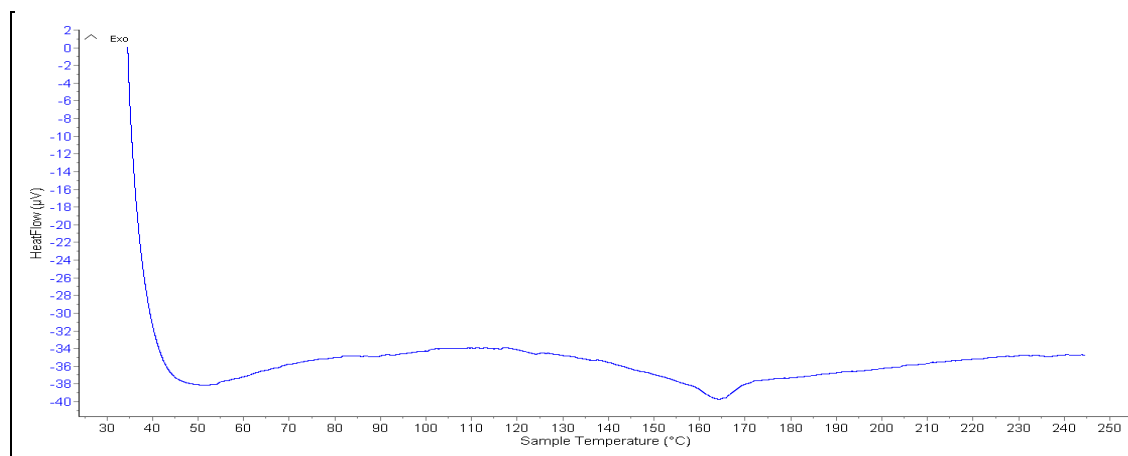


Figure (5) : DSC curve for NR/PP

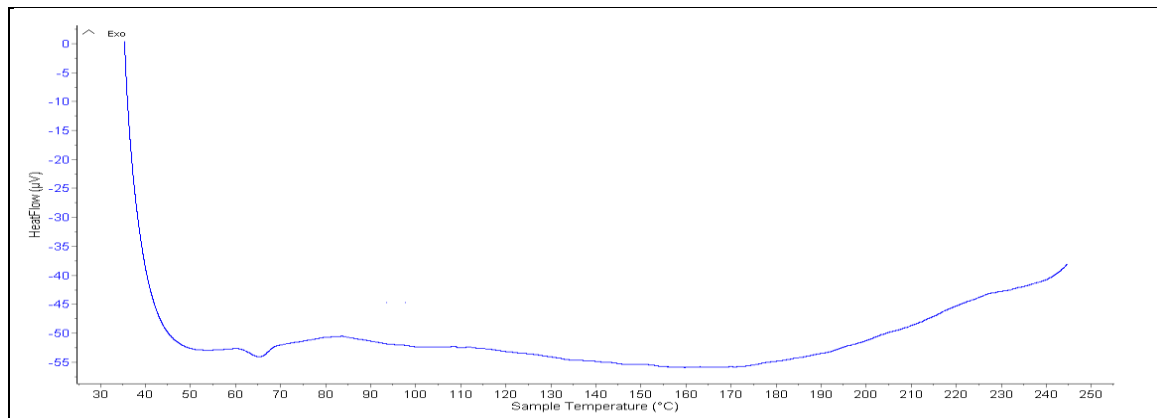


Figure (6): DSC curve for NR/PVC

Figure (3, 4, 5, 6) show the DSC curve of prepared sample with NR/PE, 70/30phr, NR/PP, NR/PS and NR/PVC 85/15phr. From this figure, it can be recognized that, the glass transition take placed at a temperature of 38⁰C NR/PE ,48⁰C NR/PS,45⁰C NR/PP and 44⁰C NR/PVC . It was indicated by the increase in heat flow. It is the glass transition temperature,heat at increased rate while the sample starts withdrawing. Next it arrives atthe point of melting, and it completely melts, heat absorption also decreases. And continues till its degradation starts. At this timeit can be notedthat the melting point as 235⁰C NR/PE and 163⁰C NR/PS, 2530C NR/PS and 196⁰C NR/PS. DSC for the rest of the sample also was done ^[30].

TABLE (5) THE GLASS TRANSITION, MELTING TEMPERATURE AND CRYSTALLIZATION TEMPERATURE OBTAINED FROM (DSC)

sample	T _m	T _g	T _c
NR/PE	235 °C	38 °C	130 °C
NR/PS	163 °C	48 °C	103 °C
NR/PP	235 °C	45 °C	167 °C
NR/PVC	196 °C	44 °C	67 °C

The effect of aging on the mechanical properties of rubber compounds

Table (6) is illustrated the effect of aging on the mechanical properties of rubber compounds with different loading of resole. From it can be seen that slight decrease in tensile strength and elongation values for rubber compounds with different loading of resole this may be show after 6 days at 80 °C. On aging there is improvement of resin crosslinking and the commencement of the previously crosslinked resin that may be the main reason for this behavior. There are highly increasing at the values of the hardness and modulus on aging. The cross-linked that created after 6 days and generally all bonds not suffered any breakage on aging; this may be good explanation for this enlargement. The truth that the new cross-linking can be created between the polymer chains through aging also may be give explanation to increasing the hardness and modulus values on aging. Thermal ageing at a temperature up to 80 °C for different time equal to 6 days was subjected to the blends of NR with PE, PS. Then the mechanical properties were measured and the retained values were calculated and are listed in Table (7). Table data proved that the binary blends have slight increase in tensile strength, modulus and decrease elongation values (NR/PE, NR/PS) blends. As a result of the presence of PE, PS in NR blends, the ageing is resist for the rubber blends.

TABLE (6) MECHANICAL PROPERTIES OF RUBBER COMPOUNDS AFFECTED BY AGING

Resole	Tensile strength	Modulus	Elongation	Hardness
2.5	3	4.4	140	29
5	5	5.3	153	37
7.5	9	7.43	166	44
10	14	8.23	125	49
12.5	2	8.75	165	53
15	4	9.14	95	59

TABLE (7) MECHANICAL PROPERTIES OF NR/THERMOPLASTIC BLENDS AFFECTED BY AGING

Thermoplastic	Tensile strength	Modulus	Elongation	Hardness
NR/PE	14	10	115	66
NR/PS	7.5	20	88	52
NR/PP	12	30	187	45
NR/PVC	4	50	99	39

5. CONCLUSIONS

The following conclusions can be reminded after this study, the addition of resole compositions improve the properties of the natural rubber and thermoplastic /Natural rubbers blends. The tensile strength, modulus and hardness values are a maximum for high resole content compounds while elongation at break and compression set reduced. The solvent uptake decreased in linear pattern while a filler loading was increasing and there is clearer effect in the greatly swelling solvents. Best mechanical properties are achieved when (10 phr) of resole is present. But the mechanical properties of NR compounds are reduced at an increase in resole loading exceeding (10 phr). The study has investigated the effect of thermoplastic (PE, PS, PP, PVC) on natural rubber properties, NR70phr/PE30phr based binary blends resulted to the best loading according to the tensile properties, while NR 85phr/ PS 15phr, NR 85phr/ PP 15phr, NR 85phr/ PVC 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. Also it is able to be observed that the different loading of resole to compounds of rubber behind 6 days at 80 °C shows small diminish in tensile strength, elongation, and tear strength values.

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