# RESULT
&
DISCUSSION

RESULTS AND DISCUSSIONS

Epoxidation of Natural Rubber [100].

The epoxidation process of natural rubber with peracetic acid 59% was carried out by reacting hydrogen peroxide with acetic acid   in presence of small quantities of conc. sulfuric acid as a catalyst. Factors such as; concentration of peracetic acid, time of epoxidation and overall reaction temperature were investigated. Sets of experiments were carried out to careen these variables to select the optimum conditions. The chemical properties of the obtained products such as OH group content, and epoxy group content were evaluated.

The electron repelling group (CH_3 – group) in peracetic acid, could make possible the formation of hydroxonium ion OH^+ [101, 102]. The formation of hydroxyl groups, in presence of peracetic acid, may be due to the fission of epoxide rings which takes place during the preparation and treatment of the epoxidized linseed oil. The possible reactions which may lead to the fission of the epoxide rings are illustrated in the following equation:
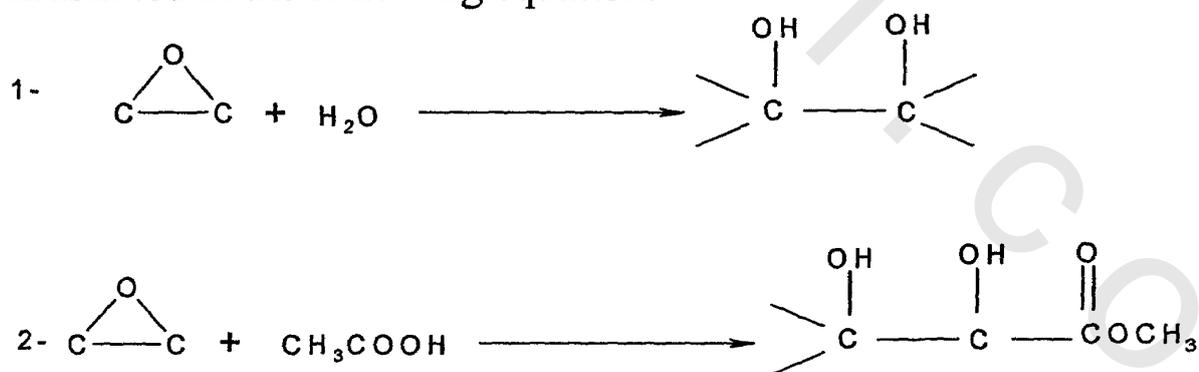
- Effect of Peracetic Acid Quantity

Different molar ratios of peracetic acid/10gm natural rubber dissolved in 1litre toluene were used. The effect of peracetic acid concentration on the properties of the obtained epoxidized natural rubber for experiments carried out at constant stirring for 15hrs at room temperature (30°C), and the obtained results are given in Table (4a).

Table (4a): Effect of Peracetic Acid (Aqueous Solution, 59%) quantity on the Properties of the Obtained Epoxiodized Natural Rubber.

Quantity of Peracid/10gm N.R.	Epoxy Group Content, %	Hydroxyl Value, mg KOH/g. NR
19	19	11
38	25	16
76	32	20
114	38	25

Data given in Table (4a) show that, with increasing the quantity of peracid relative to N.R (10g), from 19 to 114 gm, the epoxy group content, and hydroxyl value of the obtained epoxidized NR increases. For economical reasons the optimum quantity of peracetic acid was chosen (38gm) at the mentioned other conditions and the optimum conditions of the other determining factors, such as overall reaction time and temperature are evaluated for this quantity.

- Effect of Reaction Time

Stirring was carried out for different overall reaction times at 30°C and the properties of the obtained epoxidized natural rubber with peracetic acid (38ml conc. 59% to 10gm NR) are given in Table (4b), and illustrated in Figs (7 and 8).

Table (4b): Effect of Reaction Time at 30°C on the Properties of the Epoxidized Natural Rubber with Peracetic Acid.

Time of Reaction, hrs	Epoxy Group Content, %	Hydroxyl Value, mg KOH /g. NR
0	0	0
2	17	13
4	29	26
6	25	45
8	14	59
10	10	70

The obtained results show that with increasing the time of reaction the epoxy group content, increases. The maximum value of epoxy group was obtained after 4h (29), then began to decrease till (10) after 10h. However the hydroxyl value increased progressively with the overall reaction time. It is possible that increasing the time of reaction increases the probability of reaction between epoxy groups and the contents of the reaction medium. The fission of epoxy groups could be mostly due to the presence of H_2O which reacts with the epoxy group to give glycol, which leads to an increase in the values of hydroxyl group of the molecule.
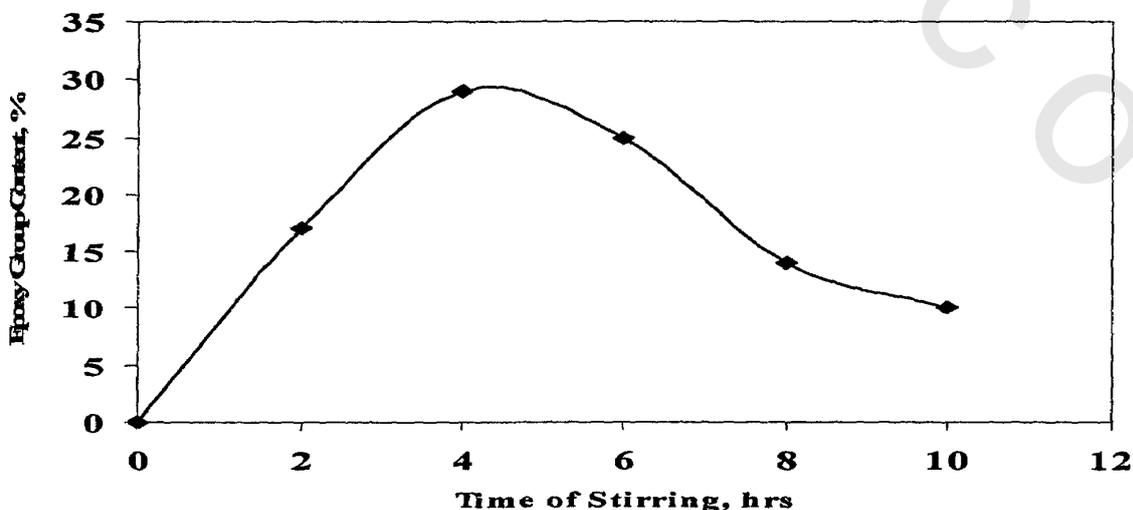
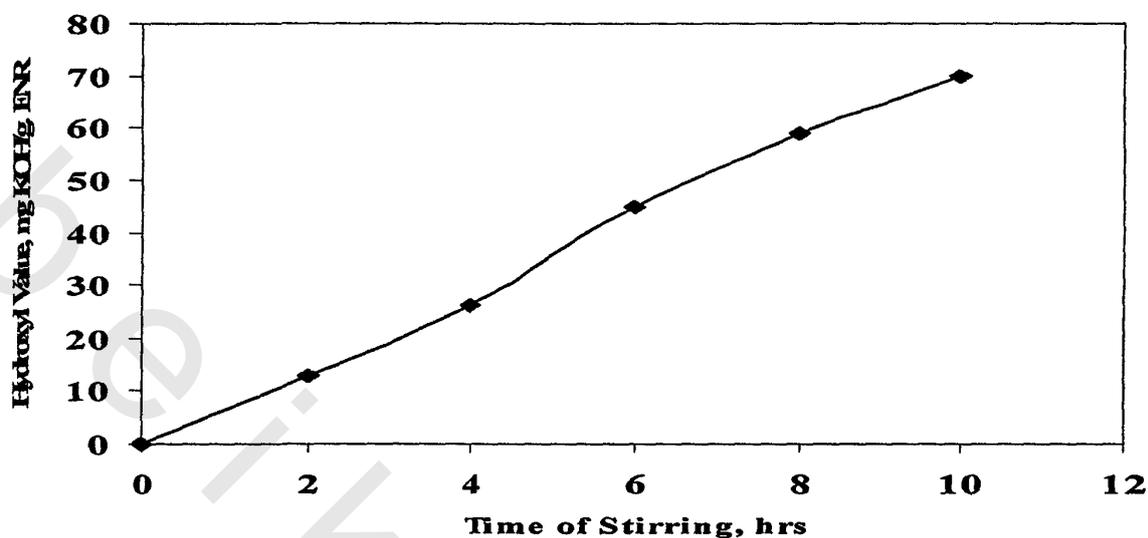Fig (7): Effect of Stirring Time on Epoxy Group Content

Fig (8): Effect of Stirring Time on Hydroxyl Value.

The I.R spectrum for the epoxidized natural rubber as compared with that of non-epoxidized natural rubber. Fig (9a) shows the epoxy absorption band at 1233.9 and 2851 cm^{-1} and Fig (9b) shows the hydroxyl absorption band at 3537.3 cm^{-1} [103].
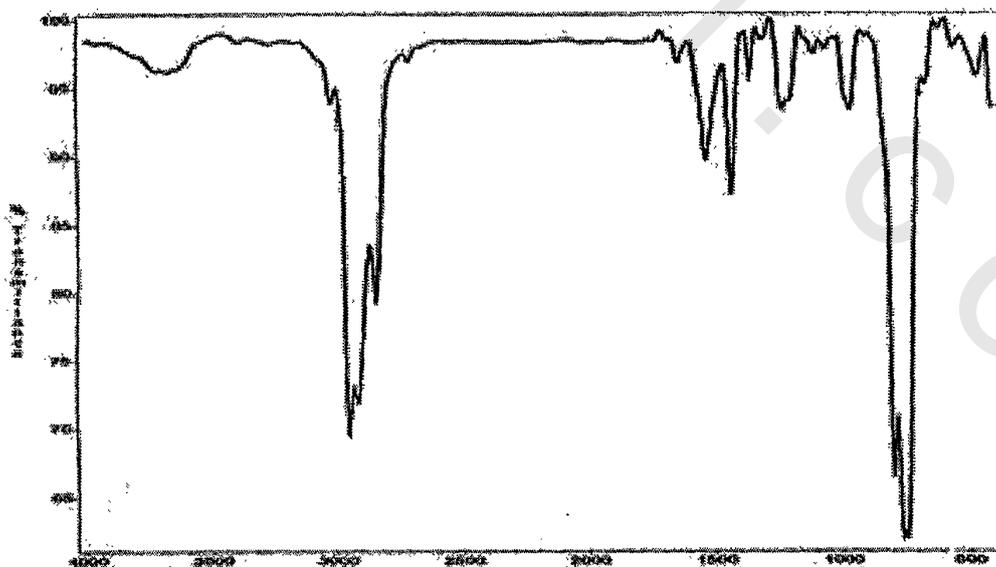

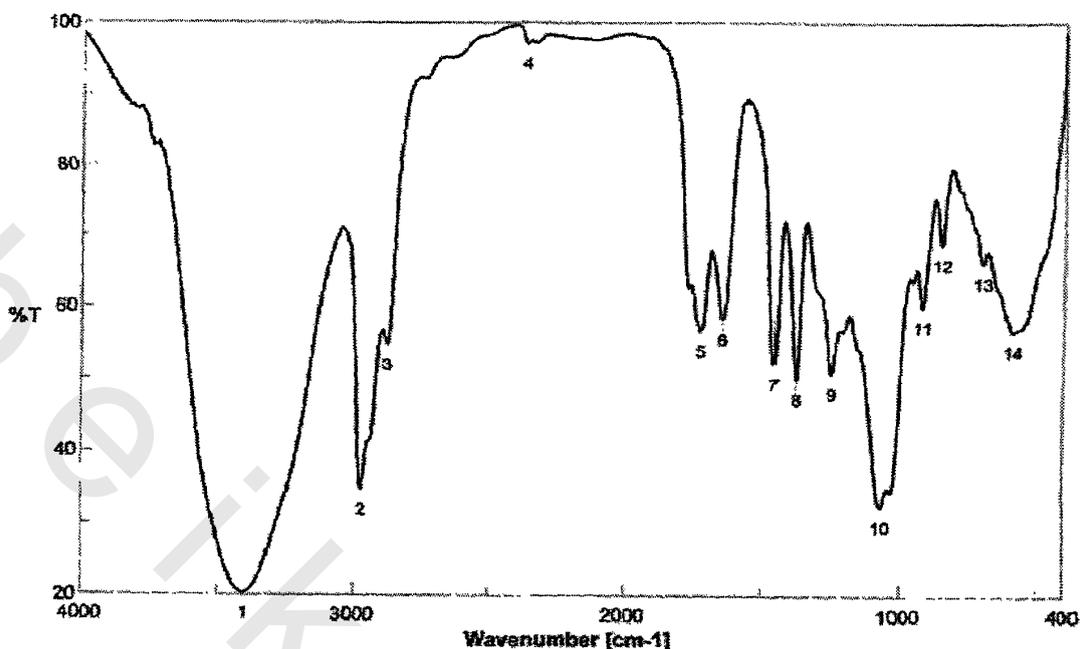**Fig (9a): IR spectrum of the non epoxidized natural rubber**

Fig (9b): IR spectrum of the epoxidized natural rubber

Epoxidation of natural rubber is a long-standing technique to improve the properties of the rubber such as solvent resistance, gas permeability and mechanical properties, in addition to high tensile strength and tear strength that the rubber inherently holds.

The epoxidation has been mainly carried out in latex stage using freshly prepared peracetic acid, performic acid, or the mixture of hydrogen peroxide and organic acid, i.e. formic acid or acetic acid. The epoxy groups of the rubber were confirmed to be stable under well-controlled condition. In contrast, they resulted in mostly ring-expanded and ring-opened secondary derivatives in the presence of excess amounts of acetic acid and hydrogen peroxide.

Thus, it is interest to investigate the relationship between structure and properties of epoxidized natural rubber (ENR).

The epoxy group contents, distribution of epoxy groups, ring-opened or ring-expanded groups and glass transition temperature (Tg) are the

important factrs to find this relationship. By analysis of the Tg data, it was found that, the increase of epoxy group content increases the Tg value from 381°C to 400 °C as shown in fig (10 a and b) respectively[104].
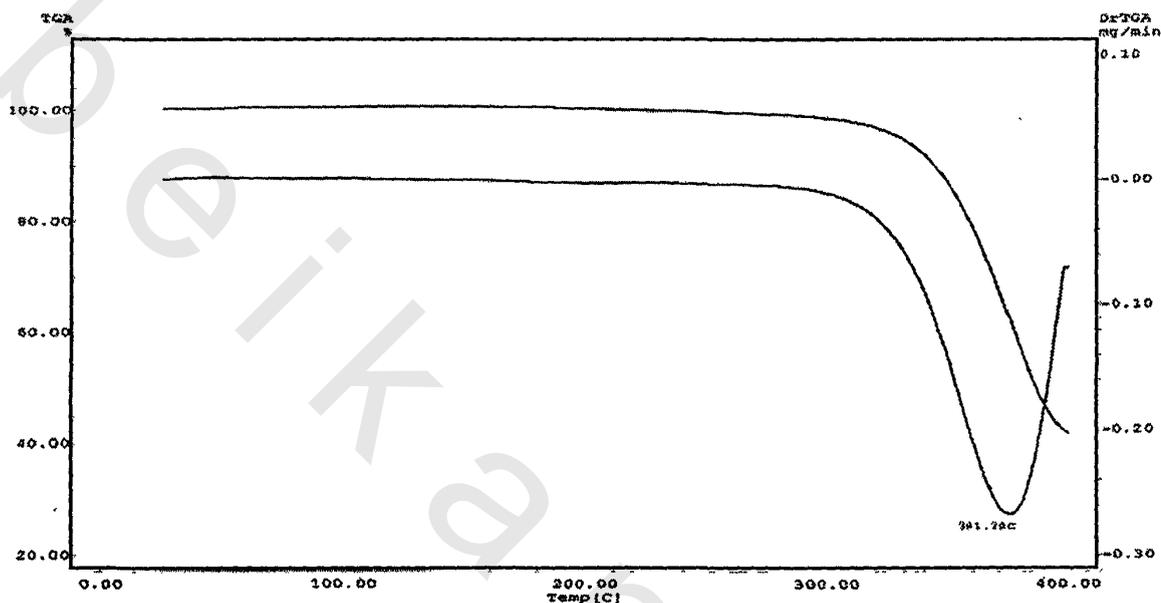

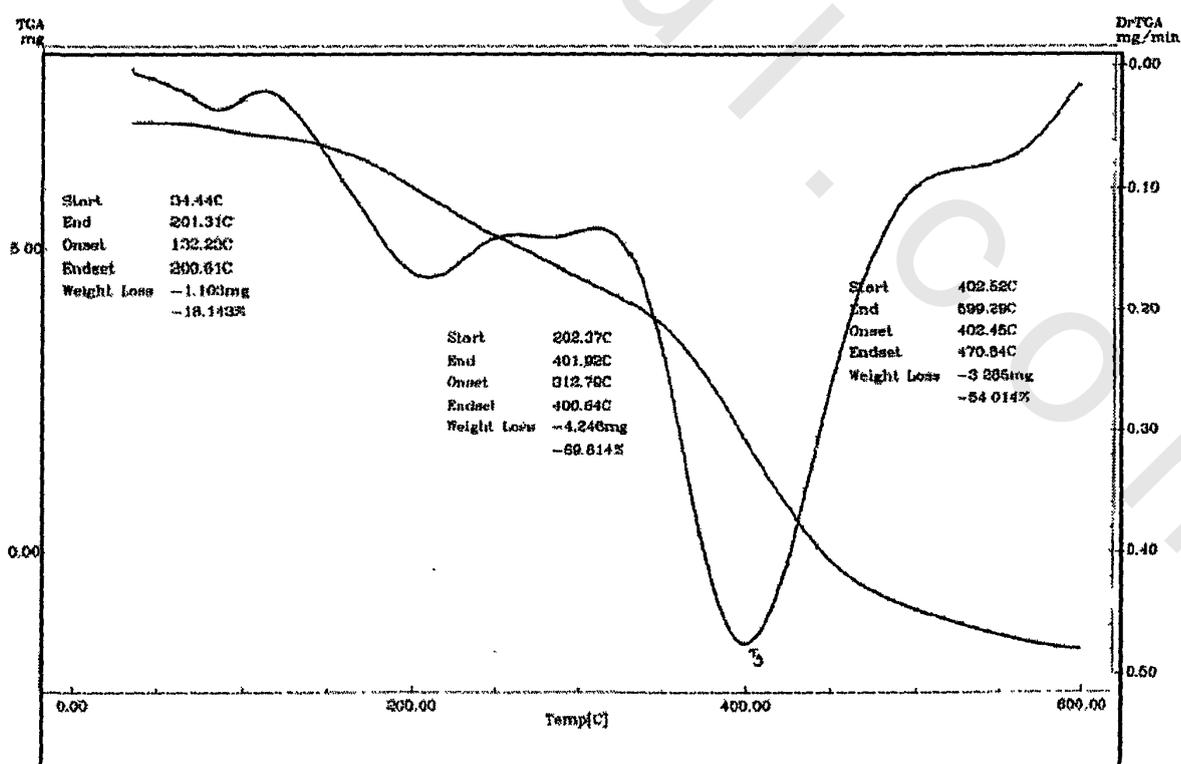**Fig (10a): T_g of the non epoxidized natural rubber**

Fig (10b): T_g of the epoxidized natural rubber

- Epoxidation of Styrene Butadiene Rubber (SBR).

The epoxidation process of SBR with peracetic acid was carried out using the same screening to obtain optimm conditions as well as ENR.

- Effect of Reaction Time

Stirring was carried out for different overall reaction times at 30°C and the properties of the obtained epoxidized styrene butadiene rubber with peracetic acid (38ml conc. 59% to 10gm SBR) are given in Table (5), and illustrated in Figs (11 and 12).

Table (5): Effect of Reaction Time at 30°C on the Properties of the Epoxidized Styrene Butadiene Rubber with Peracetic Acid.

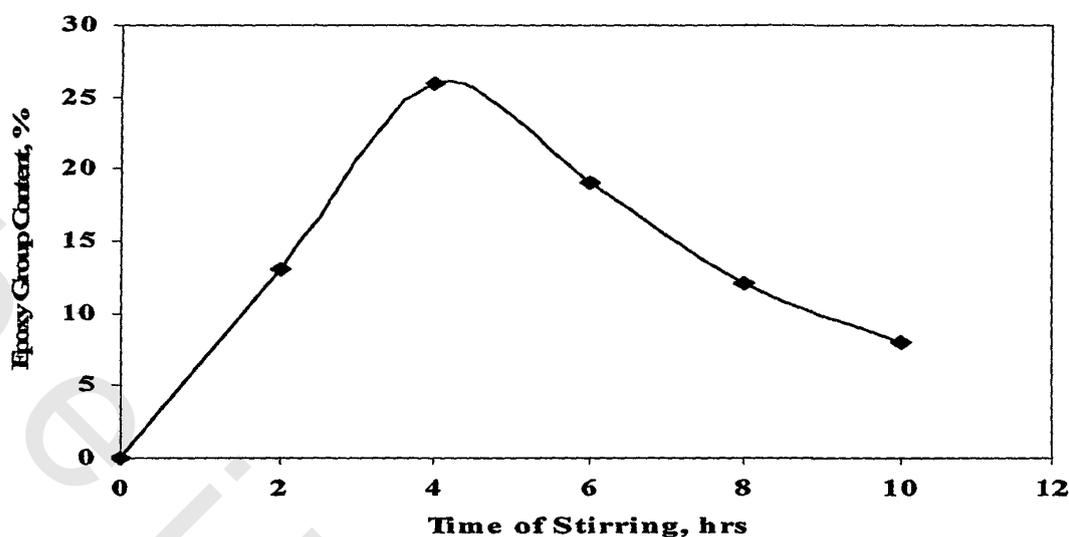| Time of Reaction, hrs	Epoxy Group Content, %	Hydroxyl Value, mg KOH /g. Oil
0	0	0
2	13	10
4	26	19
6	19	34
8	12	46
10	8	58

Fig (11): Effect of Stirring Time on Epoxy Group Content
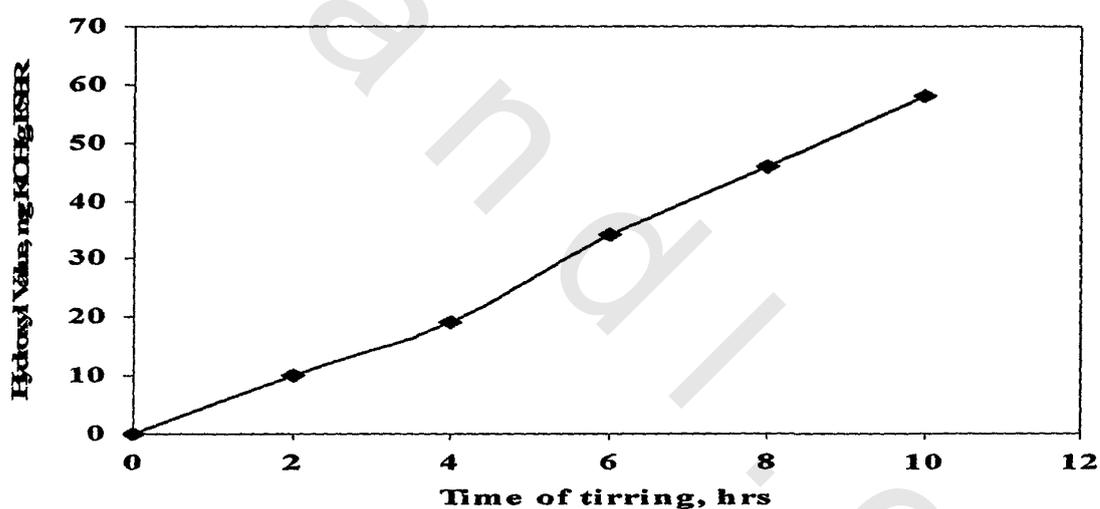
Fig (12): Effect of Stirring Time on Epoxy Group Content

The obtained results show that with increasing the time of reaction the epoxy group content, increases. The maximum value of epoxy group was obtained = 26 after 4h, then began to decrease till = 8 after 10h. However the hydroxyl value increased progressively with the overall reaction time. It is possible that increasing the time of reaction increases the probability of reaction between epoxy groups and the contents of the reaction medium. The fission of epoxy groups could be mostly due to the presence of H_2O which reacts with the epoxy group

to give glycol, which leads to increase the hydroxyl group of the molecule.

Comparison between ENR, and ESBR.

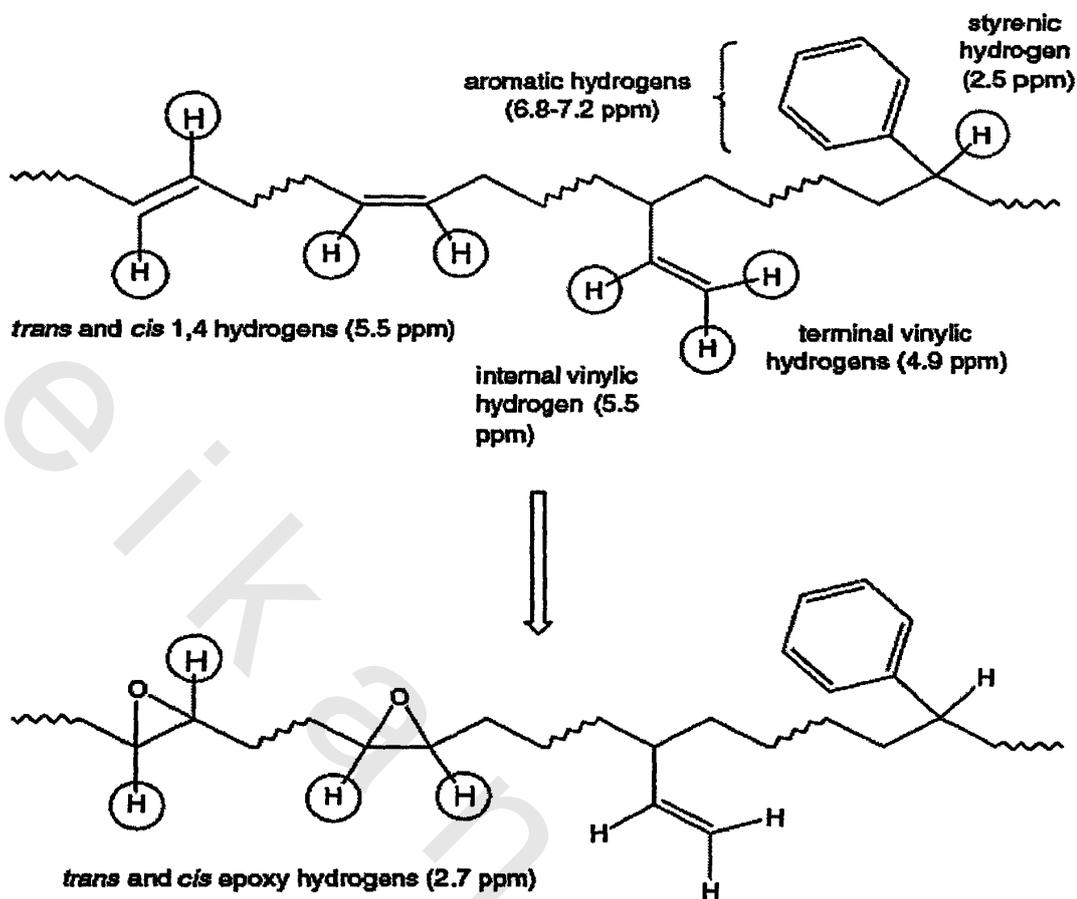Experiments were carried out to study the difference resulting from the epoxidation process at the same mentioned condition 59% peracetic acid concentration 38 mg added to 10gm NR, and SBR, for stirring time of 4h, and at 30 °C, The data are listed in table (6)

Table (6): Physical Properties of NR, ENR, SBR, and ESBR.

Sample	Epoxy Group Content, %	Hydroxyl Value	Iodine value
NR	0	0	185
ENR	29	26	57
SBR	0	0	209
ESBR	26	19	80

It can be concluded from the obtained data in Table 6, that, the hydrogen peroxide was not consume in case of NR and SBR. But in case of ENR and ESBR, it was consumed to stem the epoxide group along of the rubber chain. The epoxide groups in ENR were greater than those found in case of ESBR.

This fact can be attributed by the difficulty that the catalytically species has to reach the olefinic bond due to the presence of a phenyl ring[105].

aromatic hydrogens (6.8-7.2 ppm)

styrenic hydrogen (2.5 ppm)

trans and cis 1,4 hydrogens (5.5 ppm)

internal vinylic hydrogen (5.5 ppm)

terminal vinylic hydrogens (4.9 ppm)

trans and cis epoxy hydrogens (2.7 ppm)

Schematic representation of Starting and Epoxidized SBR

Asphalt Formulations for Pavement.

- Evaluation of Asphalt Formulations.

Formulations based on asphalt 60/70 penetration grade produced from Suez Co. (L), consist of blends obtained by mixing ENR, together with the curing agent (MA). Many sets of selected experiments were carried out to investigate the necessary times for their curing, amount of curing agent, (5 samples for asphalt type were prepared).

- Effect of Curing Time on the Physical Properties of the Obtained Formulations.

Each sample consisted of 95% asphalt (L)g + 5 % (ENR +5 % MA), and the physical properties for these samples were investigated by

testing the penetration (0.01mm), and softening point, °C for different times (5, 10, 15, 20, and 30hrs).

The data given in Table (7) and Fig (13) show that, the value of penetration (0.01mm) measured for the samples based on asphalt (L) decreased with increasing curing time till reaching the lowest value (41 for 20 hrs) and then remained unchanged with further increase of curing time. The value of softening point, °C also increased with the curing time for the tested samples. The highest value of softening point (49°C) was obtained after 20 h.

Thus that the tested formulation exhibited the highest hardness character at curing time of 20h.

The lowest value of PTS (0.02633) and the highest values of PI (-1.0977) were obtained after curing time of 20 h.

Table (7): Effect of Curing Time (hrs) on The values of Penetration, Softening Point, PTS, and PI for Formulations Consisting of 95% Asphalt (L) + 5% [ENR+5% (MA)] Cured at 150-170°C.

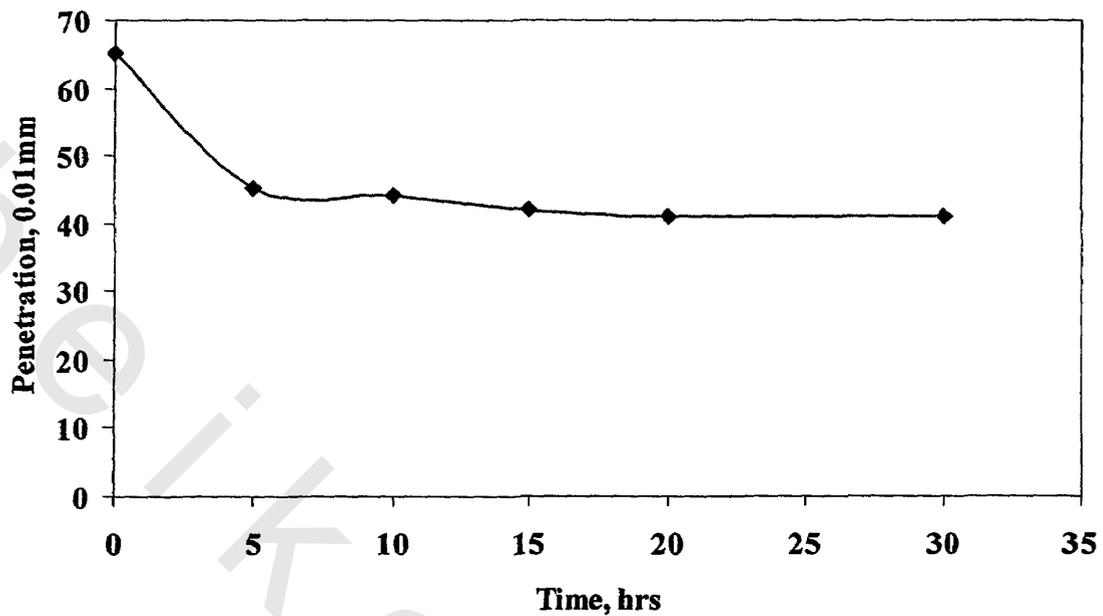| Asphalt Used	Curing Time, (hrs)	5	10	15	20	30
Suez 60/70	Penetration (0.01mm)	45	44	42	41	41
	Softening Point °C	47.3	47.8	48.5	49	48.3
	PTS	0.0264	0.02635	0.02638	0.02633	0.02671
	PI	-1.119	-1.102	-1.4881	-1.0977	-1.1876

Fig (13a): Effect of curing time, hrs on the values of penetration, (mm), for mixtures consisting of 95% asphalt (L) + 5% (ENR + 5% MA), cured at 150-170°C.
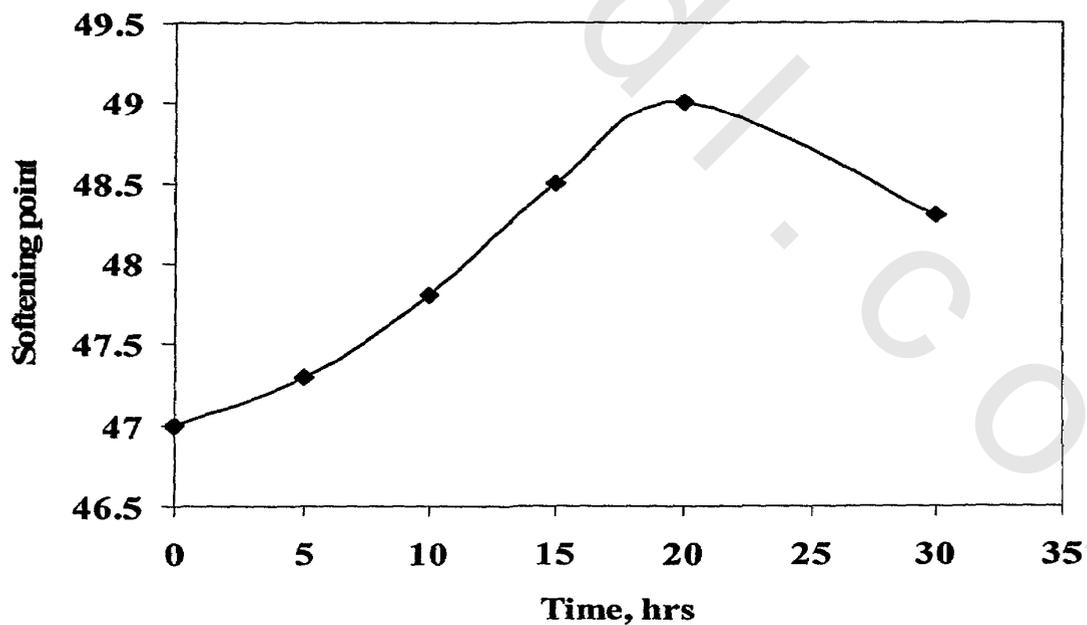

Fig (13b): Effect of curing time, hrs on the values of softening point, °C for mixtures consisting of 95% asphalt (L) + 5% (ENR + 5% MA), cured at 150-170°C.

- Effect of the Quantity of Curing Agent, % on the Values of Penetration, and Softening Point of the Prepared Formulations

Asphalt samples consisting of 95% asphalt + mixture consisting of 5% (ENR + MA). The mixture was made in different ratios (10–40w/w). The curing time was in the range of 150–170°C, at 20h, and the resulted samples were subjected to measure the penetration and softening point.

The obtained results in (Table 8 and Fig 14a) show that the values of penetration for all tested samples remain relatively unchanged with increasing MA%, until reaching the lowest value (38mm), at 40% of MA. The values of softening point of asphalt formulation increased gradually and record the highest value of (52 °C at 40% MA).

The values PTS of the tested formulations decreased with increasing the MA%. The lowest PTS value was (0.0254 at 40% MA). The values of PI increase gradually and reached the maximum value (-0.870) at 40% (MA). Such results indicated that the best hardness for asphalt formulations can be obtained in presence of 40% MA.

Table (8): Effect of The percentage of Curing Agent Malic anhydride (MA), of The weight of ENR on The values of Penetration, Softening Point, PTS, and PI for Formulations Consisting of 95% Asphalt (L)+ 5% (ENR+5-40% (MA) Cured at 150-170°C for (20) hrs, for Asphalt 60/70.

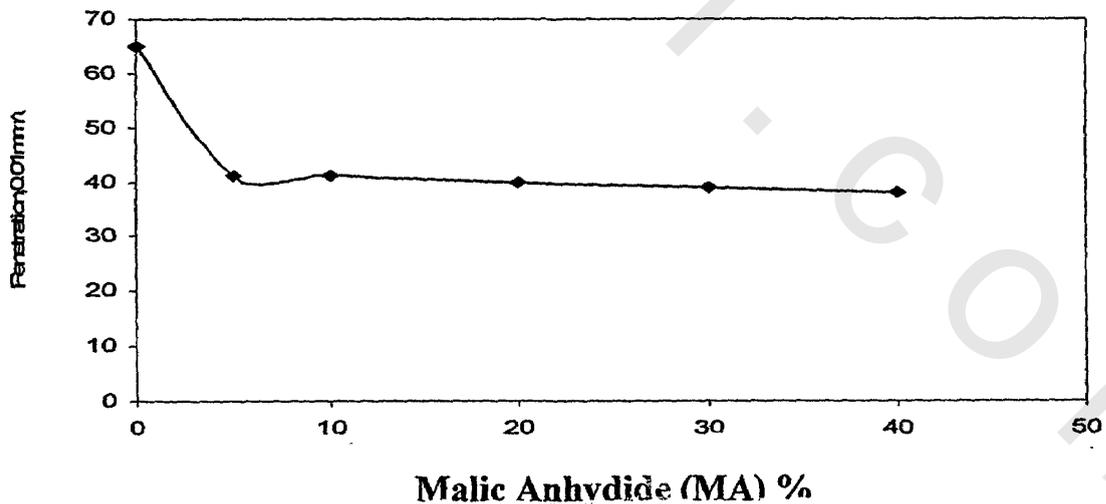| Asphalt used	Curing Agent, %	5	10	20	30	40
Suez 60/70	Penetration (0.01mm)	41	41	40	39	38
	Softening Point °C	49	49	50	51	52
	PTS	0.0263	0.0263	0.0260	0.0257	0.0254
	PI	-1.0899	-1.0899	-1.0179	-0.944	-0.870

Fig (14a): Effect of MA%, on the values of penetration, (mm), for mixtures consisting of 95% asphalt (L) + 5% (ENR +5-40% MA), cured at 150-170°C.
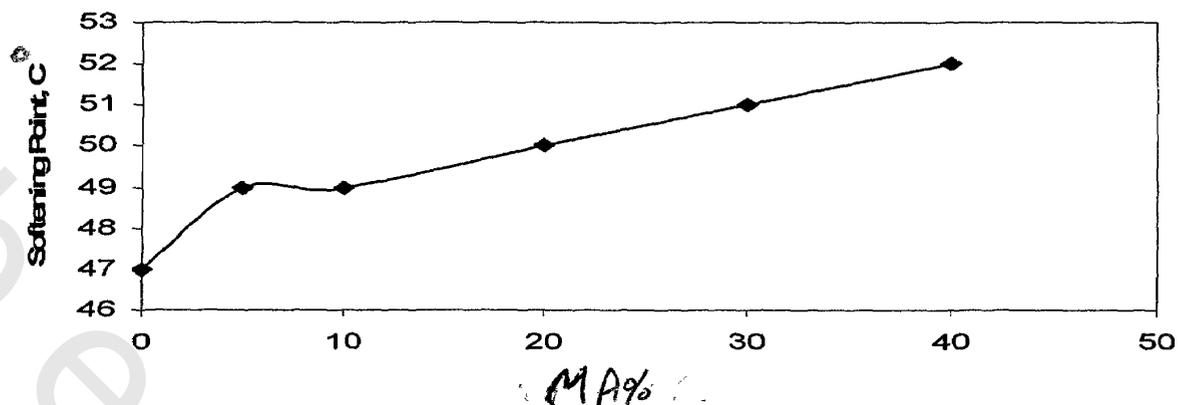
Fig (14$_b$): Effect of MA%, on the values of softening point, °C for mixtures consisting of 95% asphalt (L) + 5% (ENR + 5-40% MA), cured at 150-170°C.

We can according to the above mentioned data use asphalt modified with ENR in different percentage with 5, 10, and 15% each containing 40% MA at hot mix temp 150-170 °C for 20 hrs stirring. The mixture can then be used to be mixed with aggregate which was subjected to sieve analysis (c.f. Table 9 (a, b)).

Mechanical Properties of Asphalt concrete and it is Modification with epoxidized natural rubber (ENR).

In this part it is necessary to compare the mechanical properties of asphalt concrete (pentration grade of asphalt used 60/70 produced by Suez Co.) with the prepared ENR in the ratios 5, 10, and 15%, each quantity of ENR contains 40% by weight malice anhydride. Another sample of asphalt was used in hall no.3 in the inteternational Egyptian Cairo air port.

Asphalt 60/70 penetration grade and its formulations modified with epoxy resin based on epoxidized natural rubber (ENR) were mixed with the same grade of aggregates. The aggregates were 50% Dolomite as coarse aggregates + 45% sand as fine aggregate + 5%

Limestone powder as mineral filler. The Job Mix Formula of the surface course asphalt mix, 25mm max. agg. is listed in Table (9a).

Table (9a): Final Grading & Tolerance of the Surface Course Asphalt Mix, 25mm Max. Agg. Size.

Sieve Size, mm	Proposed JMF, % Passing	JMF Tolerance	
	JMF	Lower Limit	Upper Limit
25	100	93	100
19	96	89	100
12.5	78.6	71.6	85.6
9.5	69.2	62.2	76.2
4.75	54	47	61
2.36	39.2	35.2	43.2
1.18	31.2	27.2	35.2
0.6	21.8	17.8	25.8
0.3	11.7	7.7	15.7
0.15	6.8	5.8	7.8
0.075	4.5	3.5	5.5

Table (9b):Calculations of the Job Mix Formula of the Surface Courrse Asphalt Mix, 25mm Max. Agg.

Sieve Size,mm	C. Agg. 25mm:19mm		C. Agg. 10mm:4.75 mm		C. Agg. 14mm:10mm		C. Agg. 10mm:4.75 9mm		Filler (Crushed Limestone)		F. Agg Sand (C+N)		JMF (Total)	Limits of Project Technical Specification (Min.-Max.)
	%Passing		%Passing		%Passing		%Passing		%Passing		%Passing			
	100	5	100	18	100	7	100	20	100	5	100	45		
25	19.6	0.98	100	18	100	7	100	20	100	5	100	45	100	100
19	0.7	0.04	100	18	100	7	100	20	100	5	100	45	96	76-98
12.5	0.3	0.02	12.5	2.25	89.6	6.3	100	20	100	5	100	45	78.6	66-86
9.5	0.0	0.0	1.1	0.2	5.9	0.4	92.8	18.6	100	5	100	45	69.2	57-77
4.75			0.3	0.05	0.8	0.1	19.6	3.9	100	5	100	45	54	40-60
2.36			0.0	0.0	0.4	0.03	2.8	0.6	100	5	74.6	34	39.2	26-46
1.18					0.0	0.0	0.0	0.0	100	5	58.3	26	31.2	17-37
0.6									100	5	37.3	17	21.8	11-27
0.3									79.2	4.9	15.2	6.8	11.7	7-19
0.15									89.7	4.5	5.2	2.3	6.8	6-16
0.075									73.3	3.7	1.9	0.9	4.5	3-6

Marshall Test was used to determine the specification and qualification of the tested samples. The items studied were stability, flow, density (unit weight), air voids, voids of mineral aggregate voids filled with asphalt (VFA), and densification of the compacted paving mixtures. The results are given in Tables (10-15), and Figs (15-20).

- Effect of ENR Quantity on the Density of Asphalt Concrete Mixture.

Results given in Figs (15-20) show that the density (unit weight) gm/cm^3 of asphalt paving mixture (AP) increases with increasing the percent of asphalt. This could probably be due to increasing the interlocking between fine and coarse aggregates [58]. The curves for density of the tested samples (asphalt paving mixture modified with epoxidized natural rubber 5% (ENR + 40%MA), 10% (ENR + 40%MA), 15 % (ENR + 40%MA) (ENR) to (AP) acquire the same shape as (AP) mixture.

The density values of asphalt paving (AP) mixtures are lower than the corresponding values for (APENR) at ratio of (5% LENR + 40% MA). Whereas the values of density for (10% LENR + 40 % MA), 15 % (LENR + 40 % MA), are relatively higher than the corresponding values for (AP) mixture at 4.5, 5, 5.5, 6, and 6.5 % of asphalt.

However, at 4.5, 5, 5.5, 6, and 6.5 % asphalt to aggregate, the order of density values is 15% >APENR > 10% APENR > 5% APENR >AP mixtures.

- Effect of ENR Resin Quantity on the Stability of Asphalt Concrete Mixture.

The stability of AP mixture maximum load resistance to deformation increases with increasing the amount of the added asphalt to

aggregate due to its influence on the interparticle friction [58]. The stability reached to the maximum value (11500 N) for asphalt mixture at 5.5 percent asphalt by weight of aggregate. With further increasing the quantities of asphalt the interparticle friction is reduced mainly due to increase the asphalt film thickness at the contact between aggregate particles [58]. This result was indicated by the voids filled with asphalt (VFA) 77.4 % at 5.5 percent of asphalt and 88.28 % at 6.5 percent of asphalt as given in Tables (10-15).

The values of stability for APENR mixtures are 16632 N in the case of mixture which contains 15 % (LENR + 40% MA), the corresponding value of (VFA) was 83.4 % at the ratio of asphalt (5.5 % by wt. aggregate).

It was found also in Tables (10-15) that the values of stability decrease with increasing the quantity of asphalt where the percentages of (VFA) are very high 93.5 % at 15 % (LENR) at 6.5 % of asphalt at the contact between aggregate particles is very thick which causes sharp decrease in the interparticle friction[58].

The highest value of stability for (APENR) mixtures at 15 % (ENR + 40% MA) mixture seem to be due to the presence of epoxy resin as thermosetting polymer together at high temperature hardener (MA). This behaviour probably acts as a filler and cohesing agent in the mixture of the product when cooled till ambient temperature.

- Effect of ENR Resin Quantity on Plastic Flow of Asphalt Concrete Mixture.

The flow value indicates the flexibility and plasticity properties of asphalt contents under traffic load. It is inversely proportional to interface frictions. The maximum flow value, indicated in ASTM specifications, controls the plasticity and maximum asphalt content of

the mixtures, i.e. if asphalt content increases the flow value will also increase [100].

This is indicated in case of AP mixture and AP modified with epoxy resin based on ENR. The maximum stability which obtained at 5.5% asphalt percent, the highest value of flow = 3.8 mm, was exhibited at 10% ENR+40MA to AP.

On the other hand the flow value decreased to 2.9mm by increasing the added percent of ENR to AP.

This property could be due to increasing the presence of thermosettic epoxy resin formed on the surface of aggregate particles. This being the mixture to the saturate degree with coating binder, and inforces it stiffiness. At the same time it is impossible to increase the ENR percent more than 15%.

- Effect of ENR Resin Quantity on Air Voids and Densification of Asphalt Concrete Mixture.

As shown in Tables (10-15) and Figs (15-20), the value of calculated voids in mineral aggregate percent for (AP) mixtures reaches 16.35 at 5.5 % asphalt. This value increases with increasing asphalt percentage up to reache 17.02 at 6.5% asphalt. Similar trends are observed in the curves for the mixtures containing AP modified with (5, 10, 15) % ENR + 40% MA) [APENR]

The maximum value of VFA 88.25 % was achieved at 6.5 % asphalt from the results given in Table (10) it can be concluded that the voids filled with asphalt (VFA %) for these mixtures increase with increasing the percent of asphalt. Similar trends were observed in Tables (11-13). On the other hand the air void (AV %) for these mixtures decreases with increasing asphalt percent, which means an increase of void filled with asphalt (VFA %).

Since the densifications is much related to the value of (AV), densification = 100-AV .It is noticed from Figs (15-20) that the densification of both (AP), and (APENR) mixtures increases with increasing the asphalt percent.

The mixtures based on (APENR) at 15 % (LENR + 40% MA) acquire lower values of AV %, higher values of densification and voids filled with asphalt, among the mixtures of 10% (LENR + 40% MA), and 5 % (LENR + 40% MA).

- Effect of ENR Resin Quantity on Suitability of Mixture According to Marshall Method.

For asphalt paving mixture AP (asphalt 60/70 + aggregate mixtures) and asphalt paving mixtures blended with epoxy resin based on epoxydizied natural rubber (5, 10, 15)% to asphalt percentage curried with 40% maleic anhydride to ENR, (APENR) for each percentage, the following data are obtained from the Figs (15-20).

- Asphalt Paving Mixtures (AP).
Optimum Asphalt to Aggregate Mixture.
The maximum density was 2.358 gm/cm^3 at asphalt percent of 6.5
The maximum stability was 11500 N at asphalt percent of 5.5.
The flow 3.2 mm, the percent of asphalt =5.5
The suitable air void value is 3.7 at asphalt percent of 5.5
The values were 15.7 %, 76.4 %, and 3593 N/mm of mineral voids VFA and Marshall Quatant respectively.

The values of AV, VFA, flow, mineral voids, Marshall Quatant, and stability are found to be satisfactory for the limitation of the surface layer, and satisfactory for the limits of international Cairo air port project technical specification.

These data are obtained from the figures (15-20), for asphalt 60/70 blended with aggregate mixtures.

The following data are obtained from the figures (15-20), for asphalt paving mixture + (epoxidized naturall rubber + 40% MA).
- for the mixture containing AP mixture + 5% (ENR + 40 % MA) to asphalt percentage, the satisfactory limitation of surface layer and the limit of project technical specifications, at 5.5% asphalt have the following values:

Density =2.351 gm/cm^3
Stability =12600 N
Flow = 3.2mm
Air Voids= 3.5%
Mineral voids= 15.52%
VFA= 77.4%
Densification =96.5
Marshall Quatant = 3316 N/mm

- For the mixture containing AP mixture + 10% (ENR + 40 % MA).
The data obtained from the figures (15-20), at 5.5% asphalt have the following values:

Density =2.356 gm/cm^3
Stability =14865 N
Flow = 3.5mm
Air Voids= 3.3%
Mineral voids= 15.3%
VFA= 96.7%
Densification =96.7 %
Marshall Quatant = 4247 N/mm

- For mixture containing AP mixture + 15% (ENR + 40 % MA)
at 5.5% asphalt acquire the following values of properties:

Density $=2.374$ gm/cm^3
Stability $=16632$ N
Flow $= 2.9$mm
Air Voids$= 2.5\%$
Mineral voids$= 14.6\%$
VFA$= 83.0\%$
Densification $=97.5\%$
Marshall Quatant $= 3735$ N/mm

From these data it could be concluded that, the increase of epoxidized natural rubber percentage lead to increase the values of flow up to 10%.

The optimum value (2.9 mm) was achieved at 15% ENR, which being the high stability. At the same time, the air voids decreased to 2.5% so we cannot increase ENR ratio above 15 %. The properties of the mixture containing aggregates (crushed Dolomite, sand and filler limestone) and asphalt 60/70 could be improved by the addition of 15% (ENR+40%MA). In these mixture the highest stability value 16632 N, and flow value 2.9 mm were achieved.

Another comparison occurs between the best percentage of adding 15% ENR and 15% ESBR at the other conditions been keep const (40%MA)

The following data are obtained from the figures (15-20), for asphalt paving mixture + 15 (ESBR+40%MA)

The 5.5% asphalt achieved the limitation of surface layer, and the project technical specifications in international Egyptian Cairo port,the obtained data are:

Density =2.354 gm/cm^3
Stability =17222 N
Flow = 4.8mm
Air Voids=3.4%
Mineral voids= 15.4%
VFA= 78.1%
Densification =96.6 %
Marshall Quatant = 3588 N/mm

The following data are the limitation specifications of the Int. Cairo air port:

Density =2.355 gm/cm^3
Stability =12000 N
Flow = 3.4mm
Air Voids=3.3%
Mineral voids= 15.3%
VFA= 83.0%
Densification =96.7 %
Marshall Quatant = 3529 N/mm

Results and Discussion

Table (10): Properties of the Surface Course Asphalt (L) mix at Different Asphalt Contents, 25mm Max. Agg. Size

Marshall Design									
Asphalt Content, %	Bulk Specific Gravity, g / cm3	Max. Theoretical Gravity, g / cm3	Stability, N	Flow, mm	Air voids, %	Mineral voids, %	Voids Filled Asphalt, %	Densification	Marshall Quatant, N/mm
4.5	2.329	2.469	9500	2.2	5.7	15.5	63.4	94.3	4318
5	2.338	2.452	10800	2.7	4.6	15.52	70.3	95.4	4000
5.5	2.347	2.436	11500	3.2	3.7	15.7	76.4	96.3	3593
6	2.352	2.42	10020	4	2.8	15.85	82.3	97.2	2505
6.5	2.358	2.405	8750	4.6	2	16.1	87.0	98	2120

Specific Gravity of Bitumen g / cm3	1.02	Coarse Aggregate, %	50	Specific Gravity of Coarse Aggregate, %	2.67
Penetration Grade	60/70	Fine Aggregate, %	45	Specific Gravity of Fine Aggregate, %	2.63
Bulk Specific Gravity of Mix., g / cm3	2.634	Filler, %	5	Specific Gravity of Filler, %	2.58

Table (11): Properties of the Surface Course Asphalt (L1) mix at Different Asphalt Contents, 25mm Max. Agg. Size

Marshall Design									
Asphalt Content, %	Bulk Specific Gravity, g / cm3	Max. Theoretical Gravity, g / cm3	Stability, N	Flow, mm	Air voids, %	Mineral voids, %	Voids Filled Asphalt, %	Densification	Marshall Quatant, N/mm
4.5	2.338	2.469	9757	2.3	5.3	15.2	67.9	94.7	4242
5	2.348	2.452	11200	2.9	4.2	15.2	75.7	95.8	3862
5.5	2.355	2.436	12000	3.4	3.3	15.3	83	96.7	3529
6	2.359	2.42	10650	3.9	2.5	15.6	89	97.5	2731
6.5	2.361	2.405	9065	4.5	1.8	15.9	94.6	98.2	2014

Specific Gravity of Bitumen g / cm3	1.02	Coarse Aggregate, %	50	Specific Gravity of Coarse Aggregate, %	2.67
Penetration Grade	60/70	Fine Aggregate, %	45	Specific Gravity of Fine Aggregate, %	2.63
Bulk Specific Gravity of Mix., g / cm3	2.634	Filler, %	5	Specific Gravity of Filler, %	2.58

Table (12): Properties of the Surface Course Asphalt (L2) mix at Different Bitumen Contents, 25mm Max. Agg. Size

Marshall Design									
Asphalt Content, %	Bulk Specific Gravity, g / cm3	Max Theoretical Gravity, g / cm3	Stability N	Flow, mm	Air voids, %	Mineral voids, %	Voids Filled Asphalt, %	Densification	Marshall Quatant, N/mm
4.5	2.337	2.469	10150	2.5	5.4	15.26	64.7	94.6	4060
5	2.344	2.452	12350	3.1	4.4	15.34	71.31	95.6	3984
5.5	2.351	2.436	12600	3.8	3.5	15.52	77.4	96.5	3316
6	2.358	2.42	11215	4.4	2.6	15.7	83.3	97.4	2549
6.5	2.362	2.405	10370	4.9	1.8	15.9	88.9	98.2	2116

Specific Gravity of Bitumen g / cm3	1.02	Coarse Aggregate, %	50	Specific Gravity of Coarse Aggregate, %	2.67
Penetration Grade	60/70	Fine Aggregate, %	45	Specific Gravity of Fine Aggregate, %	2.63
Bulk Specific Gravity of Mix., g / cm3	2.634	Filler, %	5	Specific Gravity of Filler, %	2.58

Table (13): Properties of the Surface Course Asphalt (L3) mix at Different Asphalt Contents, 25mm Max. Agg. Size

Marshall Design									
Asphalt Content, %	Bulk Specific Gravity, g / cm3	Max. Theoretical Gravity, g / cm3	Stability, N	Flow, mm	Air voids, %	Mineral voids, %	Voids Filled Asphalt, %	Densification	Marshall Quatant, N/mm
4.5	2.346	2.469	10222	2.4	5	14.9	66.5	95	4259
5	2.351	2.452	13103	2.8	4.1	15.1	72.7	95.9	4680
5.5	2.356	2.436	14865	3.5	3.3	15.3	78.7	96.7	4247
6	2.361	2.42	14978	4	2.4	15.5	84.5	97.6	3745
6.5	2.364	2.405	13875	4.3	1.7	15.8	89.5	98.3	3227

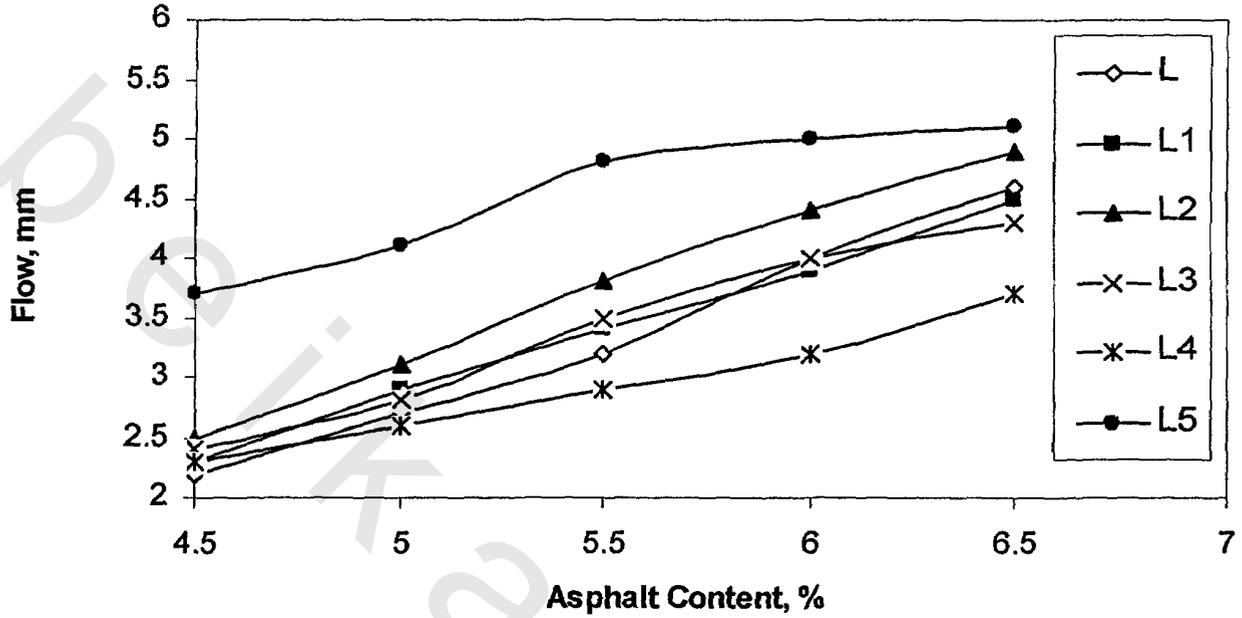|					
Specific Gravity of Bitumen g / cm3	1.02	Coarse Aggregate, %	50	Specific Gravity of Coarse Aggregate, %	2.67
Penetration Grade	60/70	Fine Aggregate, %	45	Specific Gravity of Fine Aggregate, %	2.63
Bulk Specific Gravity of Mix., g / cm3	2.634	Filler, %	5	Specific Gravity of Filler, %	2.58

Table (14): Properties of the Surface Course Asphalt (L4) mix at Different Asphalt Contents, 25mm Max. Agg. Size

Marshall Design									
Asphalt Content, %	Bulk Specific Gravity, g / cm3	Max. Theoretical Gravity, g / cm3	Stability, N	Flow, mm	Air voids, %	Mineral voids ,%	Voids Filled Asphalt %	Densification	Marshall Quatant, N/mm
4.5	2.356	2.469	14426	2.3	4.5	14.4	69.1	95.5	6272
5	2.363	2.452	16081	2.6	3.6	14.6	75.6	96.4	6185
5.5	2.374	2.436	16632	2.9	2.5	14.6	83	97.5	5735
6	2.376	2.42	15529	3.2	1.8	14.9	88.5	98.2	4853
6.5	2.378	2.405	14000	3.7	1.1	15.3	93	98.9	3003

Specific Gravity of Bitumen g / cm3	1.02	Coarse Aggregate, %	50	Specific Gravity of Coarse Aggregate, %	2.67
Penetration Grade	60/70	Fine Aggregate, %	45	Specific Gravity of Fine Aggregate, %	2.63
Bulk Specific Gravity of Mix., g / cm3	2.634	Filler, %	5	Specific Gravity of Filler, %	2.58

Table (15): Properties of the Surface Course Asphalt (L5) mix at Different Asphalt Contents, 25mm Max. Agg. Size

Marshall Design									
Asphalt Content %	Bulk Specific Gravity, g / cm3	Max. Theoretical Gravity, g / cm3	Stability, N	Flow, mm	Air voids, %	Mineral voids, %	Voids Filled Asphalt, %	Densification	Marshall Quatant, N/mm
4.5	2.348	2.469	14636	3.7	4.9	14.8	66.9	95.1	3956
5	2.352	2.452	16544	4.1	4	14.9	73.7	96	4035
5.5	2.354	2.436	17222	4.8	3.4	15.4	78.1	96.6	3588
6	2.356	2.42	16111	5	2.6	15.7	83.3	97.4	3222
6.5	2.359	2.405	13150	5.1	1.9	16.0	88.2	98.1	2578

Specific Gravity of Bitumen g / cm3	1.02	Coarse Aggregate, %	50	Specific Gravity of Coarse Aggregate, %	2.67
Penetration Grade	60/70	Fine Aggregate, %	45	Specific Gravity of Fine Aggregate, %	2.63
Bulk Specific Gravity of Mix., g / cm3	2.634	Filler, %	5	Specific Gravity of Filler, %	2.58

Fig (15) Effect of Bitumen Content (%) on the Flow
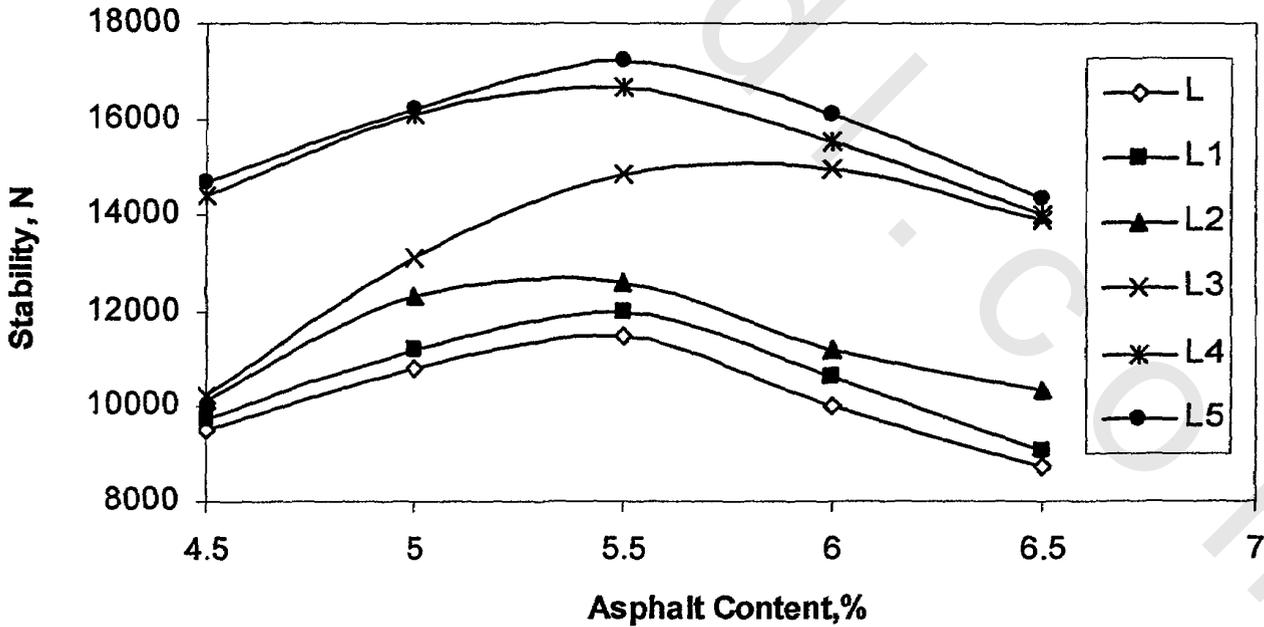
Fig (16) Effect of Bitumen Content, % on Stability, N.
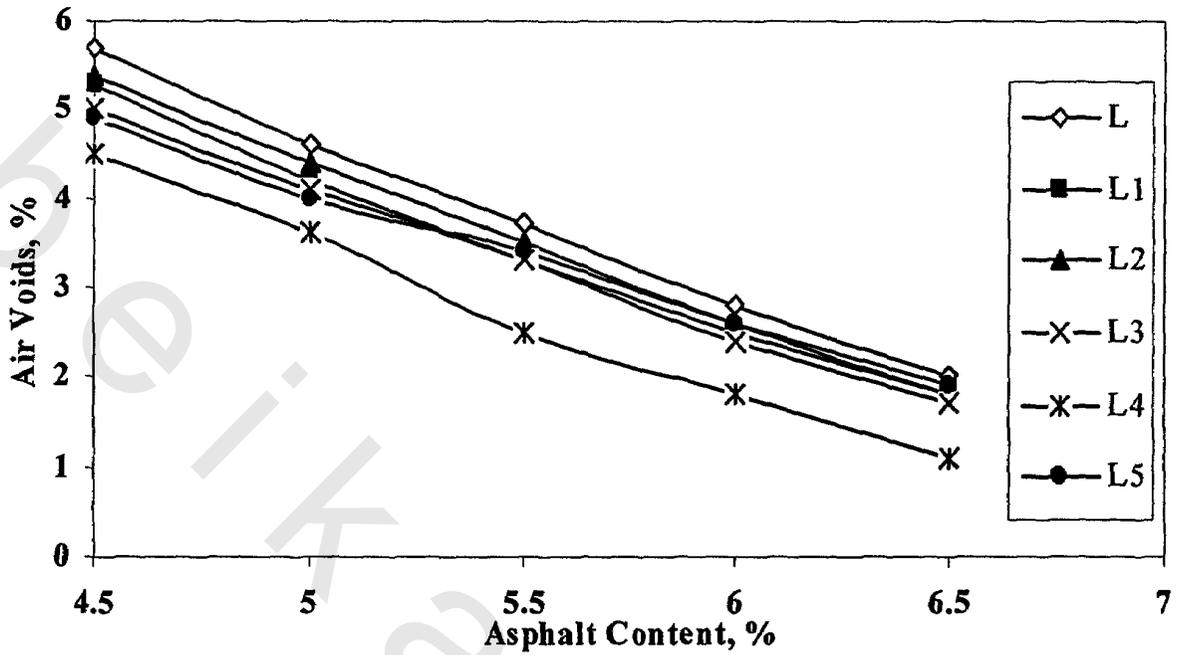
Fig (17) Effect of Bitumen Content, % on Air Voids, %
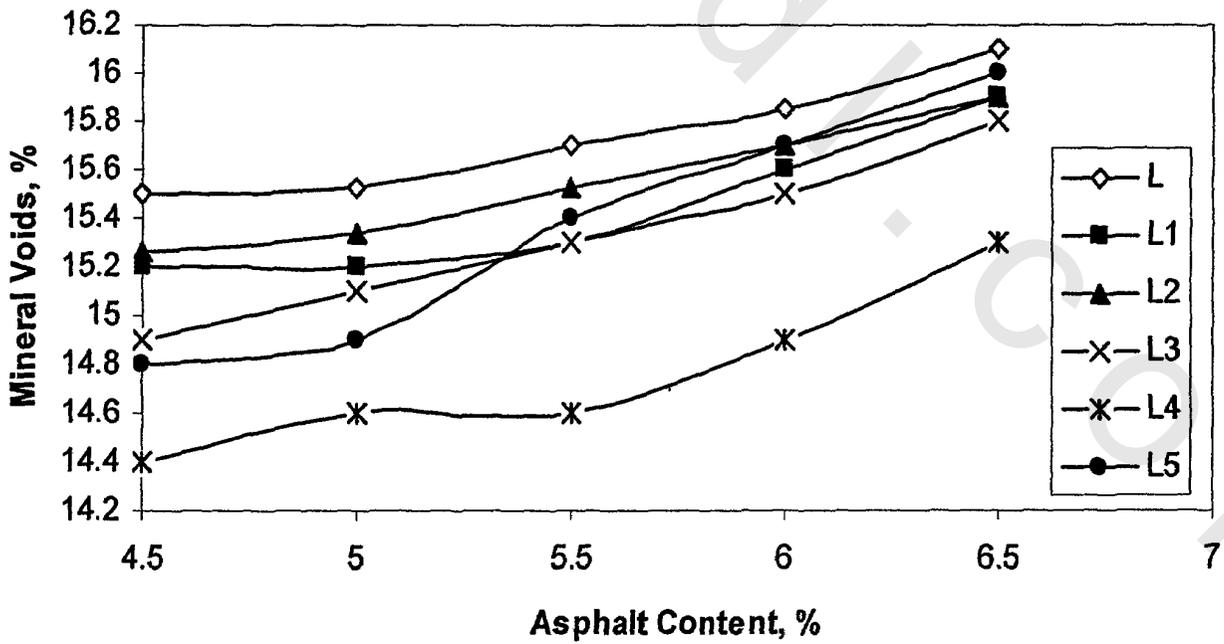
Fig (18) Effect of Bitumen Content, % on Values of Mineral Voids, %.
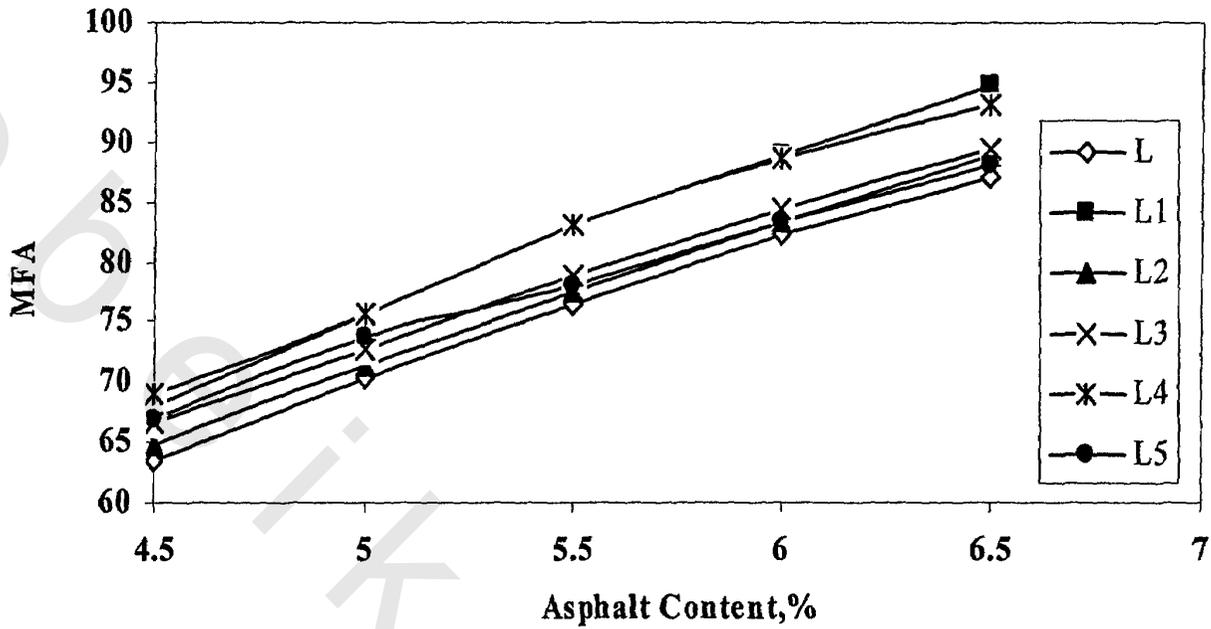
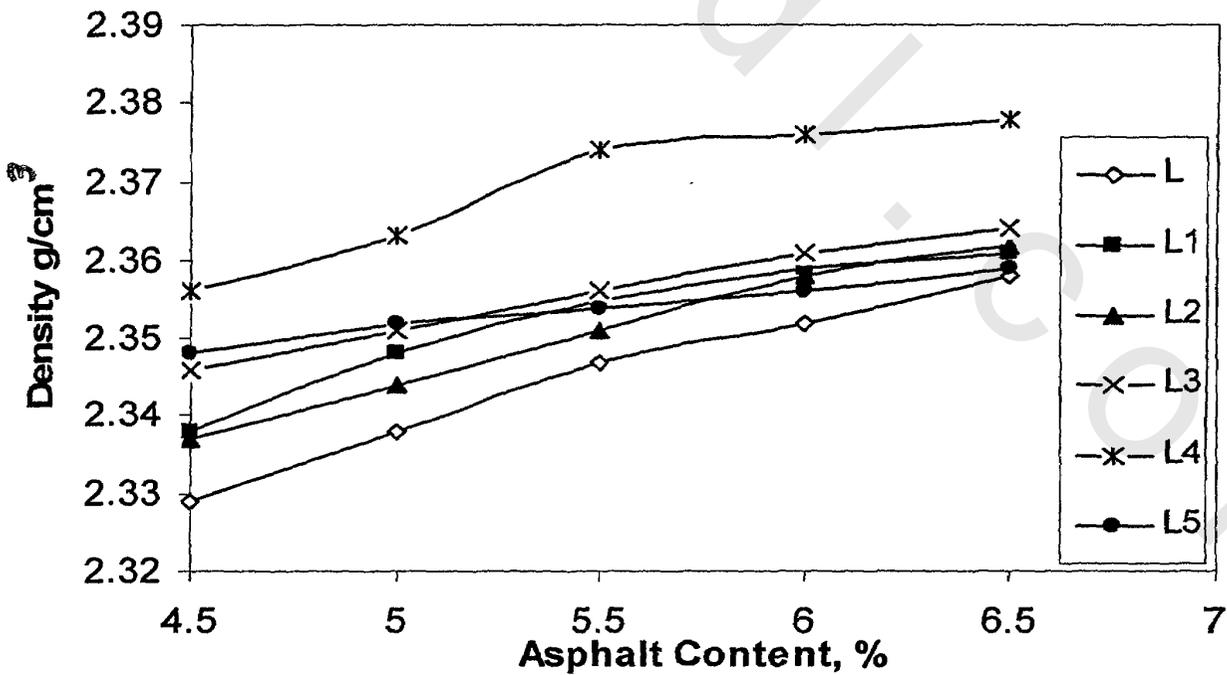**Fig (19) Effect of Bitumen Content, % on Values of Voids Filled bitumen, %.**

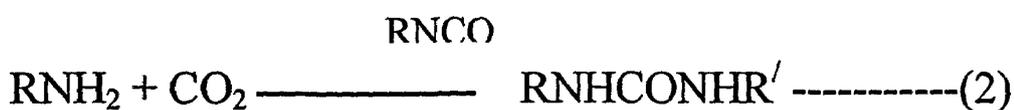**Fig (20) Effect of Bitumen Content, % on Values of Density g/cm³**

Preparation and Evaluation of Asphalt-polyurethane Foam for Different Applications

Nonionic surfactant (ethoxylated nonylphenol) was used to prepare the asphalt emulsion. Asphalt polyurethane foams were synthesized from prepared polyurethane product based on dimethyl diphenyl diisocyanate (MDI) and castor oil, in asphalt emulsion. These products were modified with polyacrylic acid, commercial [Addibond 65], and polyurethane based on epoxidized linseed oil at different NCO/OH ratios.

The urethane groups result from the reaction between hydroxyl group (from castor oil) and the isocyanate group from methyldiphenyldiisocyanate (MDI) or toluene diisocyanate.

polyol   isocyanate   urethane linkage
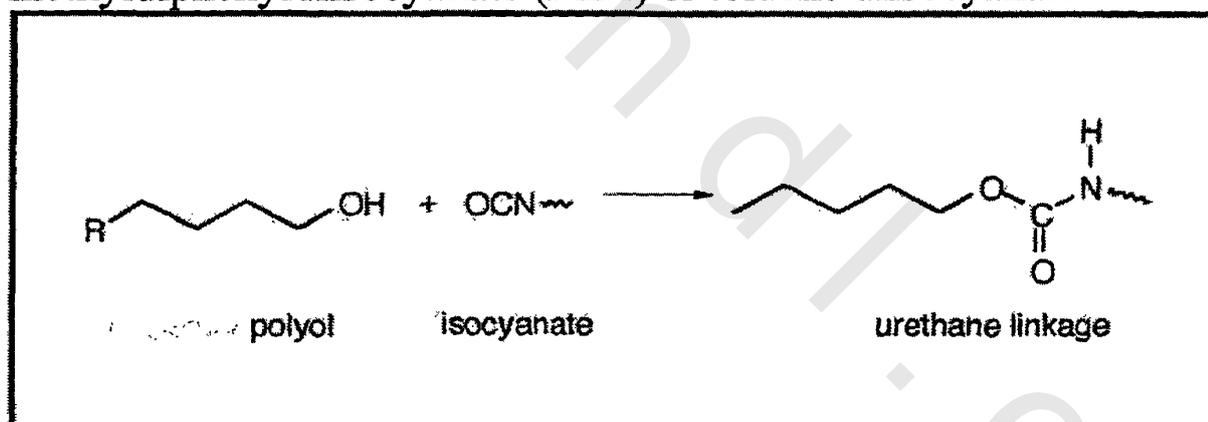
The isocyanate reacts with water to produce unstable carbamic acids, which decompose to form diamines and carbon dioxide, which acts as a blowing agent [106, 107].the reaction steps areshown in Schema 2

$$RNCO + R'COOH \longrightarrow RNHCO\,R' \text{ -----------(1)}$$

$$\qquad\qquad\qquad\qquad\qquad\text{Amide} \qquad \text{Decompose}$$

$$RNCO + H_2O \longrightarrow RNHCOOH\text{---------------}$$

$$\qquad\qquad\qquad\qquad\text{Carbamic acid}$$

$$\qquad\qquad\qquad RNCO$$

$$RNH_2 + CO_2 \longrightarrow RNHCONHR' \text{ -----------(2)}$$
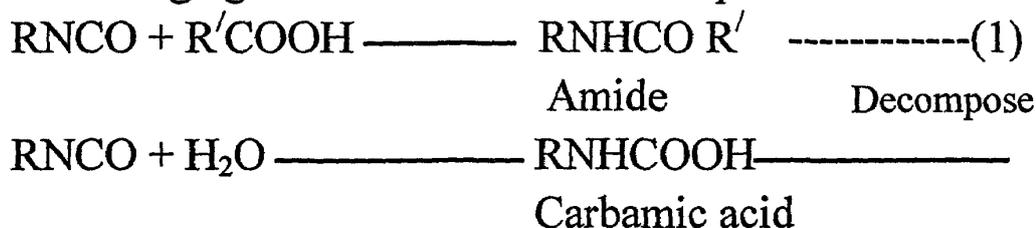
$$\qquad\qquad\qquad\qquad\text{Schema 2}$$

Reaction 1 and 2 give rise to carbon dioxide, a feature of value when forming foamed products.
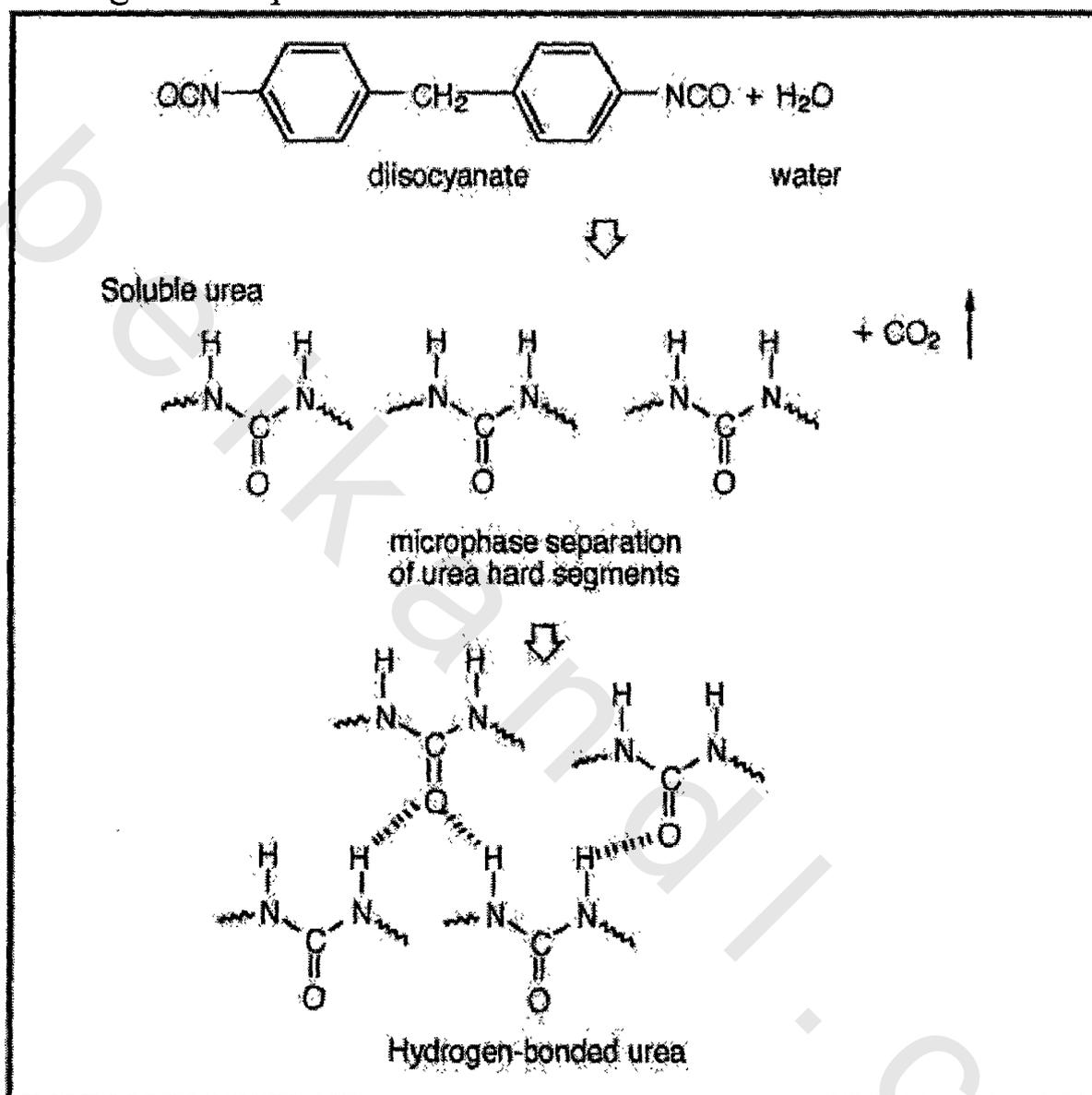
Preparation of Asphalt Polyurethane Foam.

The calculated amount of castor oil (according to the desired NCO/OH ratio) was added to constant amount of MDI (10g in each experiment with stirring, followed by triethylamine (two drops) as a catalyst. According to the OH group content of (polyol) the amounts of C.O added were accurately calculated related to the desired NCO/OH ratio. The mixture was then heated to $60+5°C$ upon stirring for 0.5hr [108-110], and the resin finally was left to dry in air till complete curing.

The calculation of NCO/OH ratio for the needed polyurethane foam product was carried out according to the following example [111].

Number of hydroxyl groups in epoxidized linseed oil = 180

Hydroxyl equivalent weight for polyol (epoxidized linseed oil) = 56100/180 = 311.66

The equivalent NCO groups is calculated from MDI of molecular weight = 250 as follows, Equivalent weight for MDI = 250/2 = 125

10g from MDI contain 10/125 = 0.08 equivalent NCO group.

In order to obtain polyurethane of ratio 1.1 (i.e. NCO/OH = 1.1) 0.08/OH =1.1

OH equivalent = 0.08/1.1 = 0.0727 equivalent
OH equivalent = weight of polyol /equivalent weight 0.0727 = weight of polyol /311.66

Weight of polyol which contains 0.0727
OH equivalent = 0.0727 x 311.66 = 22.66 gm.

Data given in Table (16), illustrate the necessary weights of   castor oil and MDI which should react to give the corresponding required ratio.

Table (16): Weights of Castor Oil (C.O) and MDI required to preparing the desired NCO/OH ratios

Used NCO/OH Ratio	Wt. Of MDI, gm.	WT. Of C.O, gm.
1.1	10	22.66
1.2	10	20.77
1.3	10	19.17
1.4	10	17.8

Curing Properties of the Obtained Films.

The data given in Table (17) show that, the products pass across three steps during the curing process. In the first step the film was tacky; the second step the film turns to slightly tacky, and in the third step it became hard.

During the process of curing, the hydroxyl groups of the castor oil react with the cyano groups in MDI molecule to form polyurethane foam product. The time necessary for curing final products (as evaluated by estimating the hardening times of the samples at room temperature), it was found that this property for the final polyurethane product depends upon the weight of the polyol used in the preparation of the desired NCO/OH ratio. The obtained results given in Table (17) indicated that the increase of NCO/OH ratio decreases the time of curing.

It can be concluded that the ratio of NCO/OH = 1.2 is the most suitable ratio from obtain the sample which was chosen to economical point of view, and easily stirred especially in presence of additives to form different formulations. These results were reached with E.A. Hassan et al [112].

Table (17): The Curing Properties for Different Ratios of (NCO/OH) Polyurethane

Ratio of NCO/OH	Wt. of Polyol, gm/10gm MDI.	Change in State with Time, hrs.		
		First Stage (Tacky)	Second Stage (Finger Print)	Third Stage (Cured)
1.1	22.66	1.3	8.45	24
1.2	20.77	1	7.30	20
1.3	19.17	0.50	6	16
1.4	17.8	0.40	4.30	12

Overall time including all the three stages.

Modification of Asphalt Polyurethane Foams

The asphalt –polyurethane foam sample for which NCO/OH ratio =1.2, was chosen for economical point of view to be modified with different percentages of commercial rubber (Addibond 65), polyacrylic acid water base, and polyurethane based on (epoxidized natural rubber + MDI) at different ratios of NCO/OH (1, 2, 3, 4, and 5) which were used during the preparation of asphalt polyurethane foams. The data given in Table (18, 19) show that, the weight necessary to prepare NCO/OH, and it is curing properties.

Table (18): Weights of Epoxidized Natural Rubber ENR and MDI used for Preparing the Desired NCO/OH Ratio.

Required NCO/OH Ratio	Wt. of MDI gm	Necessary Wt. of ENR, gm
1	10	64.1
2	10	32.05
3	10	21.37
4	10	16.02
5	10	12.82

Curing Properties of The prepared Formulations.

The data given in Table (19) show that, experiment No.1 demands very long time to be cured in air.

The data obtained from the other three experiments indicate that during the curing process the properties of the film upon changing, passed through three stages; in the first stage it was slightly tacky, in the second stage it was slightly tacky, and in the third stage it become hard.

During the process of curing, the hydroxyl groups of the ENR react with cyano group in MDI molecule to form the polyurethane product.

In addition to the sample asphalt foam in 1.2 NCO/OH, it was necessary to prepare polyurethane based epoxidized natural rubber at the ratio of NCO/OH=4 is the most suitable ratio to obtain the sample which can be easily stirred, and have the suitable curing properties with the asphalt polyurethane foam. For the ratio of NCO/OH =5 resulting in obtaining coagulation and consequently it is useless.

Table (19): The Curing Properties for Different Ratios of (NCO/OH) Polyurethane

Ratio of NCO/OH	Wt. of Polyol, gm/10gm MDI.	Change in State with Time, hrs.		
		First Stage (Tacky)	Second Stage (Finger Print)	Third Stage (Cured)
1	64.1	-	-	-
2	32.05	8	14	20
3	21.37	3	4.5	9
4	16.02	0.3	1.5	6
5	12.82	-	-	-

Table (20): Formulation of the Prepared Asphalt-Polyurethane Foams

Ingredients	Formulations, wt.%													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Asphalt emulsion, gm	55	55	55	55	55	55	55	55	55	55	55	55	55	55
Polyurethane NCO/OH 1.1	45	-	-	-	-	-	-	-	-	-	-	-	-	-
1.2	-	45	-	-	40.5	38.2	36	34.7	34.7	34.7	40.5	38.2	36	34.7
1.3			45	-	-	-	-	-	-	-	-	-	-	-
1.4	-	-	-	45	-	-	-	-	-	-	-	-	-	-
Addibond 65 (W/W of C.O) for possible modification for insulation 10%	-	-	-	-	4.5	-	-	-	-	-	-	-	-	-
15%	-	-	-	-	-	6.7	-	-	-	-	-	-	-	-
20%	-	-	-	-	-	-	9.0	-	-	-	-	-	-	-
25%	-	-	-	-	-	-	-	11.2	-	-	-	-	-	-
3% Acrylic acid	-	-	-	-	-	-	-	-	3	-	-	-	-	-
2%A+ 10% Addibond 65	-	-	-	-	-	-	-	-	-	3	-	-	-	-
Polyurethane depend on ENR at ratio (NCO/OH=4) added in ratio of 10%	-	-	-	-	-	-	-	-	-	-	4.5	-	-	-
15%	-	-	-	-	-	-	-	-	-	-	-	6.7	-	-
20%	-	-	-	-	-	-	-	-	-	-	-	-	9.0	-
25%	-	-	-	-	-	-	-	-	-	-	-	-	-	11.2

Tests carried out on the prepared Formulations:

- Sound Proofing Test

It is measured by using a special apparatus, precision integration sound level (Bruel and Kjaer, Type 2236), Denmark. A sound proofing box (60x20x60 cm). The final foam sample noise sources in addition to the microphone were put at equal distances from both sides of the sample.

The sound pressure level (SPL) was measured for every sample by the sound level meter at frequency of 31.5Hz and constant noise level. The obtained data are listed in table (21)

Table (21): Sound Pressure Level at 31.5Hz for the Prepared Asphalt Polyurethane Foams.

Samples No. Mentioned in (Table 20)	Sound test (sound pressure Level SPL, (dB)		
	Without*material	With Material	Sound reduction IL**
1		112	8
2		76	44
3		93	27
4		102	18
5		101	19
6		101	19
7	120	96	24
8		111	9
9		61	59
10		63.5	56.5
11		82	38
12		84	36
13		70	50
14		89	31

Sound proofing performance is one of the most important factors in the evaluation of sound proofing materials in many applications such as (automobiles, building construction, etc). The sound proofing performance for all the prepared asphalt foam samples, as previously mentioned in case of vibration damping, are carried out and calculated from the following equation

$$IL = SPL_{air} - SPL_{material}$$

Where, IL is insertion loss (sound reduction).
SPL_{air} is sound pressure level without material barrier.
$SPL_{material}$ is sound pressure level with material barrier.

Data given in Table (21) show that the value of $SPL_{material}$ & $1/IL$ clearly that the lower sound pressure level indicates the better sound proofing performance.

The values of sound reduction (IL) for the prepared samples proceed according to the following order of the type of modifiers added to asphalt-polyurethane foam having NCO/OH ratio = 1.2. The best sample was (no. 9) foam sample modified with 3% polyacrylic acid (IL=59.0) > (no. 10) foam samples modified with 3% {1% addibond 65 + 2% polyacrylic acid (have IL= 56.5)} > foam sample modified with 20%polyurethane (based on ENR + MDI) at NCO/OH =4 (have IL=50) (no.13)

- Vibration Damping Test

The vibration damping performance is generally represented by the velocity level (VL). The test method of the velocity levels encounters touching the sample surface to surface of the testing apparatus. The velocity level is measured by using the Integrating Vibration Meter, Type 2513 (Denmark) for all samples with the same vibrator source.

Table (22): Velocity Level at 31.5Hz for the Prepared Asphalt Polyurethane Foams.

Samples No. Mentioned in (Table 20)	Vibration test (Velocity Level Lv), (dB)		
	Air	Material	Loss factor
1		125.5	14.5
2		122	18
3		124	16
4		124	16
5		129.0	11
6		128	12
7	140	125.5	14.5
8		127	13
9		111	29
10		124	16
11		121	19
12		119	21
13		118	22
14		127	13

The vibration damping performance is represented in general by the loss factor which is calculated from the following equation.

Loss factor = velocity level (Lv) $_{air}$ − velocity level (Lv) $_{material}$

For the unmodified foam sample, it is clear from the data of loss factor given in table (22), that the value of loss factor proceed in the following order of NCO/OH= 1.2 (18) > NCO/OH=1.3 (16) >NCO/OH=1.1 (14.5).

All of these formulations in turn have appreciably lower values of loss factor as compared with the modified samples with commercial rubber [Addibond 65].

The sequence of the values of loss factor proceeds in the following order of the used modifier for the foam samples having NCO/OH=1.2: 3%polyacrylic acid (29)> foam sample modified with 20% polyurethane at NCO/OH = 4 (22).

Probably due to the increased viscoelastic behavior in the modified samples, and consequently the decreased vibration in the specimens.

Water Absorption

The test method of the water absorption is simply used to determine the affinity and efficiency of the sample for the aim of determine the pores of the sample was carried out for the prepared samples, and the results given in Table (23) show that, the water absorption (wt. %) in case the samples based on NCO/OH = 1.2 are apparently better for the modified samples, as compared with the unmodified.

This is probably due to the highest significant enhancement of the hydrophobic character of asphalt and the other additives as compared to the other tested asphalt foam samples.

Table (23): Water Absorption, % for the Prepared Asphalt Formulations Immersed in Water for 24 hr at 25 °C

Samples No.	Wt. before immersion in water	Wt. after immersion in water	Water absorption rate, (wt. %)
1	1.8495	1.8714	1.17
2	1.8644	1.9678	5.25
3	1.7592	1.8199	3.33
4	1.6988	1.7999	5.62
5	1.6368	1.6677	1.85
6	2.0917	2.1103	0.88
7	1.2200	1.2499	2.39
8	1.7196	1.7400	1.17
9	1.0000	1.0341	3.30
10	2.7611	2.8983	4.73
11	2.1385	2.1792	1.87
12	2.0861	2.1345	2.27
13	2.0343	2.1521	2.69
14	2.1086	2.1932	3.86

Thermal Stability

Results of the thermal stability of the prepared foams at 200 °C for 200h are given in Table (24). The data show that, the addition of 3% polacrylic acid to the asphalt-polyurethane samples improved the thermal stability properties (wt. loss = 1.009-2.991 %). This may be due to the fact that the added polyacrylic acid with its excessive carboxylic groups imparts higher values of cross-linking bonds and consequently can withstand higher temperatures, and longer lifetime in use without aging (destruction) as compared to the unmodified asphalt foams.

Table (24): Thermal Stability for All the Prepared Asphalt Foam Formulation at 200 °C.

Samples No. Mentioned in (Table 20)	Weight loss, % after curing time, hrs.						
	5	10	20	40	80	150	200
1	1.278	1.432	2.135	3.621	4.562	6.713	9.101
2	1.007	1.316	1.921	3.006	3.299	4.568	7.629
3	0.999	1.300	1.879	2.798	3.190	4.015	6.721
4	0.912	1.310	1.291	1.981	2.851	3.781	5.667
5	3.135	3.135	3.564	3.998	4.235	4.361	5.981
6	2.980	2.980	3.009	3.190	3.672	4.172	5.012
7	2.431	2.431	2.853	3.098	3.335	4.063	4.681
8	2.319	2.319	2.790	3.001	3.125	3.978	4.000
9	1.163	1.163	1.986	2.781	2.713	2.751	2.991
10	1.234	1.234	2.016	2.834	2.891	2.895	3.191
11	1.031	2.305	2.816	3.215	3.452	4.87	5.021
12	1.004	2.167	2.635	3.006	3.257	4.71	5.000
13	0.981	1.325	1.987	2.561	2.885	3.140	3.561
14	0.976	1.003	1.536	2.016	2.567	2.931	3.251

Differential Scanning Calorimetric Analysis (DSC) for Foamed Samples

The result of DSC analysis for samples No. 1, 2, 7, 8, 9, 10, 13, 14 (in Table 20) (c.f Figs 21-28) show no sign of physical changes up till 291.79°C for NCO/OH=1.1, 305.64°C for NCO/OH=1.2, in the morphology of the foamed samples 320°C for modification with 25% PU, 367.35°C for modification with 20% PU, 314°C for modification

with 2%A+1%Addibond, 287.05 °C for 25% Addibond, 302 °C for 20%Addibond, 378.34 °C for 3%Acrylic acid
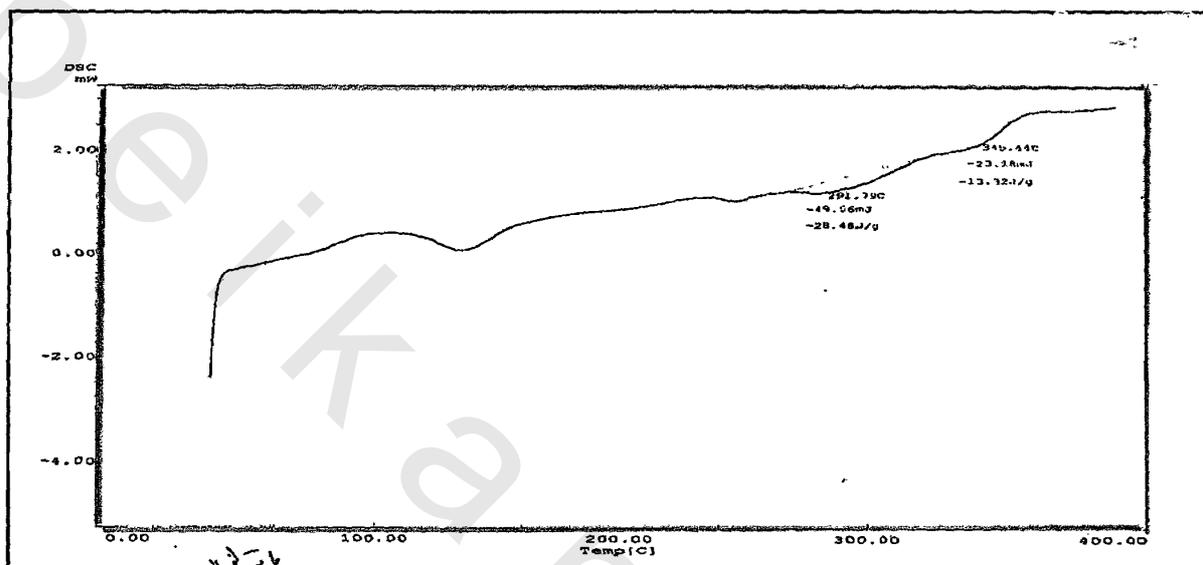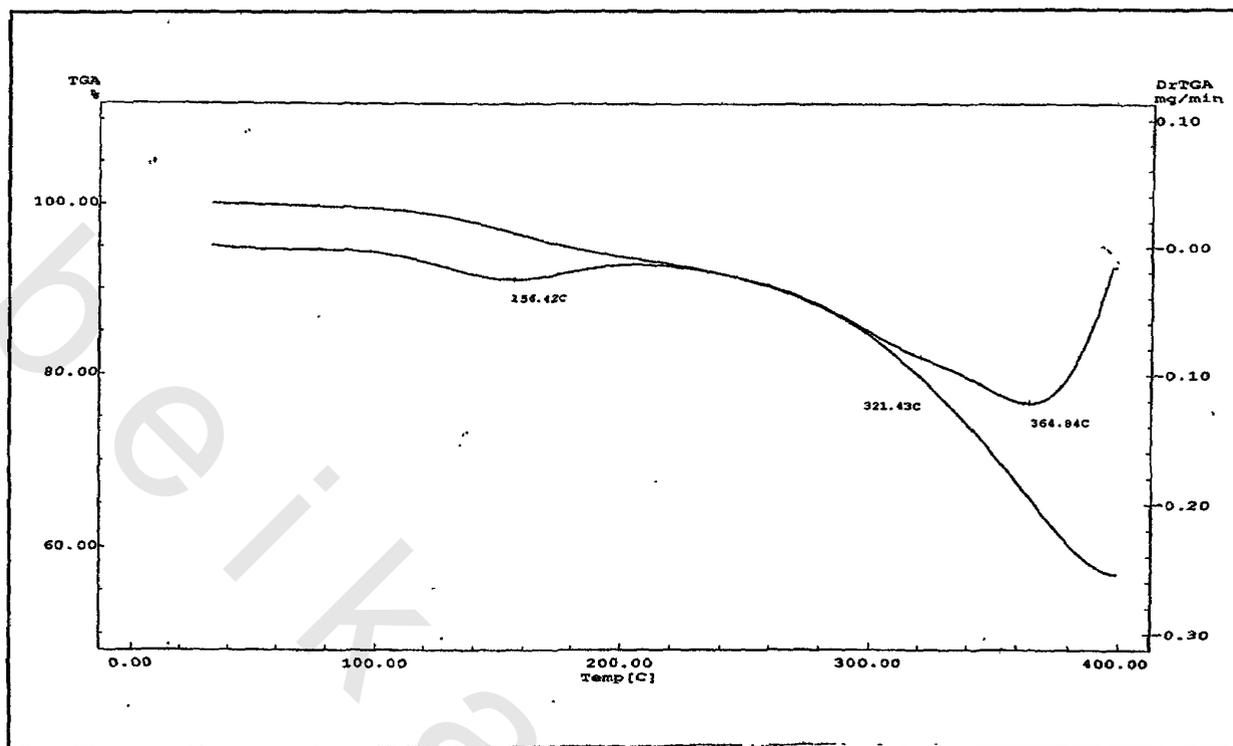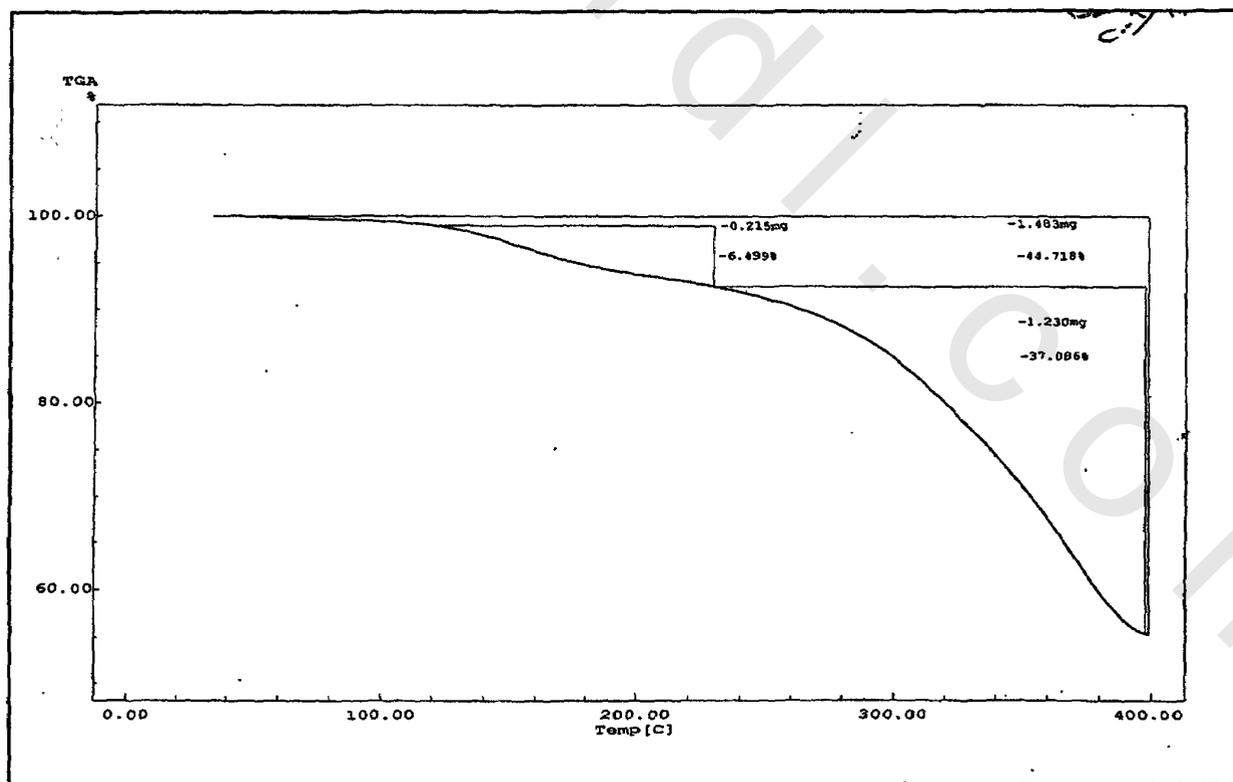

Fig (21): DSC of Asphalt Foam at NCO/OH Ratio = 1.1 wihout modification.
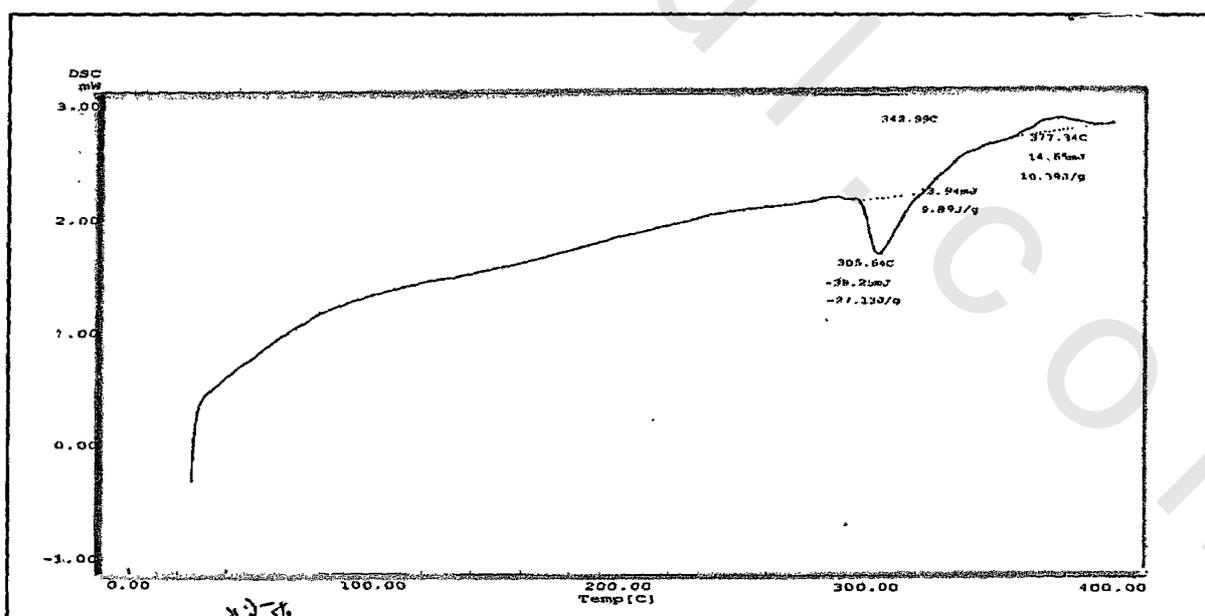
Fig (22): DSC of Asphalt Foam at NCO/OH Ratio = 1.2 without modification.
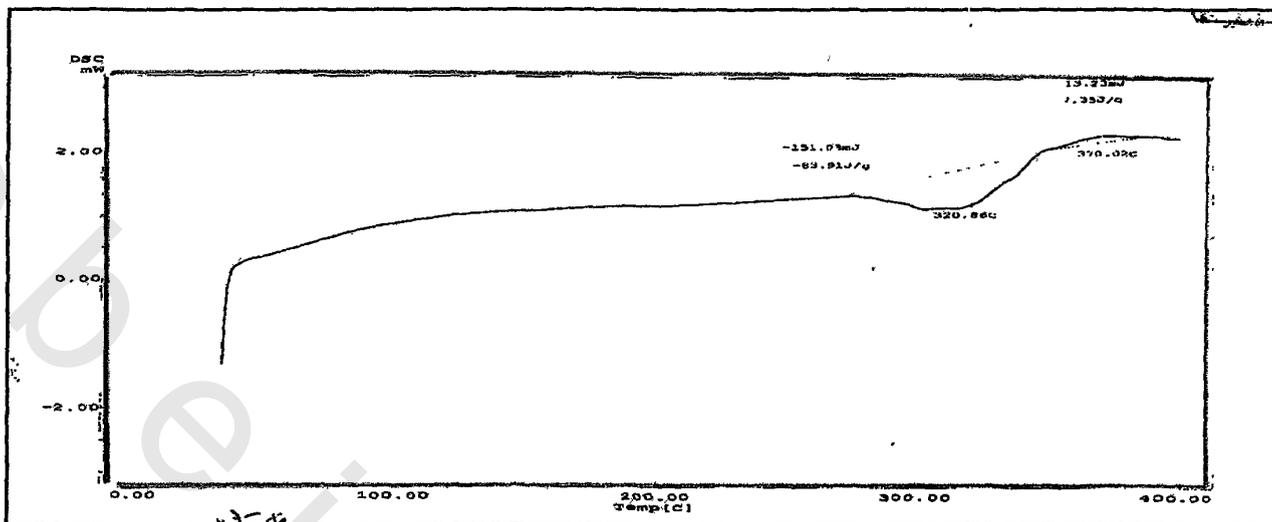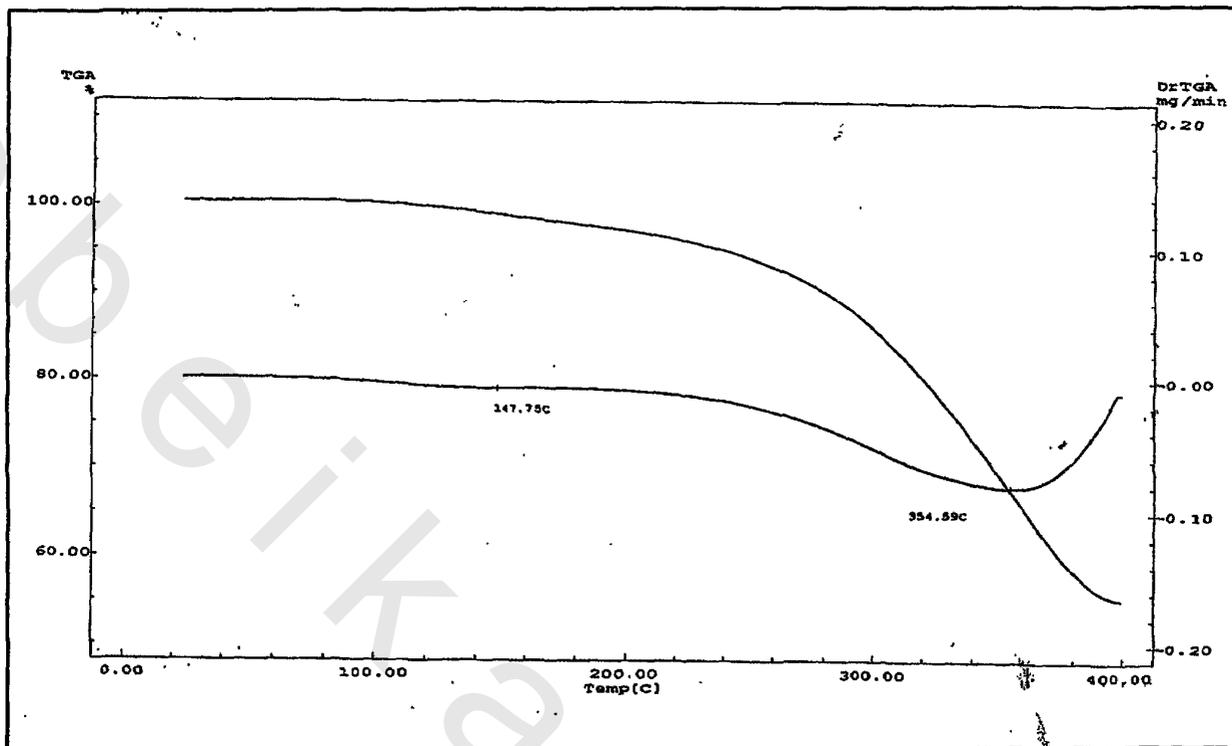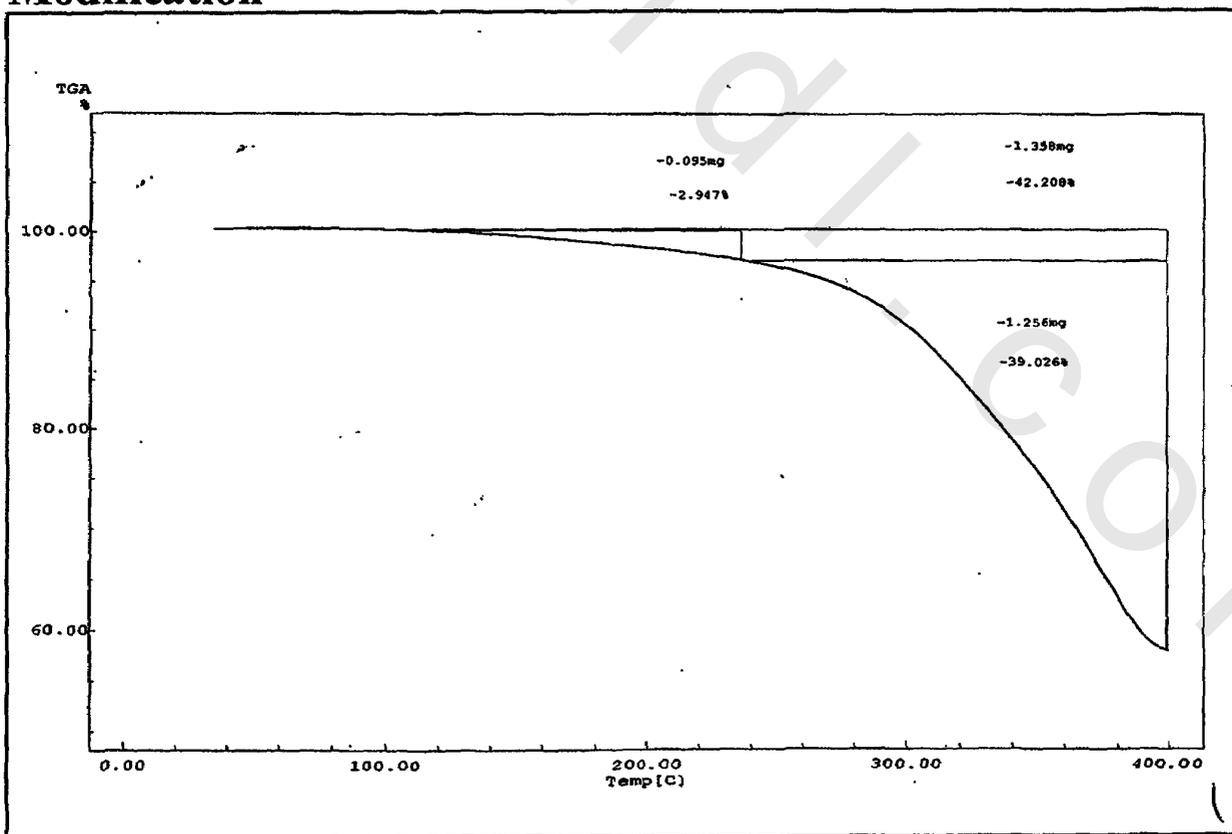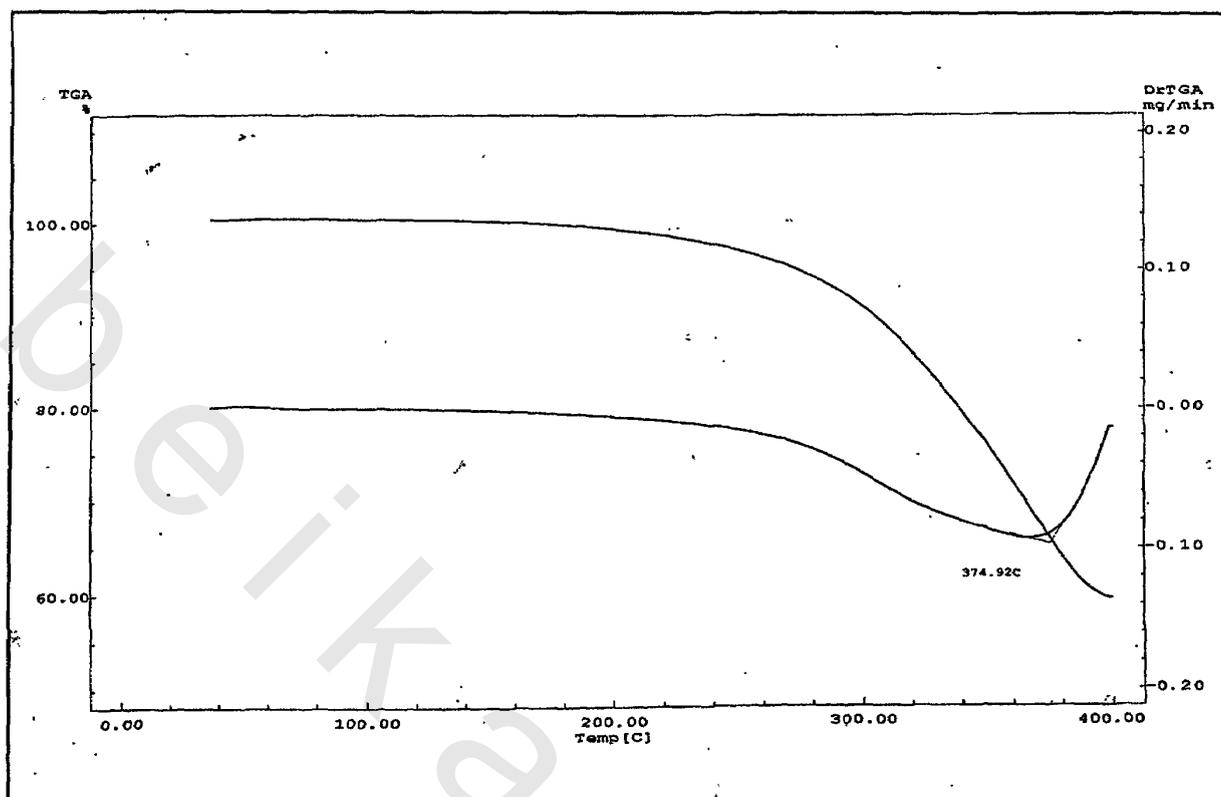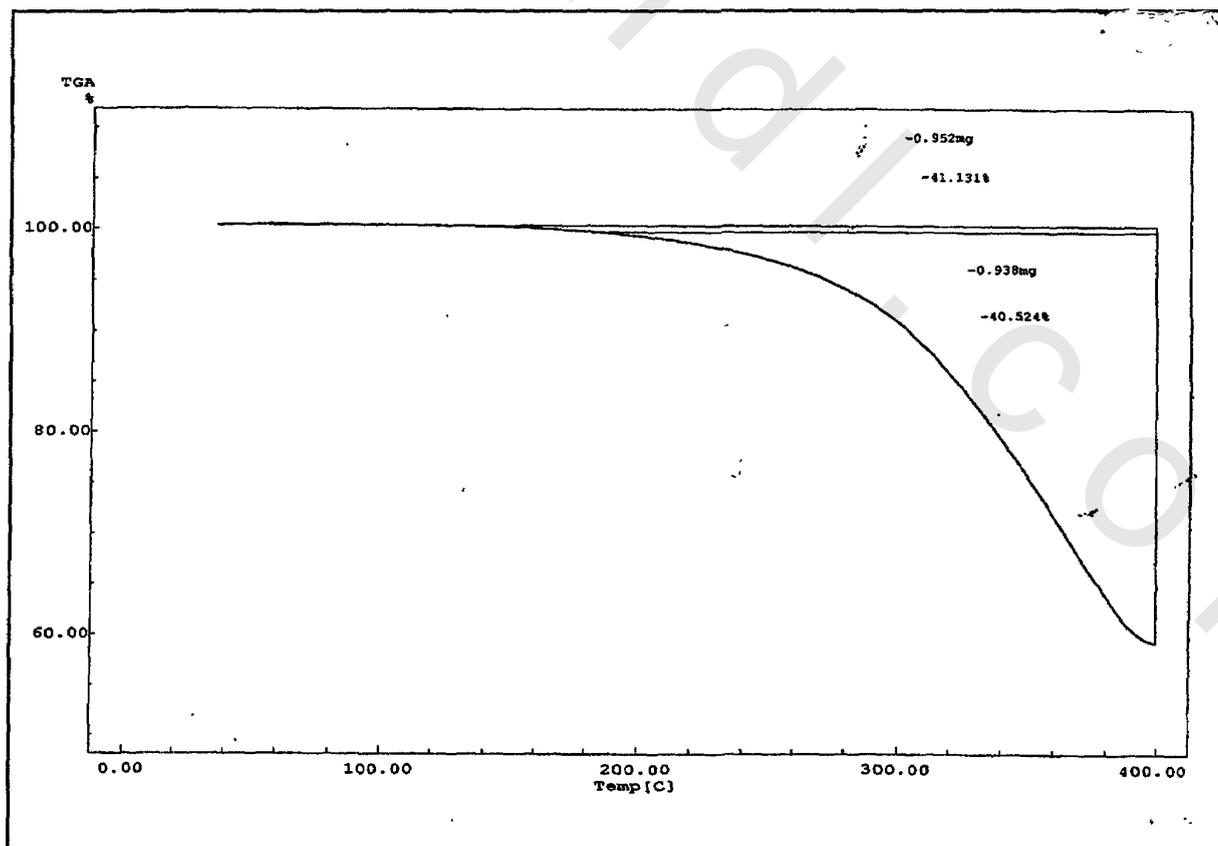
Fig (23): DSC of Asphalt Foam Modified with 25% PU
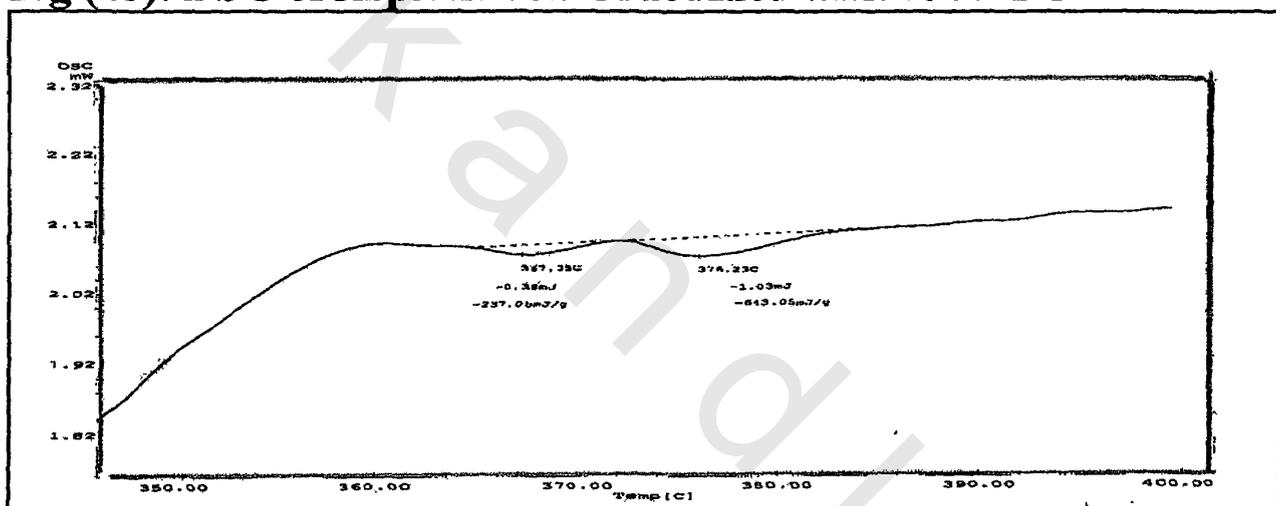
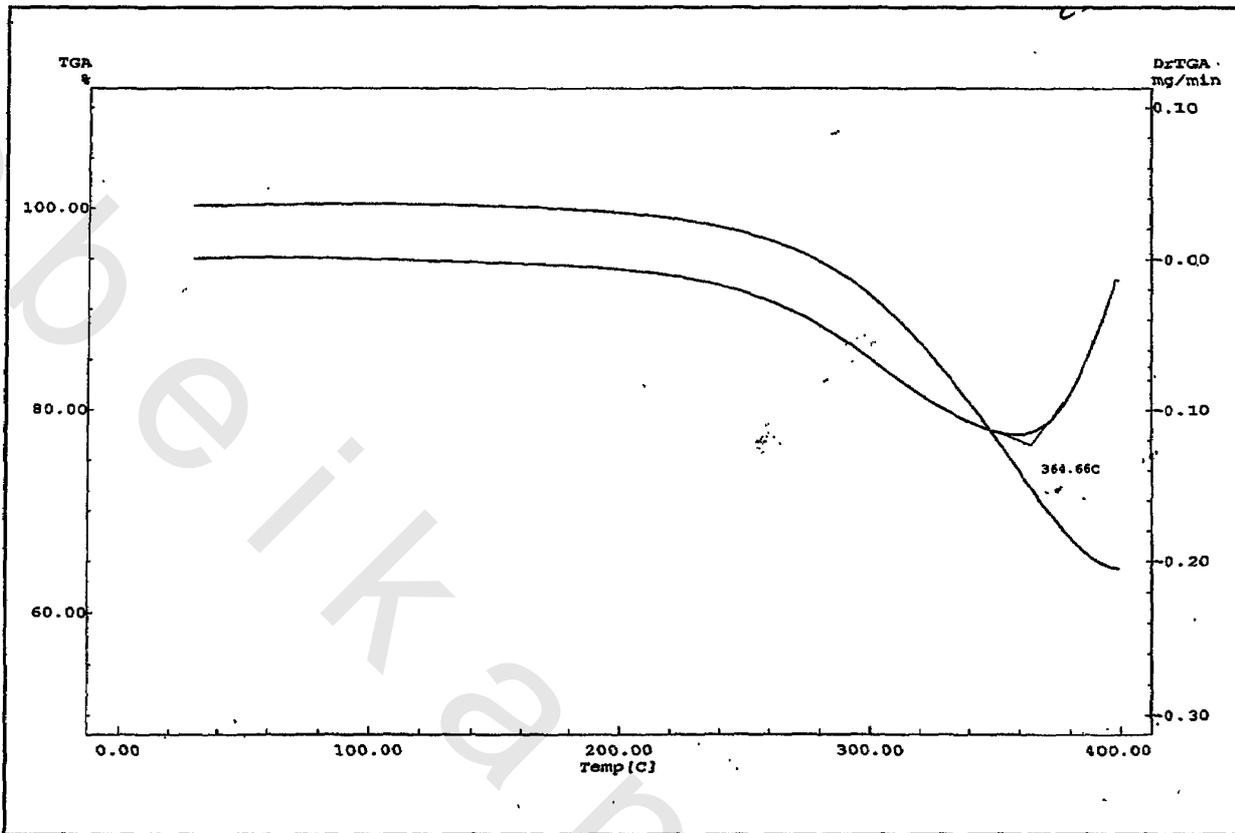

Fig (24): DSC of Asphalt Foam Modified with 20% PU
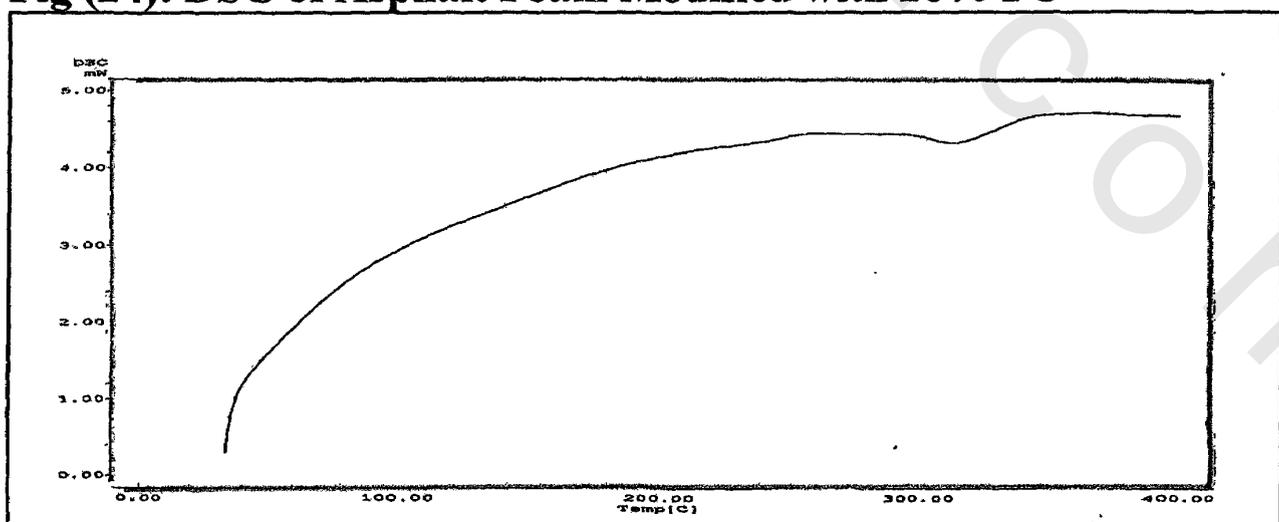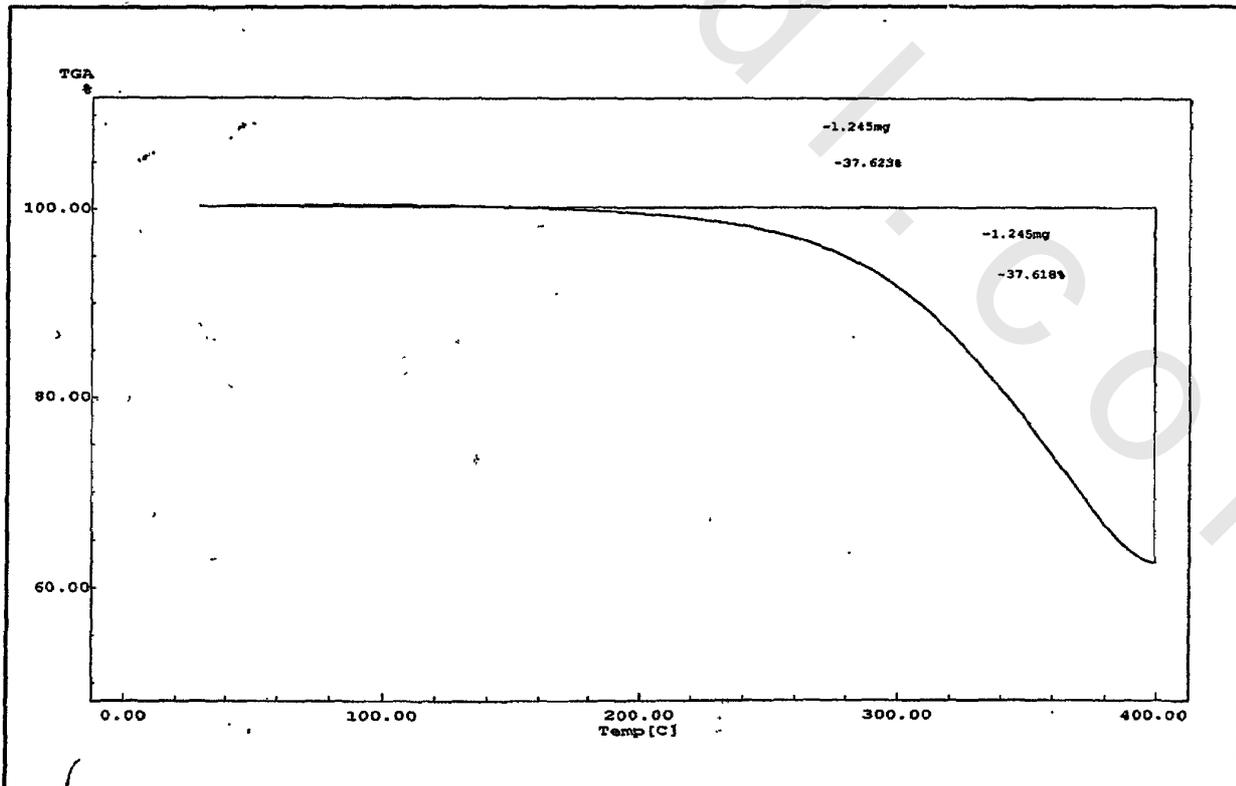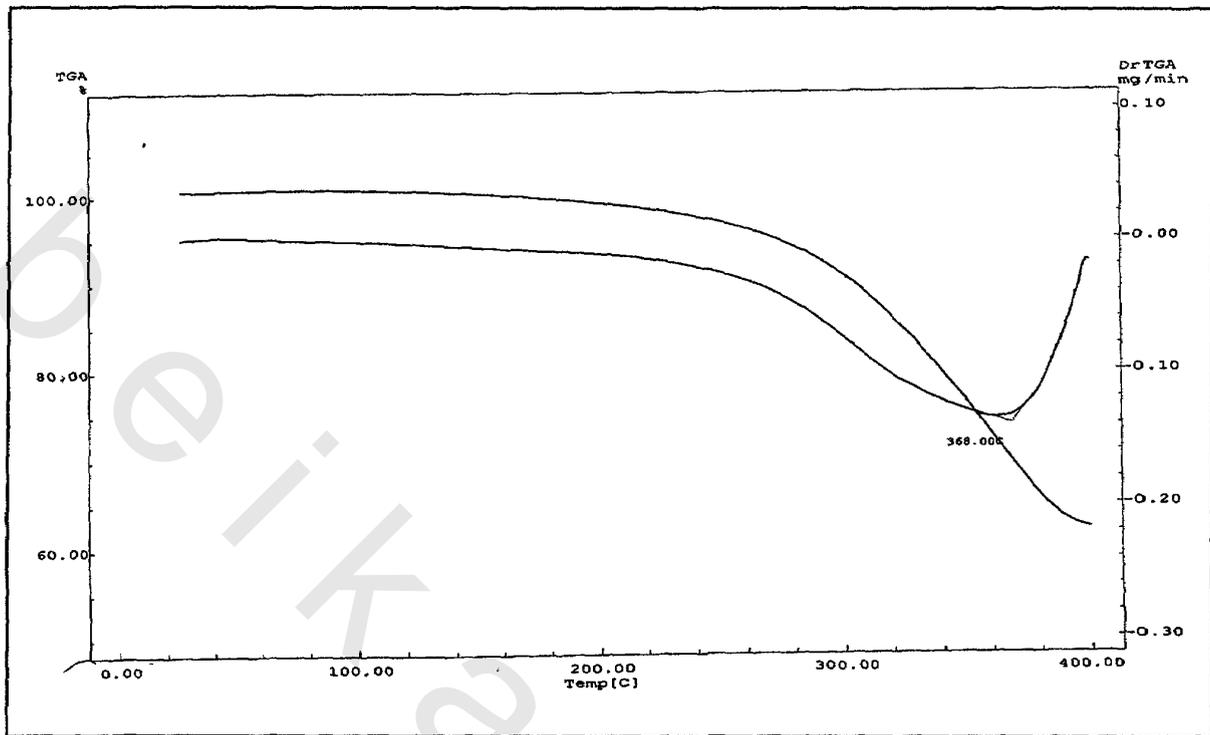

Fig (25): DSC of Asphalt Foam Modified with 2%A +1%Addibond
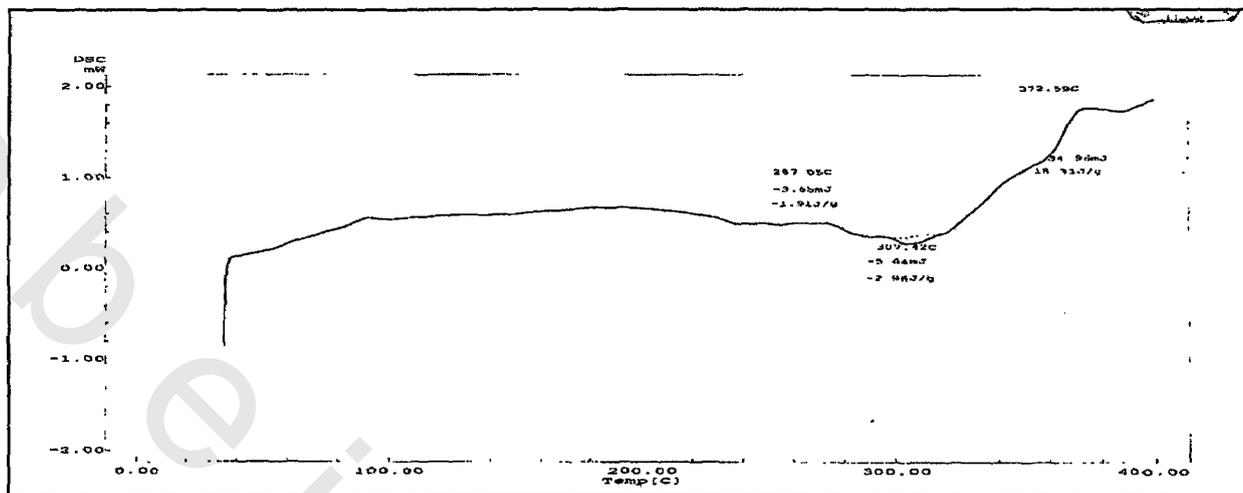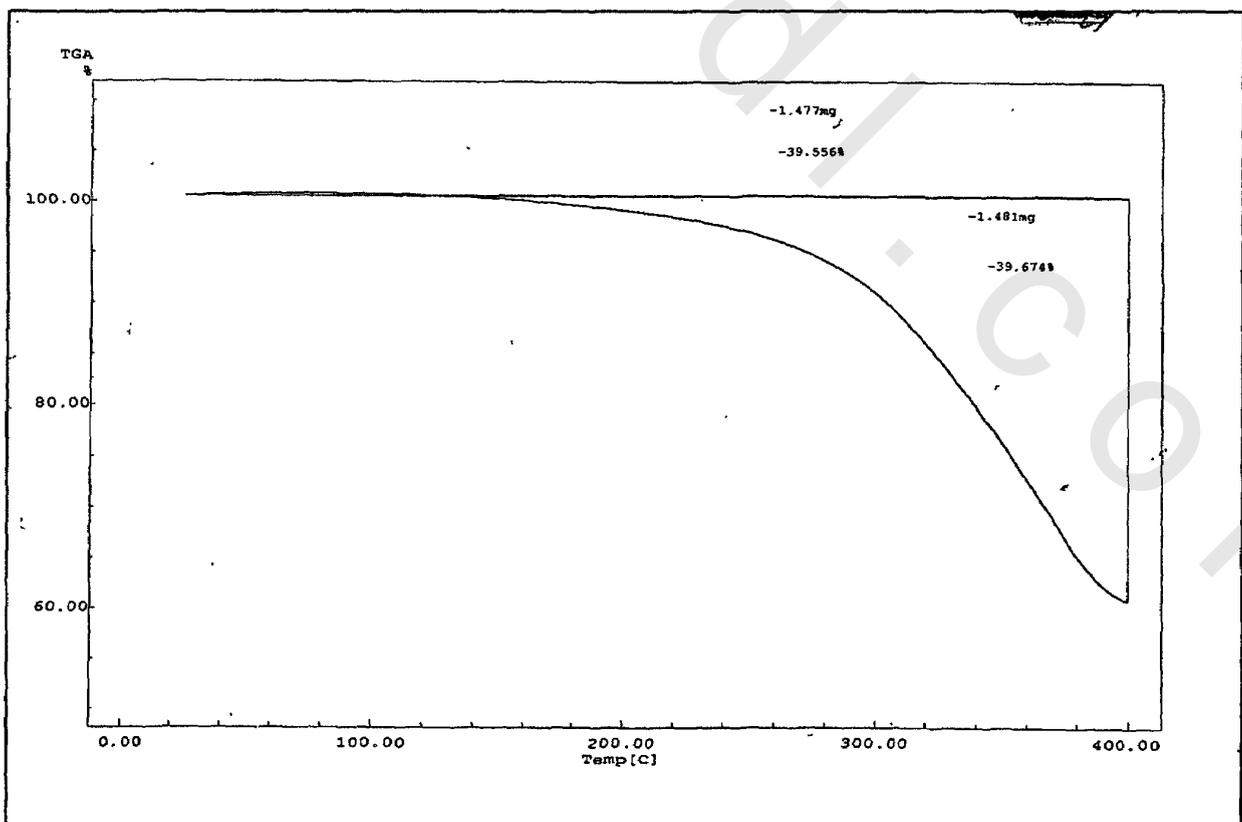
Fig (26): DSC of Asphalt Foam Modified with 25% Addibond 65
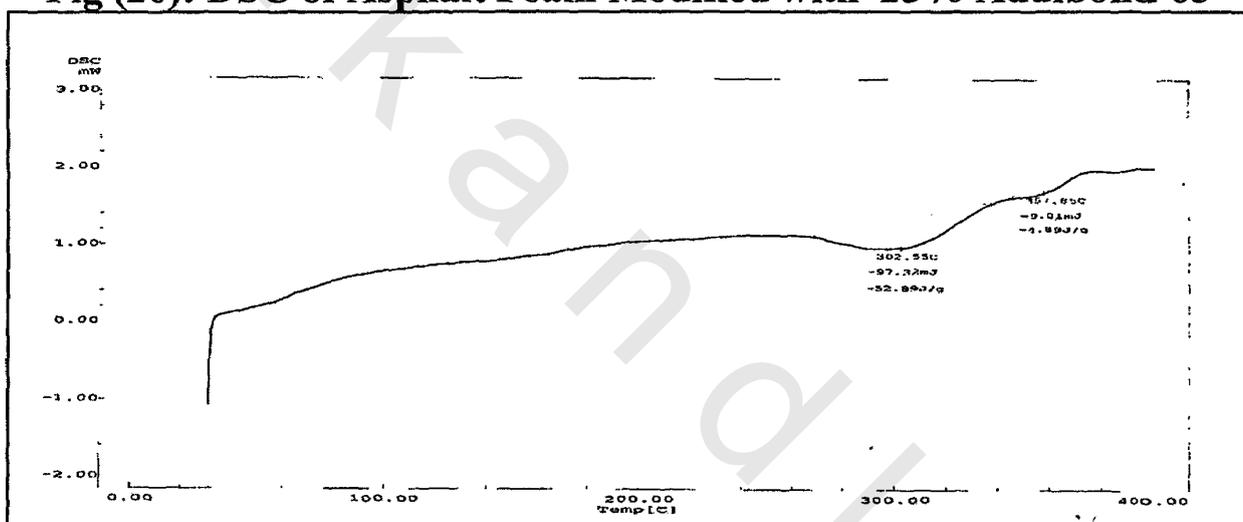
Fig (27): DSC of Asphalt Foam Modified with 20% Addibond 65
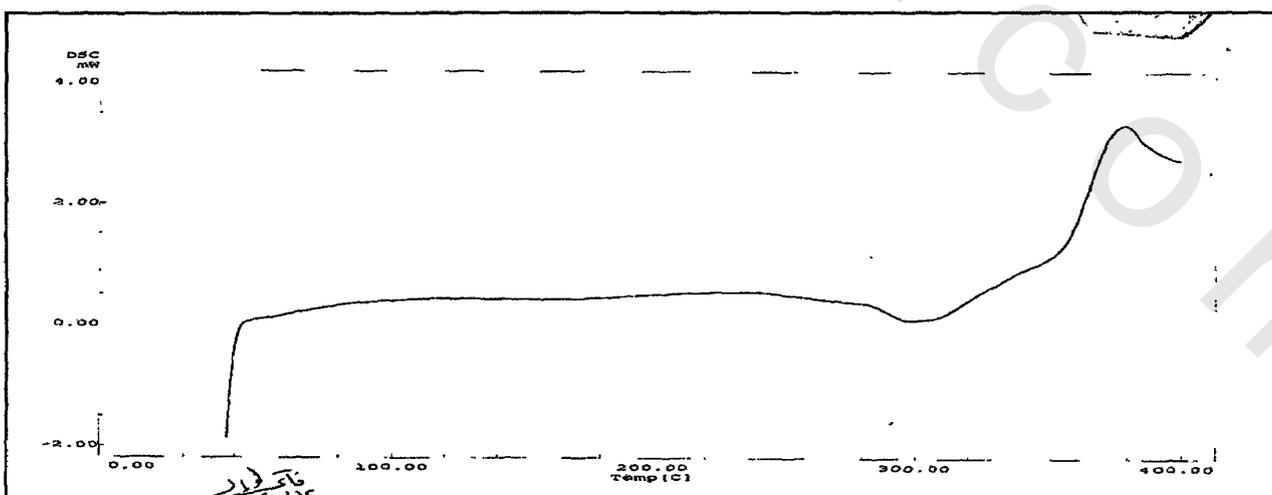
Fig (28):DSC of Asphalt Foam Modified with 3% Acrylic acid Water base

Results of Thermo-Gravimetric Analysis of the Prepared Foam.

Figs (29-36), and Table (25) illustrate the results of thermogravimetric analysis for the prepared foams. They show that they are thermally stable. The wt. loss % of the foam samples were 41.13 % at 374.92 °C for the modified foam by 25 % polyurethane; 37.618 % at 364.66°C for the modified sample by 20 % polyurethane; 39.074% at 368 °C for the modified sample by 15 % polyurethane; 43.169% at 369.2 °C for the modified sample by 2% A+ 1% Addibond 65 addition.

Table (25): Thermo Gravimetric Analysis for the Prepared Samples

Samples	Temperature °C	Wt. Loss %
Asphalt Foam +25% Pu	374.92	41.131
Asphalt Foam +20% Pu	364.66	37.618
Asphalt Foam +25% Addibond 65	368	39.074
Asphalt Foam +(2%A+1% Addibond 65)	369.20	43.169
Asphalt Foam +20% Addibond 65	163.27 364.97	8.776 45.63
Asphalt Foam +3% A	319.15 363.16	44.016 45.971
Asphalt Foam NCO/OH 1.1	156.42 321.43 364.8	6.499 37.086 44.086
Asphalt Foam NCO/OH 1.2	147.75 354.59	4.614 45.799

Fig (29ₐ): TGA of Asphalt Foam at NCO/OH Ratio = 1.1 without Modification

Fig (29ᵦ): TGA of Asphalt Foam at NCO/OH Ratio = 1.1 without Modification

Fig (30a):TGA of Asphalt Foam at NCO/OH Ratio = 1.2 without Modification

Fig (30ₑ): TGA of Asphalt Foam at NCO/OH Ratio = 1.2 without Modification

Fig (31a): TGA of Asphalt Foam mModified with 25% PU

Fig (31b): TGA of Asphalt Foam Modified with 25% PU

Fig (32a): TGA of Asphalt Foam Modified with 20% Pu

Fig (32b): TGA of Asphalt Foam Modified with 20% Pu

Fig (33a): TGA of Asphalt Foam Modified with 25%Addibond

Fig (33b): TGA of Asphalt Foam Modified with 25%Addibond
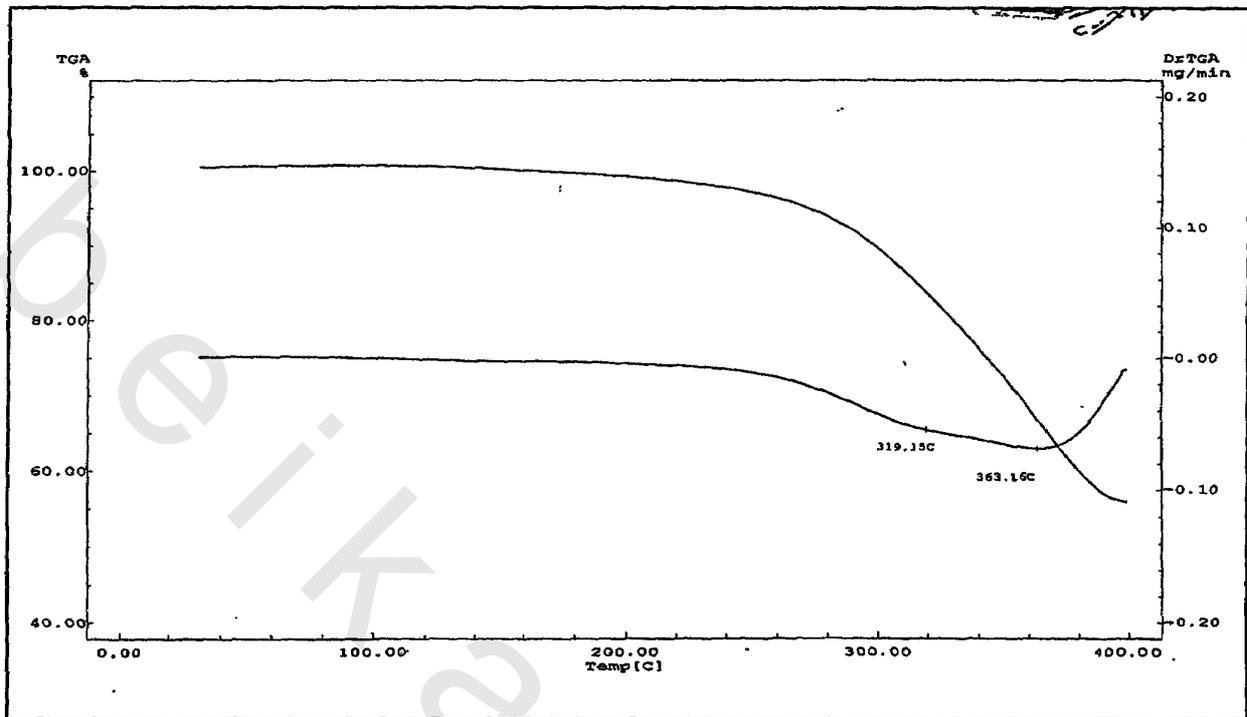
Fig (34a): TGA of Asphalt Foam Modified with 3% A
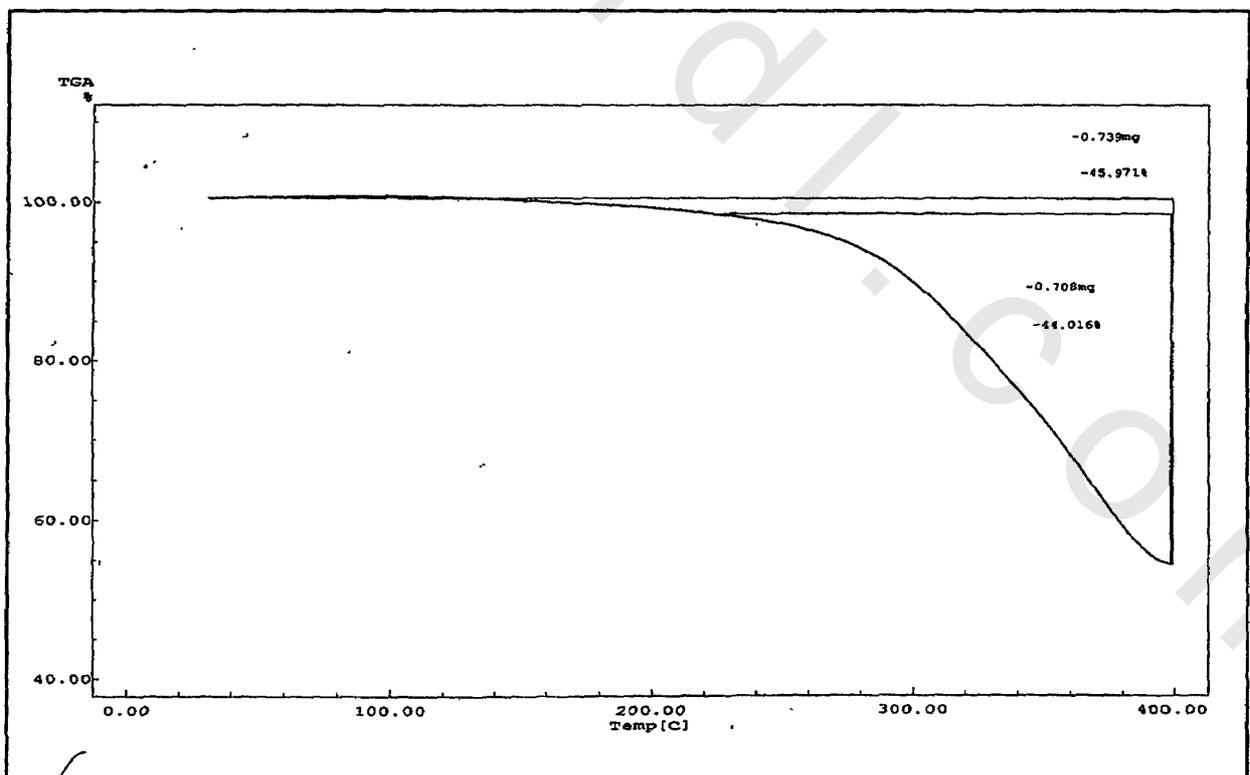
Fig (34b): TGA of Asphalt Foam Modified with 3% A
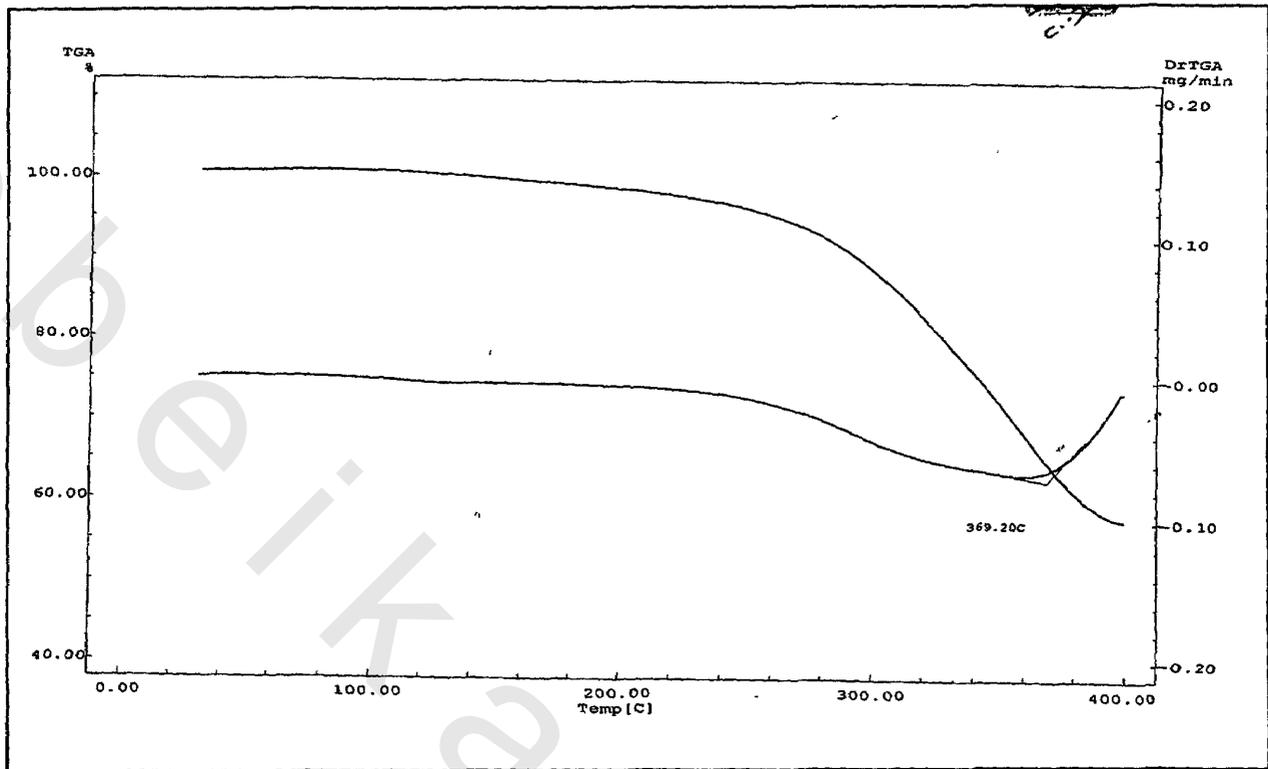
Fig (35a): Asphalt Foam Modified with (2%A+1% Addibond)
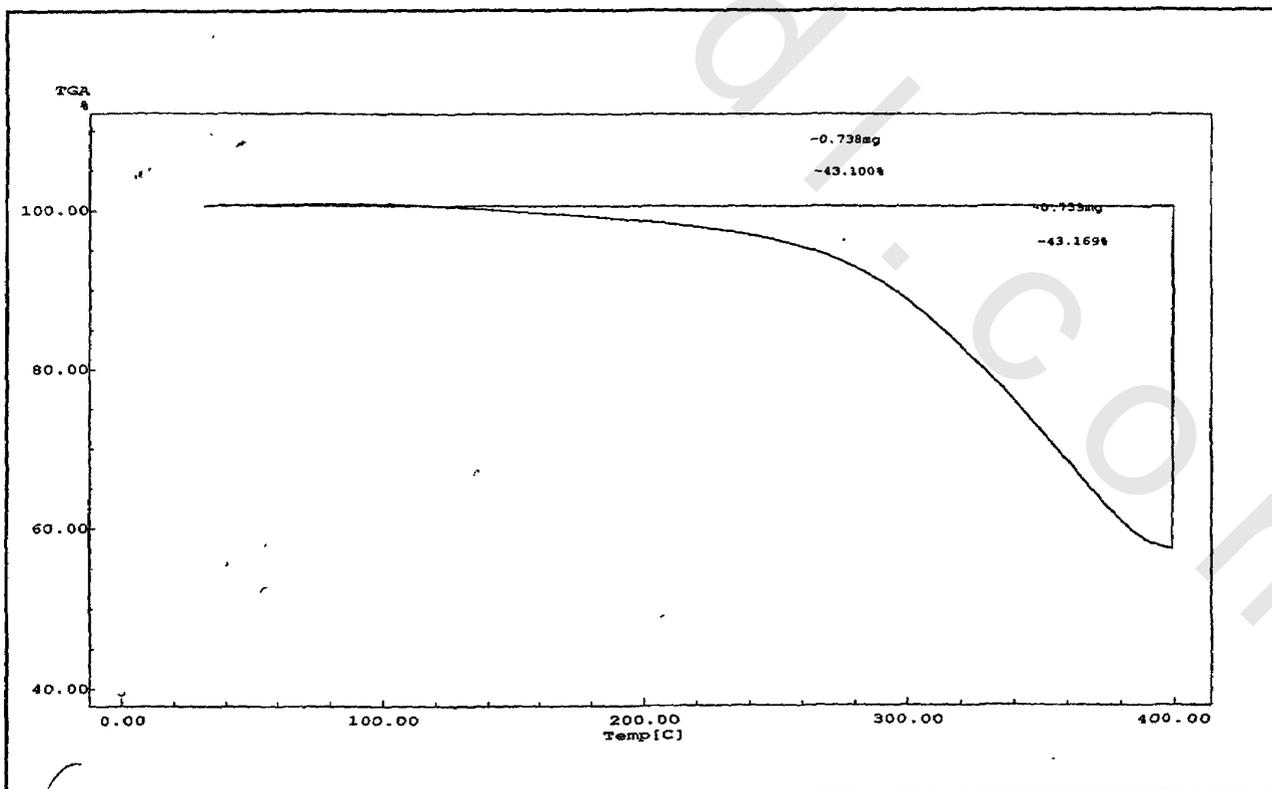
Fig (35b): Asphalt Foam Modified with (2%A+1% Addibond)
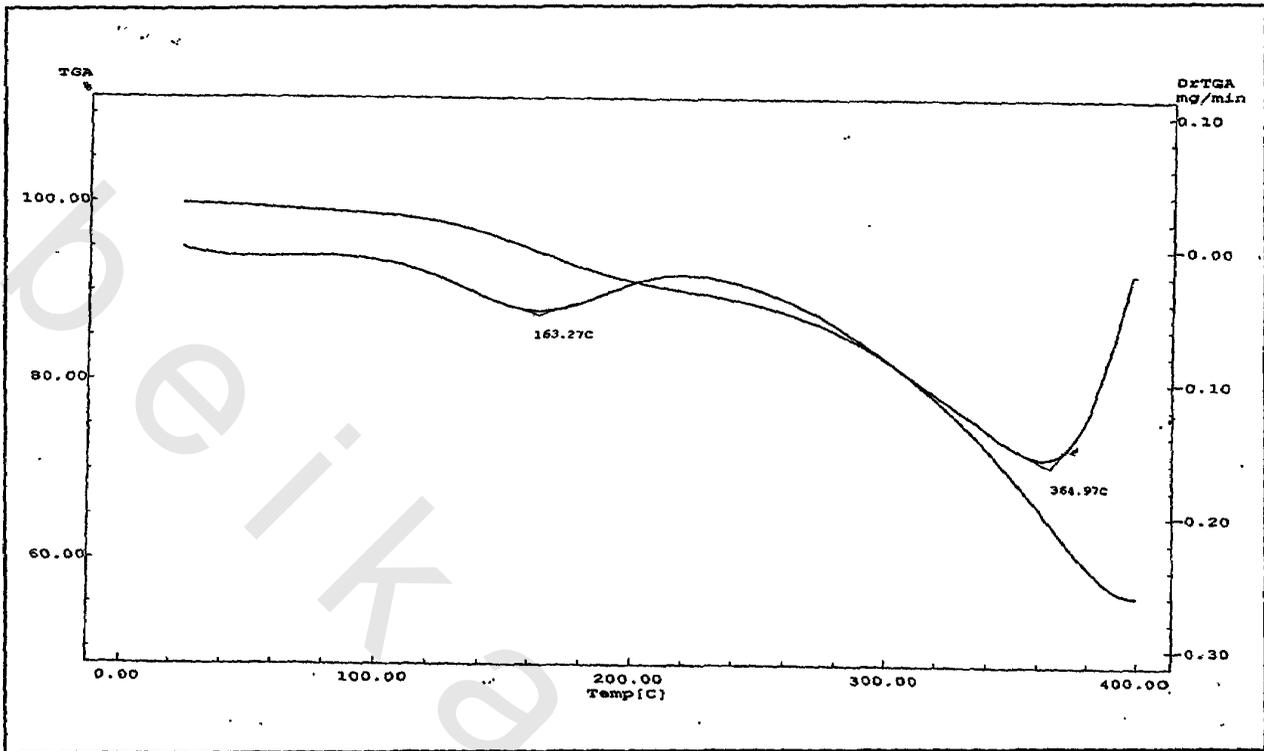
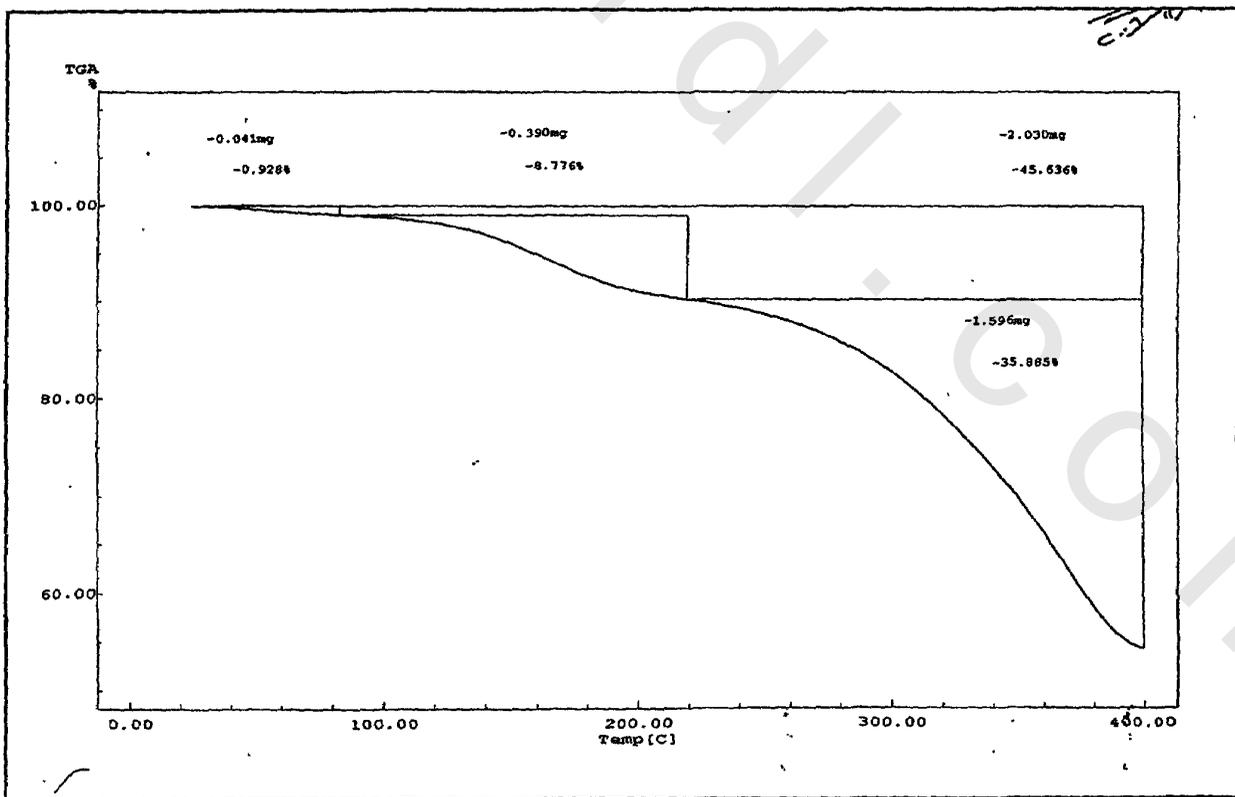**Fig (36a): TGA of Asphalt Foam Modified with+ 20% Addibond**

Fig (36b): TGA of Asphalt Foam Modified with 20% Addibond

Vulcanization Reaction for Samples Consisting of Blown Asphalt (Oxidized Asphalt) and Natural Rubber.

Rubbers are usually blended with some ingredients capable of rendering them useful in different applications. These include, vulcanizing agents, accelerators, activators, antioxidants, and fillers.

The vulcanization is considered the key process in rubber technology for producing rubber having optimum mechanical properties [113].

Crosslinking is an absolute requirement if elastomers are to have their essential property of rapidly and completely recovering from the deformation.
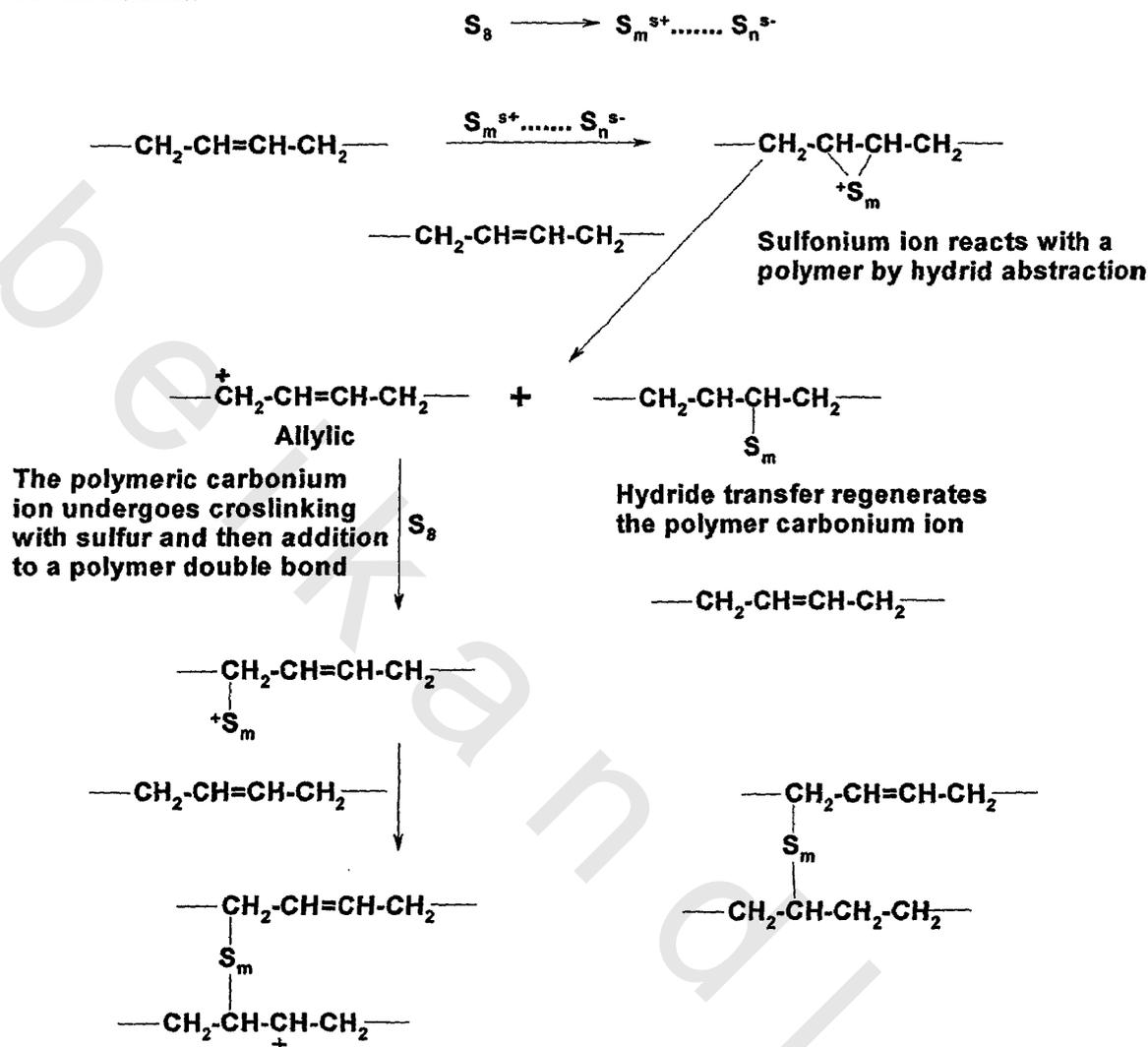
Crosslinking or vulcanization of polymers containing double bonds can be accomplished by different chemical methods such as sulpher, peroxides.

In general, the commercial vulcanization method is focued on heating using sulfur. This was the method used in this work.

Although sulfur vulcanization has been studied since its discovery in 1839 by Goodyear, its mechanism is not well understood.

Recent studies indicated that the reaction proceeds by the following ionic route.

Mechanism:-

$$S_8 \longrightarrow S_m{}^{s+} \dots\dots S_n{}^{s-}$$

—CH$_2$-CH=CH-CH$_2$— $\xrightarrow{\quad S_m{}^{s+} \dots\dots S_n{}^{s-} \quad}$ —CH$_2$-CH-CH-CH$_2$—
                                                                        $^+$S$_m$

—CH$_2$-CH=CH-CH$_2$—

Sulfonium ion reacts with a polymer by hydrid abstraction

$\overset{+}{\text{C}}$H$_2$-CH=CH-CH$_2$— **+** —CH$_2$-CH-CH-CH$_2$—
Allylic   S$_m$

The polymeric carbonium ion undergoes croslinking with sulfur and then addition to a polymer double bond S$_8$

Hydride transfer regenerates the polymer carbonium ion

—CH$_2$-CH=CH-CH$_2$—

—CH$_2$-CH=CH-CH$_2$—
 $^+$S$_m$

—CH$_2$-CH=CH-CH$_2$—

—CH$_2$-CH=CH-CH$_2$—
 S$_m$

—CH$_2$-CH=CH-CH$_2$—

—CH$_2$-CH=CH-CH$_2$—
 S$_m$

—CH$_2$-CH-CH$_2$-CH$_2$—

—CH$_2$-CH=CH-CH$_2$—
 S$_m$

—CH$_2$-CH-CH-CH$_2$—
 +

During vulcanization the addition of sulfur breaks the double bonds between the two carbon atoms and the sulfur atoms bridge the gaps between the chains [114]. An interesting reaction of rubber is its combination with sulfur; no rubber is considered technically useful if its chains are not crosslinked by a process known as curing or vulcanization.

The process of vulcanization converts the plastic properties of the raw rubber into elastic properties. However, vulcanized rubber – by itself (without modification) does not exhibit satisfactory mechanical properties. Fortunately the mechanical properties can be enhanced by the addition of carbon black fillers as a reinforcing agent [114].

Blown asphalt was used as modifier for vulcanizing natural rubber in different ratios of 5, 10, 20, 50, and 100 phr based on the natural rubber. Each ratio has been used with sulfur (S; 3.8) phr, ZNO; 2.0phr, Stearic acid; 1.0phr, TMTD; 1.0phr, MBT; 4.5phr, and carbon black; 50phr, based on the natural rubber, Table (26).

Table (26): Formulations of Vulcanized Natural Rubber, and Natural Rubber Modified with Blown Asphalt NRBA.

	VNR	VNRBA 5	VNRBA 10	VNRBA 20	VNRBA 50	VNRBA 100
NR	100	100	100	100	100	100
BA	—	5	10	20	50	100
S	3.8	3.8	3.8	3.8	3.8	3.8
ZNO	2.0	2.0	2.0	2.0	2.0	2.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	1.0	1.0	1.0	1.0	1.0	1.0
MBT	4.5	4.5	4.5	4.5	4.5	4.5
Carbon Black	50	50	50	50	50	50

The samples containing high content of blown asphalt have increased processability of samples and increased curing process. Different ratios of sulfur (3.8, 4.8, 5.8, 6.8, and 7.8) phr should be used with natural rubber modified blown asphalt at ratios of 50, and 100 phr based on the natural rubber as shown in Table (27).

Table (27): Formulations of Vulcanized Natural Rubber, and Natural Rubber Modified Blown Asphalt NRBA.

Ingredients, (g)	V.NRBA 50					V.NRBA 100				
NR	100	100	100	100	100	100	100	100	100	100
BA	50	50	50	50	50	100	100	100	100	100
S	3.8	4.8	5.8	6.8	7.8	3.8	4.8	5.8	6.8	7.8
ZNO	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0	2.0	2.0
STEATIC ACID	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
MBT	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
CARBON BLACK	50	50	50	50	50	50	50	50	50	50

In this work, the oxidized asphalt blended with the natural rubber (NR) in different ratios was formulated to obtain the vulcanized samples. Their mechanical, thermal stability, resistance to external media, swelling values, and crosslinking properties of the vulcanized samples, DSC, TGA were evaluated.

- Mechanical Properties for Samples Based on NR Modified with Different Ratios of Blown Asphalt

By the mechanical properties of polymers, one means those parameters or characteristics of the material that determine their response to applied stress. The nature of this response depends on temperature, time, and pressure, as well as on the structure, preparation conditions, and the past history of the polymer. Under some conditions such as low applied stresses and relatively low temperature, polymers may behave as linear elastic materials. Under higher applied stresses and at normal temperature, polymers may show yield phenomena like plastic deformation. Over a wide range of strain magnitudes, temperatures and test frequencies, high polymers show linear and / or nonlinear viscoelastic behavior [93].

- Tensile Strength (T.S) kgf/mm^2, and Elongation at Break % (Eb)

Values of Ts and Eb are determined for vulcanized natural rubber samples (VNR). The T.S and Eb for the vulcanized samples based on the same natural rubber materials previously subjected to blown asphalt by different percentage (5, 10, 20, 50, and 100) to 100 phr from(NR) were determined.

Tests were carried out using Tension Machine Type M-10(HUNG-TA INSTRUMENT Co. LTD), to estimate the values of tensile strength (kg/mm^2) and elongation at break (%).

The data given in Tables (28, 29, and 30), and Figs (37, 38), the obtained tensile strength kgf/mm^2 data of the tested samples are ranked in the following order:

VNRBA$_{50-3}$; (46.5 kgf/mm^2)> VNRBA$_{50-2}$; (45.8 kgf/mm^2)> VNRBA$_{20}$ (44.9 kgf/mm^2)> VNRBA$_{10}$ (44.5 kgf/mm^2)> VNRBA$_5$ (44.1 kgf/mm^2)>VNR (43.9 kgf/mm^2) >VNRBA$_{100-4}$ (38.1 kgf/mm^2)> VNRBA$_{100-3}$ (36.4 kgf/mm^2).

The obtained result show that the value of the tensile strength (46.5 kgf/mm^2) and the elongation at break (958%) of the sample VNRBA$_{50-3}$ (vulcanized natural rubber modified with 50% blown asphalt + 5.8g sulfur/100g NR) is the highest as compared with the other samples.

The values of elongation at break (%), for the same tested samples were ordered as the following order:

VNRBA$_{50-3}$; (958%) > VNRBA$_{50-2}$; (949%) > VNRBA$_{20}$ (946%) > VNRBA$_{10}$ (930%) > VNRBA$_5$ (918%) > VNR (905%)> VNRBA$_{100-4}$ (890%) > VNRBA$_{100-3}$ (875%).

- Absorbed Energy (kgf/mm) During The process of Deformation.
Absorbed energy (kgf/mm) is the value of the needed for the work done to break the tested sample. Absorbed energy values for the above mentioned tested samples concerning tensile strength are given in Tables (28, 29, and 30). The obtained results show that the values of absorbed energy for the tested samples were ranked as the following order:

$VNRBA_{50-3}$ (10.3 kgf/mm) > $VNRBA_{50-2}$ (9.9 kgf/mm) > $VNRBA_{20}$ (9.3 kgf/mm)> $VNRBA_{10}$ (8.9 kgf/mm) > $VNRBA_5$ (7.8kgf/mm)> VNR (6.3kgf/mm) > $VNRBA_{100-4}$ (6.5) > $VNRBA_{100-3}$ (6.2).

From these values, it is clear that the increase depends on the added quantity of BA.

- Young's Modulus, kgf/mm^2

Values of Young's modulus calculated for the above mentioned tested samples as given in Table 28. These data show that the Young modulus increases with increasing the quantity of added blown asphalt.

Table (28): Mechanical Properties at Room Temperature for the Prepared Vulcanized Natural Rubber, and Vulcanized Natural Rubber Modified with Blown Asphalt.

Samples	Tensile Strength (kgf/mm^2)	Elongation At Break (%)	Absorbed Energy (kgf.mm)	Young's Modulus (kgf/mm^2)
VNR	43.9	905	0.280	6.3
$VNRBA_5$	44.1	918	0.356	7.8
$VNRBA_{10}$	44.5	930	0.395	8.9
$VNRBA_{20}$	44.9	946	0.433	9.5
$VNRBA_{50}$	-	-	-	-

Table (29): Mechanical Properties at Room Temperature for the Prepared Vulcanized Natural Rubber Modified with 50phr Blown Asphalt + Different Percentages of Sulfur.

Samples	Tensile Strength (kgf/mm^2)	Elongation atBreak (%)	Absorbed Energy (kgf.mm)	Young's Modulus (kgf/mm^2)
VNRBA$_{50-1}$	-	-	-	-
VNRBA$_{50-2}$	45.8	949	0.455	9.9
VNRBA$_{50-3}$	46.5	958	0.510	10.3
VNRBA$_{50-4}$	-	-	-	-

1=3.8g sulfur,   2=4.8g sulfur,

3=5.8g sulfur,   4=6.8g sulfur,

Table (30): Mechanical Properties at Room Temperature for the Prepared Vulcanized Natural Modified with 100phr Blown Asphalt + Different Percentage of Sulfur.

Samples	Tensile Strength, (kgf/mm^2)	Elongation at Break, (%)	Absorbed Energy, (kgf.mm)	Young's Modulus, (kgf/mm^2)
VNRBA$_{100-1}$	-	-	-	-
VNRBA$_{100-2}$	-	-	-	-
VNRBA$_{100-3}$	36.4	875	0.231	6.1
VNRBA$_{100-4}$	38.1	890	0.253	6.5
VNRBA$_{100-5}$	-	-	-	-

From data illustrated in Tables (29, 30) and Fig (37,38) we can noticed that the optimum quantity of adding blown asphalt was 50% to natural rubber achieve the highest values of tensile strength and elongation at break. However 100% adding blown asphalt to natural rubber cause deformation in the vulcanized matrix
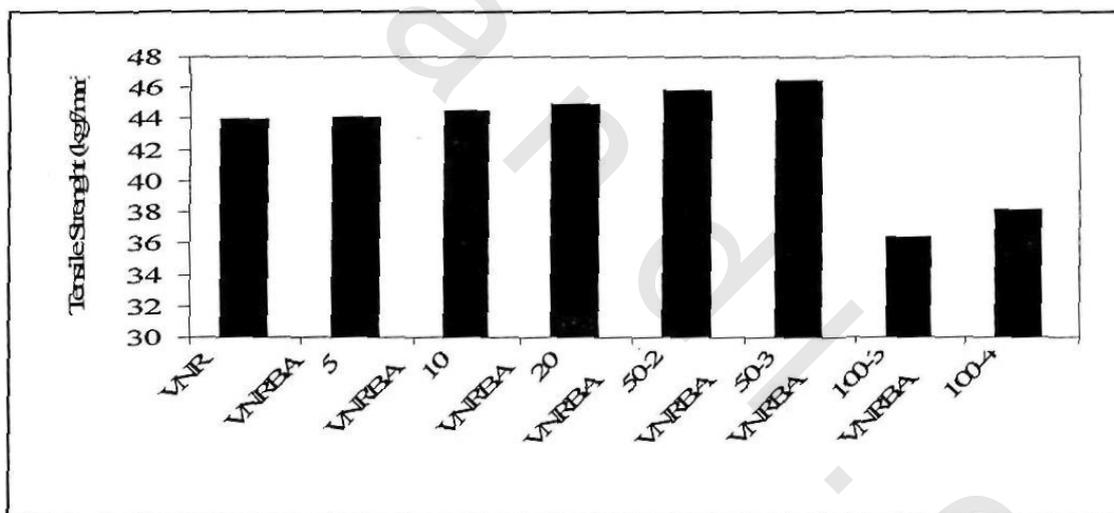
Fig (37): Tensile Strength Value (kgf/mm^2), for vulcanized Rubber, and Modified Vulcanized Rubber with Blown Asphalt.
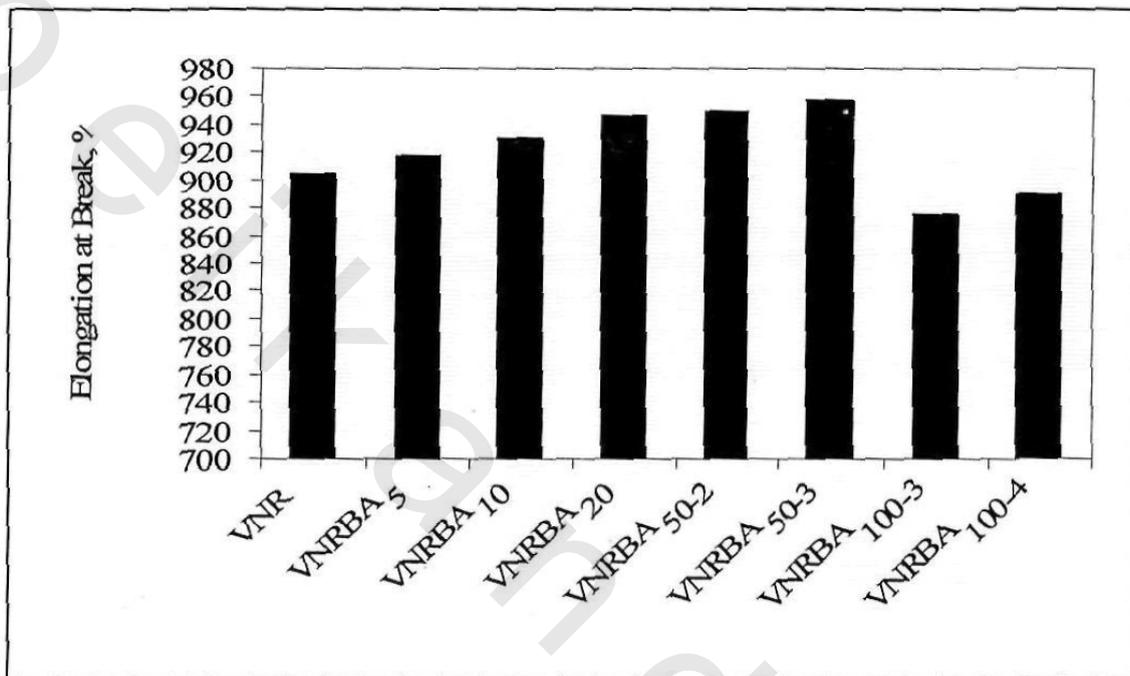
Fig (38): Elongation at Break, (%), for vulcanized Rubber, and Modified Vulcanized Rubber with Blown Asphalt

- Thermal Stability

The studied samples based on the vulcanized natural rubber, and the modified natural rubber with the blown asphalt (VNR, $VNRBA_5$, $VNRBA_{10}$, $VNRBA_{20}$, $VNRBA_{50-2}$, $VNRBA_{50-3}$, $VNRBA_{100-3}$, $VNRBA_{100-4}$) were placed in furnace at 200 ^{o}C individually, and then withdrawn from the furnace after fixed time intervals; cooled to room temperature and weighted. The weight loss for each cold sample was recorded in Table (31), and illustrated in Fig (39).

Table (31): Thermal Stability (wt. loss, %) for Vulcanized Rubber, and Different Formulations of Rubber Modified Blown Asphalt Heated at 200 °C .

Curing Time, hrs	Weight loss, % after different curing times, hrs.						
	5	10	20	40	80	150	200
VNR	0.973	1.231	1.452	1.612	2.181	2.651	3.110
VNRBA$_5$	0.952	1.093	1.215	1.379	1.876	2.153	2.630
VNRBA$_{10}$	0.931	0.970	1.191	1.214	1.635	2.014	2.410
VNRBA$_{20}$	0.901	0.934	1.034	1.165	1.497	2.000	2.237
VNRBA$_{50-2}$	0.927	1.082	1.087	1.412	1.987	2.261	2.783
VNRBA$_{50-3}$	0.873	0.895	0.912	0.985	1.031	1.321	1.892
VNRBA$_{100-3}$	0.973	1.123	1.365	1.571	2.131	2.491	3.051
VNRBA$_{100-4}$	0.821	0.830	0.900	0.981	1.025	1.132	1.681
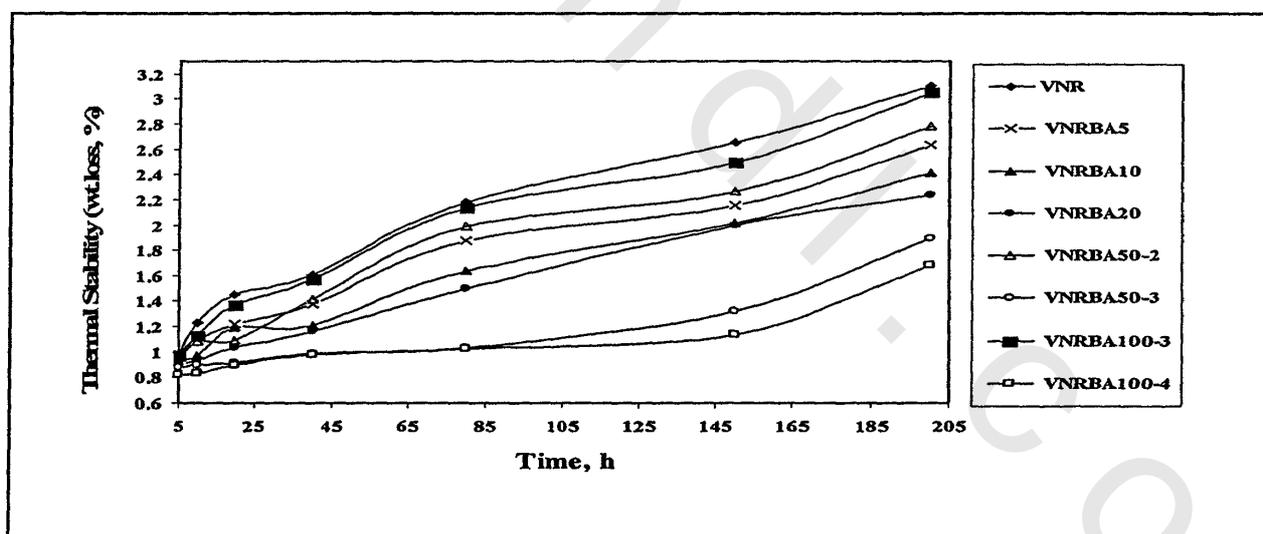
Fig (39): Thermal Stability (wt. Loss, %) for Vulcanized Rubber, and Different Formulation of Rubber Modified with Blown Asphalt.

The obtained data given in Table (31) and Fig (39) show that, the vulcanized natural rubber modified with blown asphalt samples acquired wt. loss values % lower than for vulcanized natural rubber

without such modification. For example: VNRBA$_5$ has wt. loss = 2.630%, while the corresponding wt. loss of VNR, wt. loss equals 3.110% (curing time was 200 h for the two samples). This means that the modification of the vulcanized natural rubber with the blown asphalt and sulfur increases the thermal stability. The decrease of wt. loss %. could be due to increasing the crosslinking value (1/Q) of the treated samples.

The obtained results after heating the samples up to 200 °C show that the values of (wt. loss %) generally increases with increasing the time of heating of the tested samples. For example, the wt. loss of the sample VNRBA$_{50-3}$ after different heating time is ordered as; wt. loss = 0.873% after 5 h < 0.895% after 10 h < 0.912% after 20 h < 0.985% after 40 h < 1.031% after 80 h < 1.321% after 150 h < 1.892% after 200 h.

- Resistance to External Media.
Swelling and Crosslinking Values

The time dependence of degree of swelling, after different time values, for the vulcanized rubbers (VNR), and also vulcanized rubber modified with blown asphalt (VNRBA$_5$, VNRBA$_{10}$, VNRBA$_{20}$, VNRBA$_{50-3}$, VNRBA$_{100-4}$) have been studied. After post-curing time (15 min, at 155 °C), in solvent (benzene and kerosene) individually, at room temperature, as shown in Table, 32, and Figs, 40-43, from the obtained data it can be concluded that

1-The swelling values (Q%) and crosslinking values (1/Q) change with the percent of added (blown asphalt) relative to the rubber in the process.

As example the values of swelling, (Q%) in benzene after 24 h for post curing samples proceed in the following order; VNRBA$_{20}$ (1.149%) < VNRBA$_{10}$ (1.161%) < VENRBA$_5$, (1.45%) and also for

VNR, (1.58%). This means that the values of swelling (Q%) decrease with increasing the percent of added (BA) to the rubber in the process. This is inversely proportional to the corresponding values of crosslinking (1/Q) as follows; for the $VNRBA_{20}$ (0.870%) >$VNRBA_{10}$ (0.864%) > $VENRBA_5$, (0.689%) and also for VNR, (0.632%).

This means that the values of crosslinking increase with increasing the percent of added (blown asphalt) as shown in Table (32), and illustrated in Figs (40-43).

Similar behavior was obtained when the percent of blown asphalt was increased. The sulfur percent must be increased to increase the swelling values in benzene after 24 h for the post cured samples.

The values of swelling (Q%) decrease with increasing the percent of added (sulfur) to the rubber in the process. This is inversely proportional to the corresponding values of crosslinking (1/Q)

2- The swelling values, % (Q%) and crosslinking values (1/Q) depend on the time of immersion of the studied samples in the solvents.

The values of swelling (Q%) of the post cured samples after post-curing time, in benzene, [$VNRBA_5$ after 24 h, was (1.45%), $VNRBA_5$ after 12 h, was (1.32), $VNRBA_5$ after 6 h, was (1.13%), $VNRBA_5$ after 1 h, was (0.676%), and $VNRBA_5$ after 30 min was (0.460%).

Generally the values of swelling increase with increasing immersion time for the tested samples. It was found also that the crosslinking 1/Q values decrease with increasing the time of immersion in the following order;

VNRBA$_5$ (0.689%) at 24 h < VNRBA$_5$ (0.757%) at 12 h < VNRBA$_5$ (0.884%) at 6 h < VNRBA$_5$ (1.479%) at 1 h < VNRBA$_5$ (2.173) at 30 min.

This means that the increase of the immersion time gives chances of the solvent (benzene or kerosene) to penetrate into the chains of the tested samples. This penetration probably destroys the found links between the sample chains.

3– The swelling values (Q), and crosslinking values (1/Q) are affected by the type of solvent, the given data of 1/Q for post cured VNRBA$_{5-3}$, in benzene, for 24 h, at room temperature was (1.002%) > (0.971%) for the corresponding value of 1/Q in kerosene.

Generally the studied samples in benzene achieve higher swelling values Q (%) and lower crosslinking values (1/Q) as compared with obtained with the corresponding samples in kerosene. This may be due to the high molecular weight of kerosene which hindrances its penetration via the sample chains.

Table (32): Swelling Values (Q), and Crosslinking Values (1/Q) in Benzene, and Kerosene, at Room Temperature for Post Cured Vulcanized Rubber, and Vulcanized Rubber Samples Modified with Blown Asphalt.

Sample	Time	Benzene		Kerosene	
		Q	1/Q	Q	1/Q
VNR	0.5	0.513	1.949	0.371	2.695
	1.0	0.953	1.049	0.877	1.140
	6	1.468	0.681	1.287	0.777
	12	1.500	0.666	1.351	0.740
	24	1.580	0.632	1.456	0.686
VNRBA$_5$	0.5	0.460	2.173	0.421	2.375
	1.0	0.676	1.479	0.643	1.555
	6	1.13	0.884	1.103	0.906
	12	1.32	0.757	1.23	0.813
	24	1.45	0.689	1.39	0.719
VNRBA$_{10}$	0.5	0.341	2.932	0.322	3.105
	1.0	0.531	1.883	0.480	2.083
	6	0.961	1.040	0.869	1.150
	12	1.013	0.987	0.927	1.078
	24	1.161	0.861	0.967	1.034
VNRBA$_{20}$	0.5	0.329	3.039	0.310	3.225
	1.0	0.528	1.894	0.468	2.136
	6	0.946	1.057	0.857	1.167
	12	1.003	0.997	0.916	1.092
	24	1.149	0.870	0.956	1.046
VNRBA$_{50-3}$	0.5	0.297	3.367	0.279	3.584
	1.0	0.489	2.044	0.426	2.347
	6	0.893	1.119	0.810	1.234
	12	0.961	1.040	0.872	1.146
	24	1.002	0.998	0.931	1.075
VNRBA$_{100-4}$	0.5	0.265	3.773	0.243	4.11
	1.0	0.436	2.293	0.409	2.44
	6	0.851	1.170	0.803	1.24
	12	0.936	1.068	0.859	1.164
	24	0.945	1.058	0.907	1.102
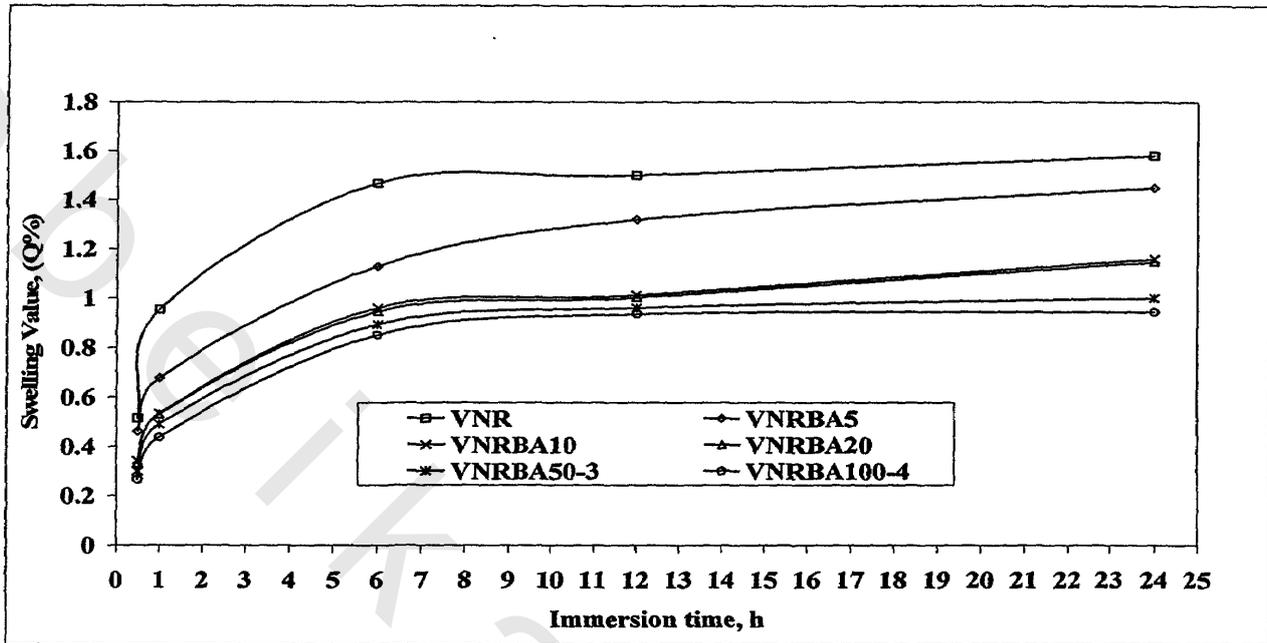
Fig (40): Change in the Swelling Values (Q%) in Benzene at room Temperature with immersion Time for Different Samples o Vulcanized Rubber, And Rubber Modified with Blown Asphalt.
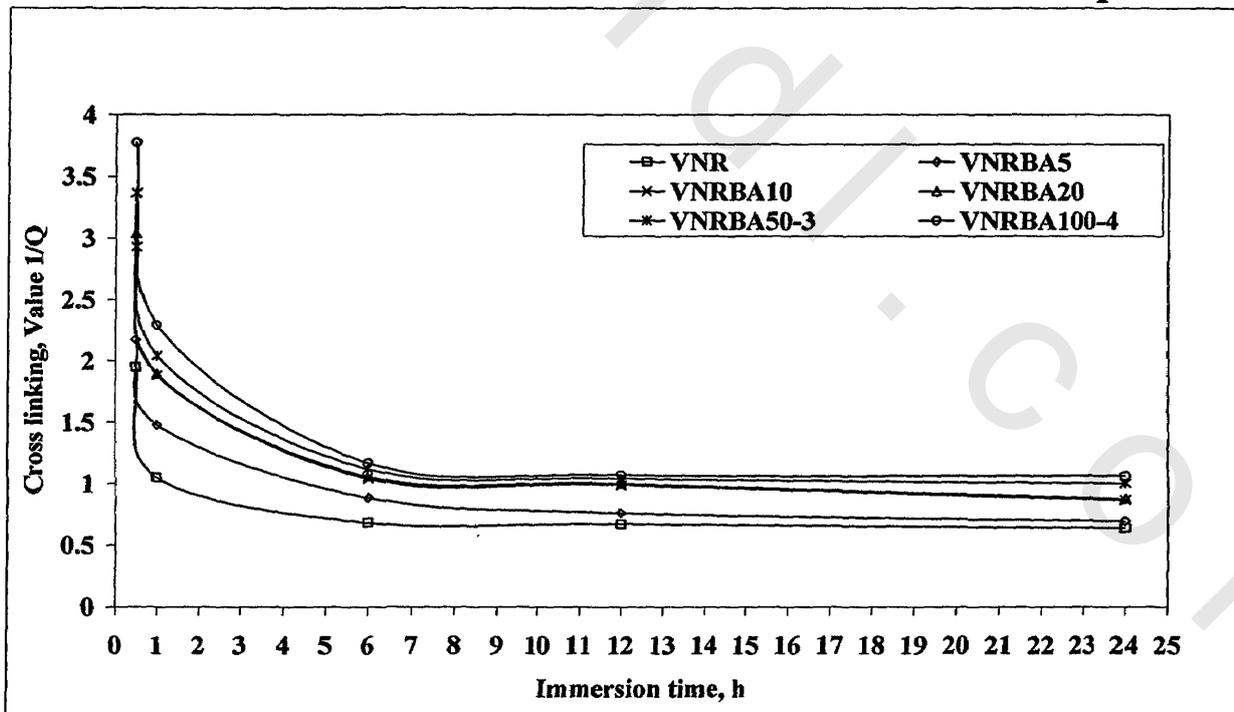
Fig (41): Change in the Crosslinking Values (1/Q%) in Benzene with immersion Time at room Temperature for Different Samples of Vulcanized Rubber, And Rubber Modified with Blown Asphalt
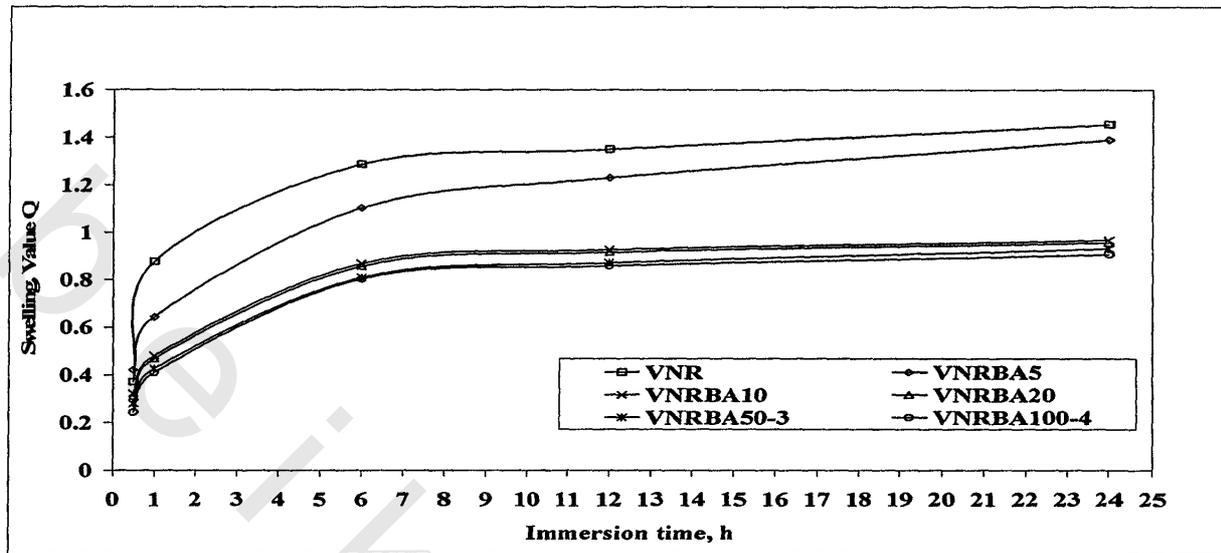
Fig (42): Change in the Swelling Values (Q%) with immersion Time in Kerosene at room Temperature for Different Samples of Vulcanized Rubber, And Rubber Modified with Blown Asphalt
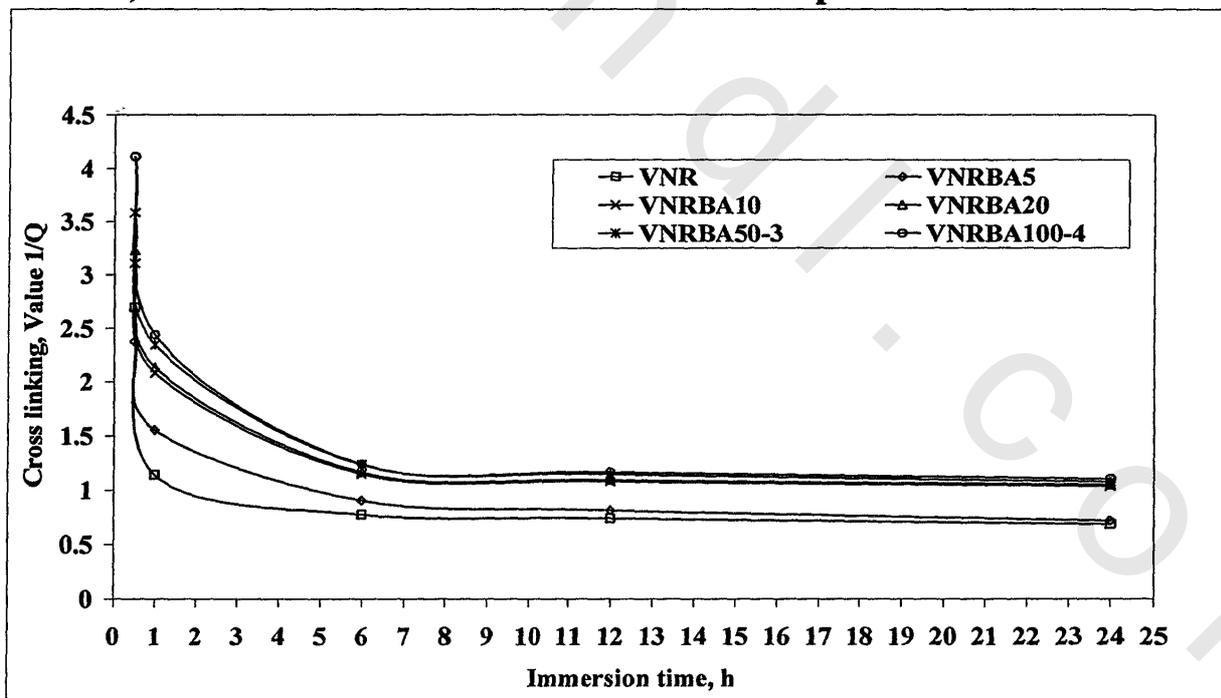
Fig (43): Change in the Crosslinking Values (1/Q%) with immersion Time in Kerosene at room Temperature for Different Samples of Vulcanized Rubber, And Rubber Modified with Blown Asphalt

Resistance to Chemicals (wt. loss, %)

The chemical resistance in wt. loss% was investigated at room temperature for vulcanized sample in water, acetone, H_2SO_4, and kerosene illustrated in Table (33) for 3 weeks interval.

Generally all tested samples show high resistance in the studied media and the values of wt.loss,% depend on the chemical composition of the tested modified rubber samples.

The resistance against 10% H_2SO_4, for the tested vulcanized samples such as; $VNRBA_{100-4}$, (wt. loss, 0.937%) < $VNRBA_{50-3}$, (wt. loss, 1.147%) >$VNRBA_{20}$, (wt. loss, 1.217%) < $VNRBA5$, (wt. loss, 1.362%) < VNR, (wt. loss, 1.521%).

The difference of the chemical resistance represented by wt. loss % can be explained by the difference of their chemical constitution as shown in Table (33).

Table (33): Chemical Resistance (wt. Loss, %) in different Media at Room Temperature for Vulcanized Samples.

Samples	Time of immersion week	Water	Acetone	H_2SO_4, 10%	Kerosene
VNR	1	0.029	1.403	0.973	2.871
	2	0.35	1.960	1.351	3.164
	3	0.38	2.109	1.521	3.581
VNRBA$_5$	1	0.010	1.351	0.909	2.317
	2	0.019	1.613	1.003	2.553
	3	0.023	1.785	1.362	2.948
VNRBA$_{20}$	1	0.00	1.296	0.874	2.275
	2	0.00	1.487	0.982	2.431
	3	0.00	1.914	1.217	2.731
VNRBA$_{50-3}$	1	0.00	1.083	0.894	1.932
	2	0.00	1.157	0.935	2.164
	3	0.00	1.290	1.147	2.405
VNRBA$_{100-4}$	1	0.00	0.842	0.650	1.841
	2	0.00	0.971	0.691	2.059
	3	0.00	1.036	0.937	2.231

Differential Scanning Calorimetric Analysis (DSC) for Vulcanized Samples

The results of DSC analysis as shown in Figs (44-48) show no sign of physical changes in the morphology of the samples up to (365.37°C, 394.84 °C) for VNRBA$_{100-4}$, 382.51°C for VNRBA$_{50-3}$, (187.03°C, 297.18 °C 378.11 °C) for VNRBA$_{50-2}$, 356°C for VNRBA$_{20}$, and 352.30°Cfor VNR,
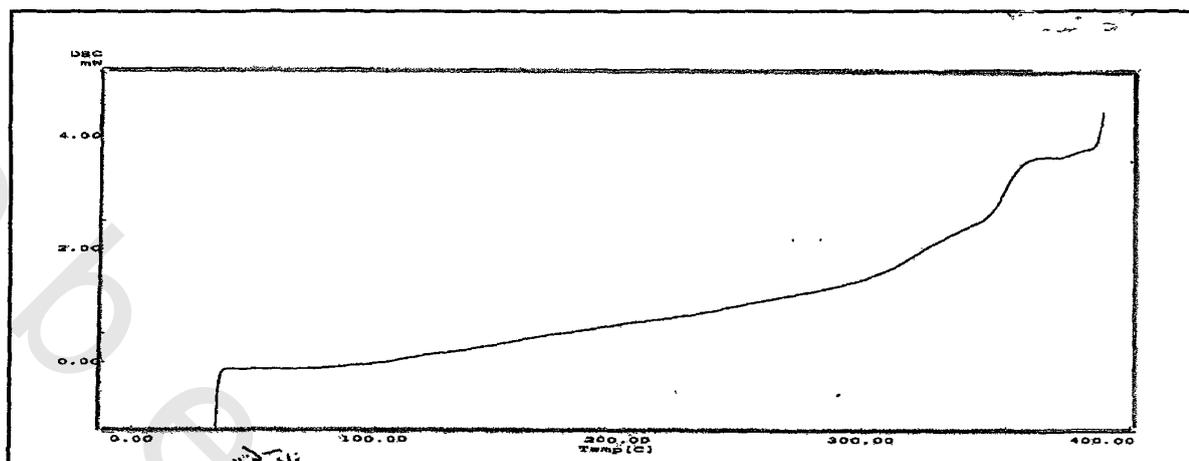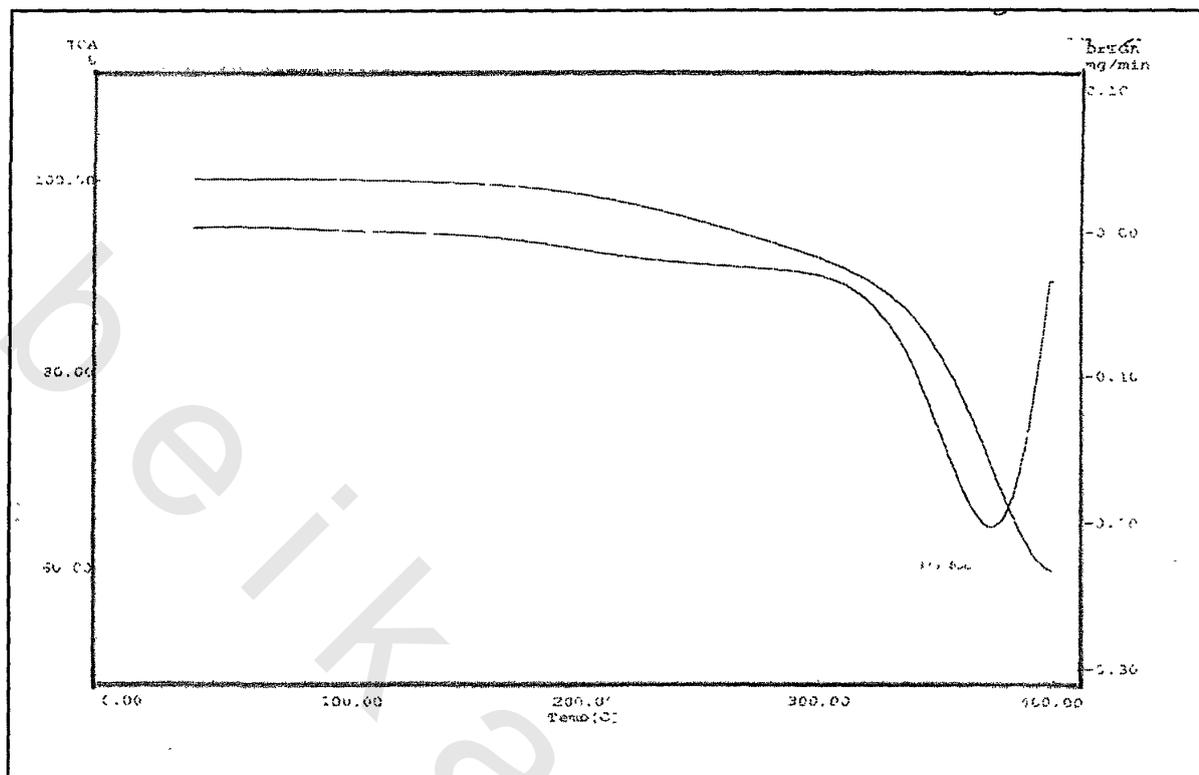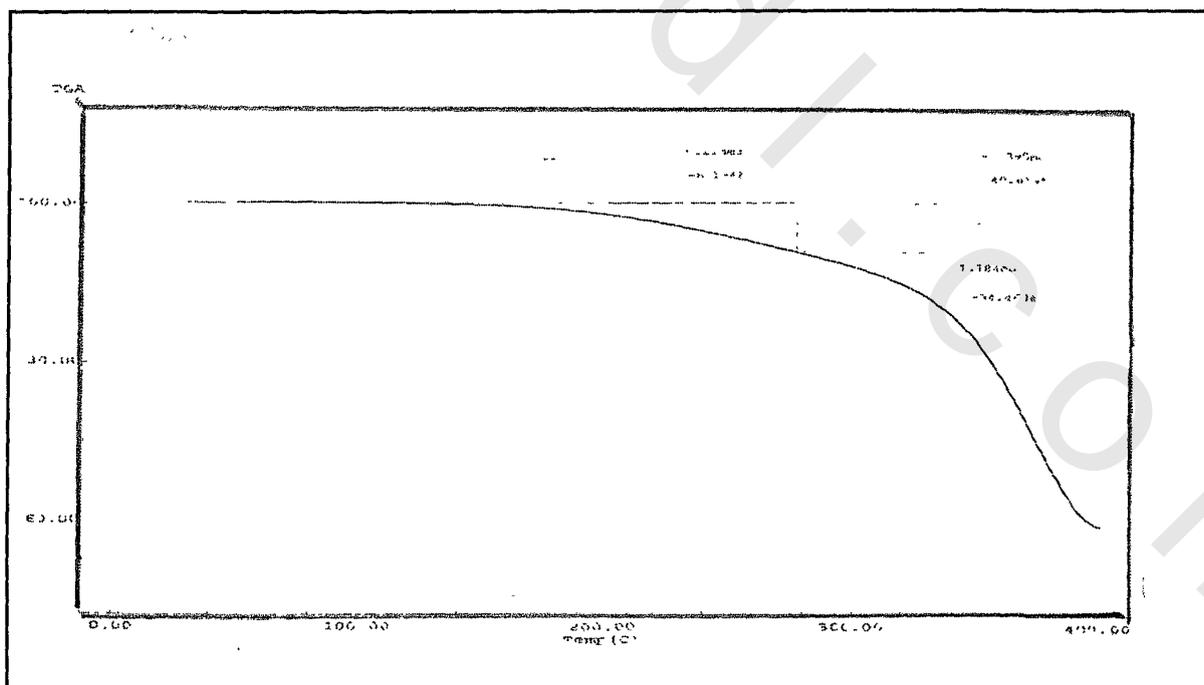
Fig (44): **DSC for Vulcanized Natural Rubber Modified with (100g Blown Asphalt+ 6.8 g Sulfur/100g NR (VNRBA$_{100-4}$)).**
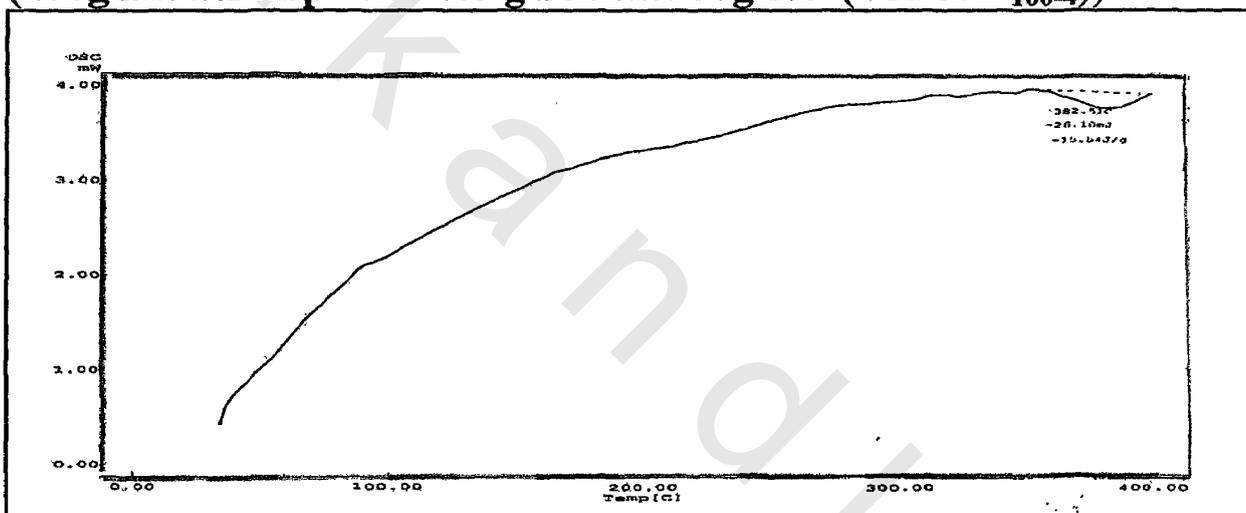
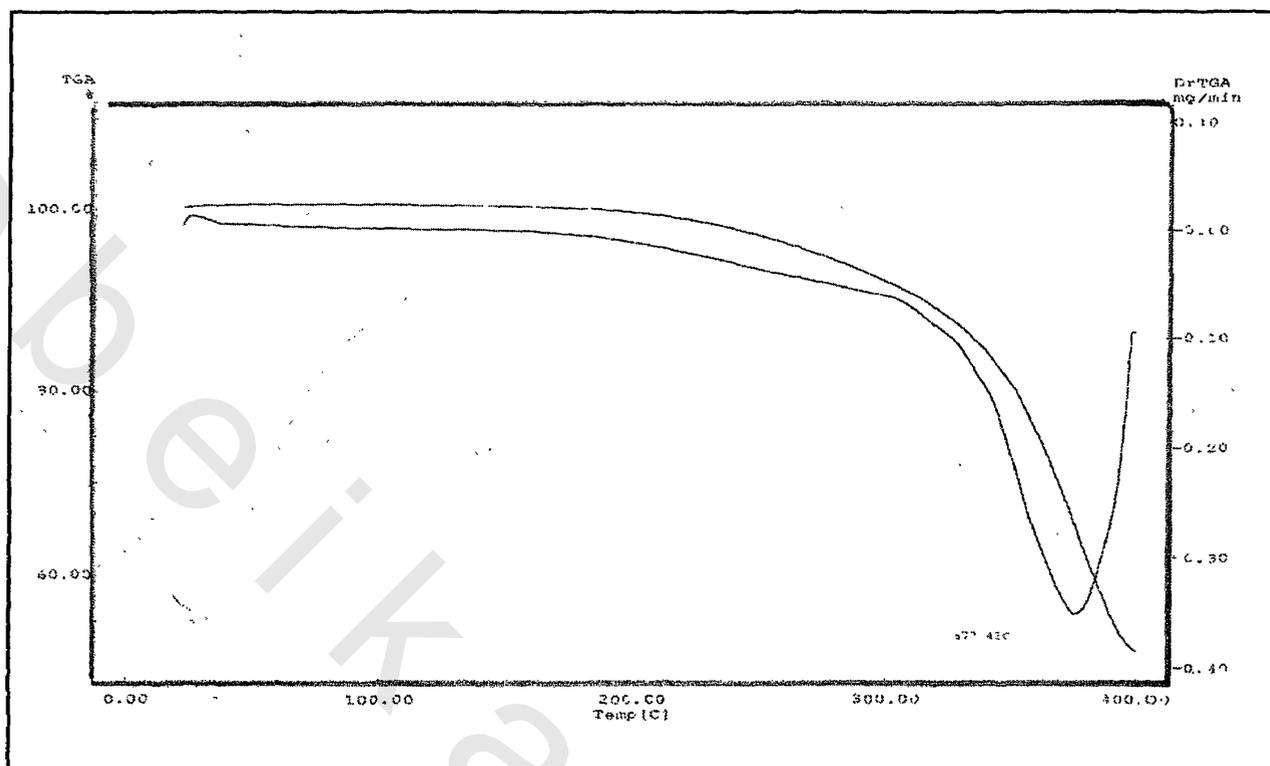Fig (45): DSC for **Vulcanized Natural Rubber Modified with (50g Blown Asphalt+ 5.8 g Sulfur/100g NR (VNRBA$_{50-3}$)).**
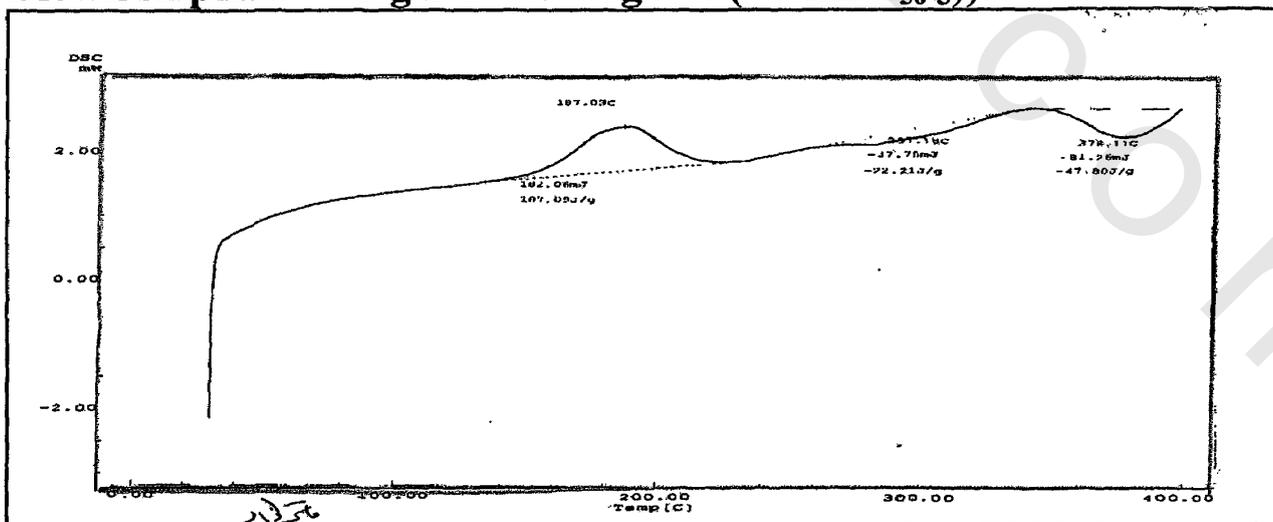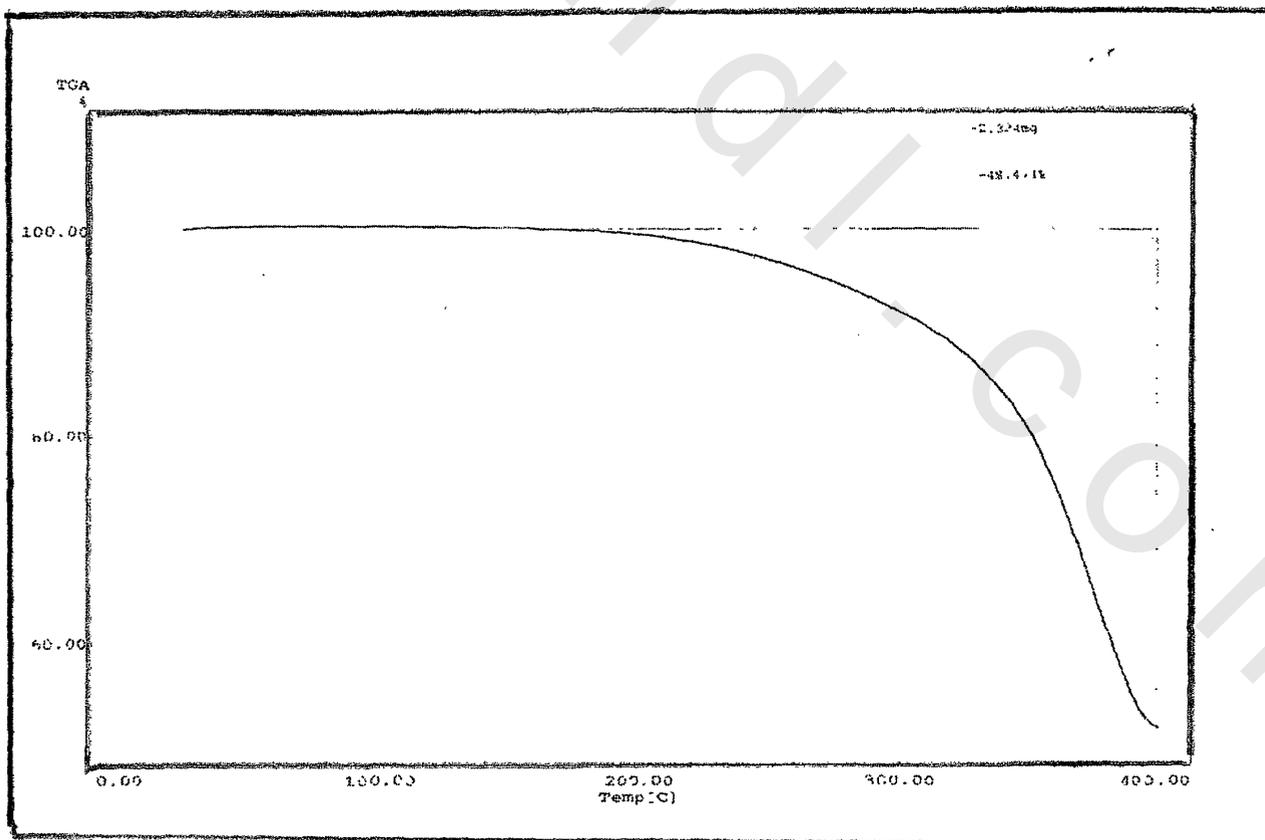

Fig (46): DSC for **Vulcanized Natural Rubber Modified with (50g Blown Asphalt+ 4.8 g Sulfur/100gNR (VNRBA$_{50-2}$)).**
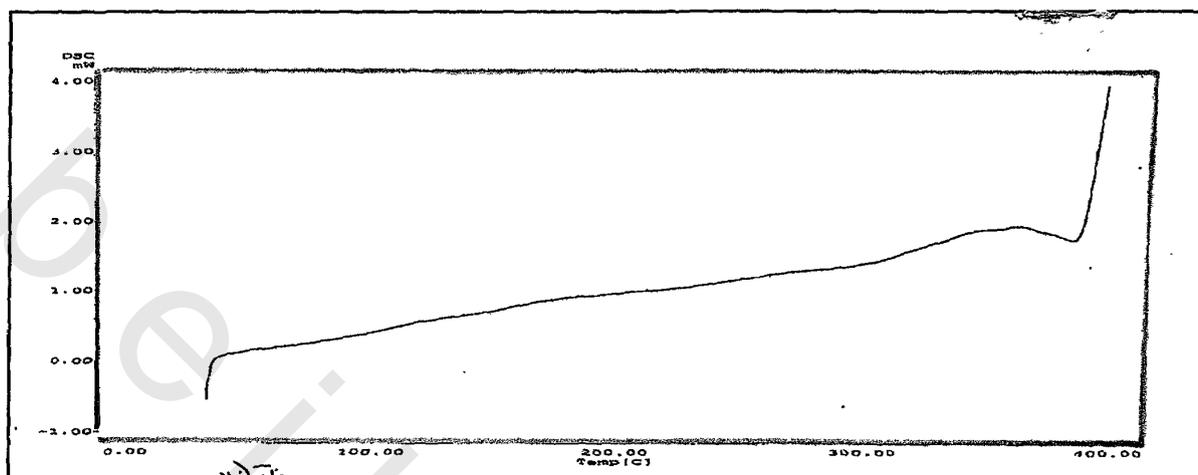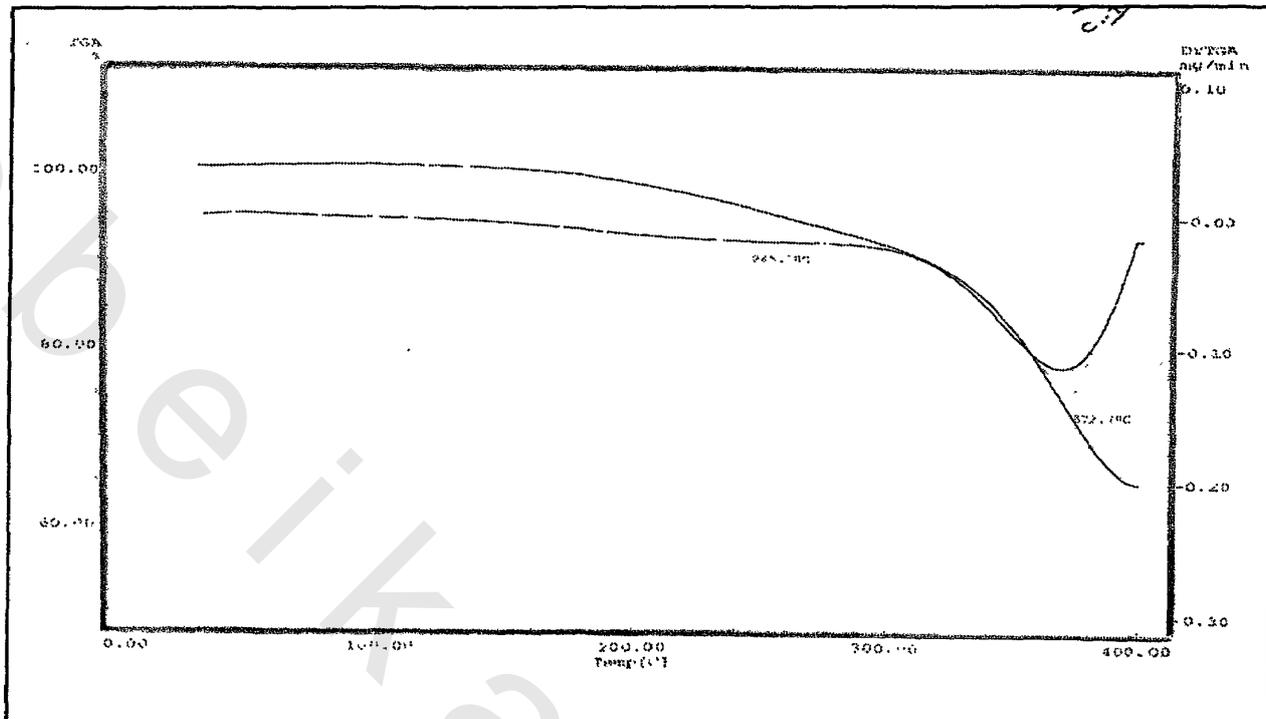
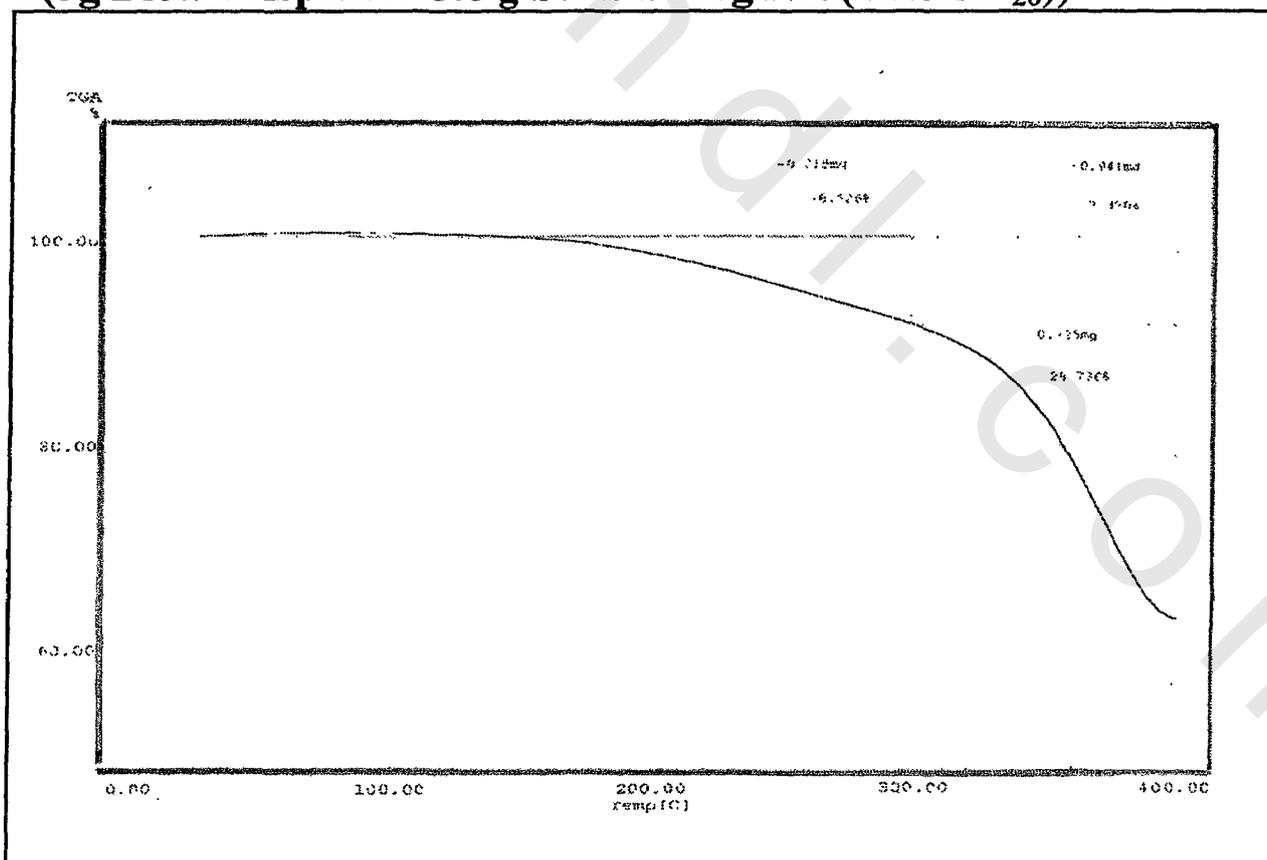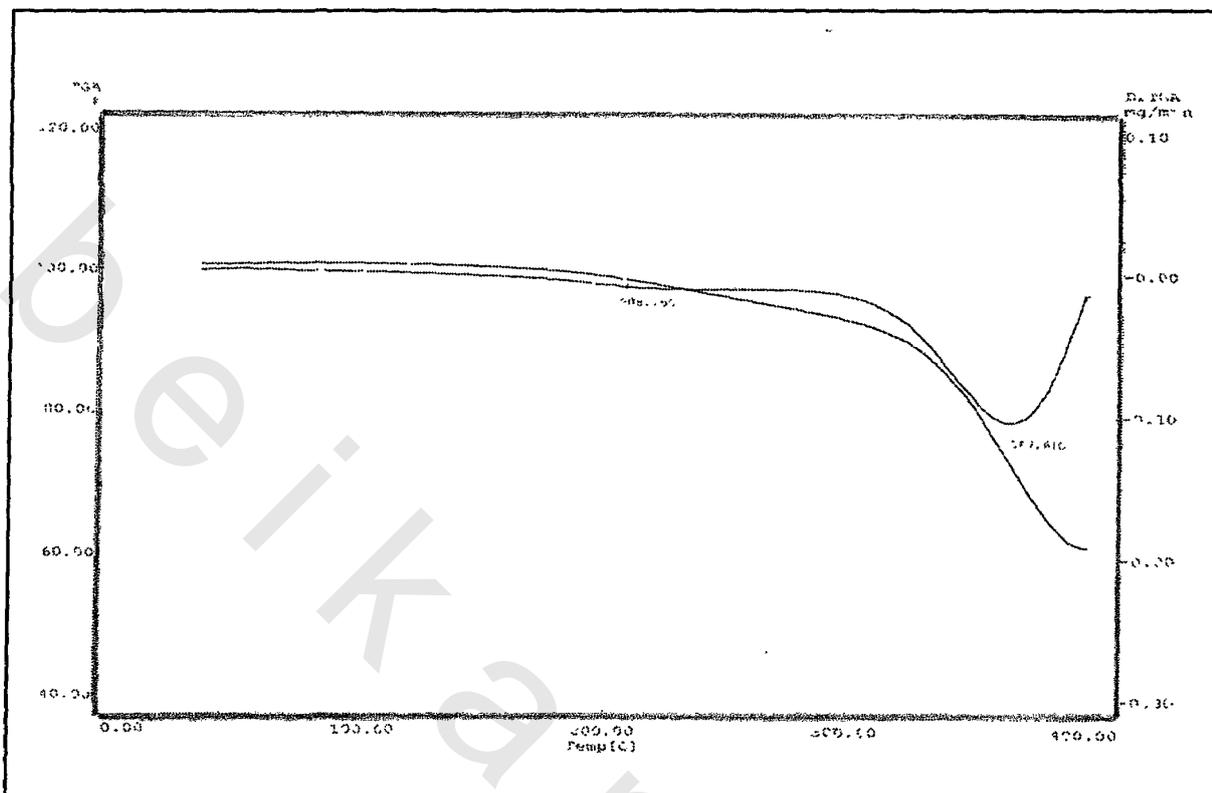Fig (47): DSC for **Vulcanized Natural Rubber Modified with (5g Blown Asphalt+ 3.8 g Sulfur/100g NR (VNRBA$_{20}$)).**
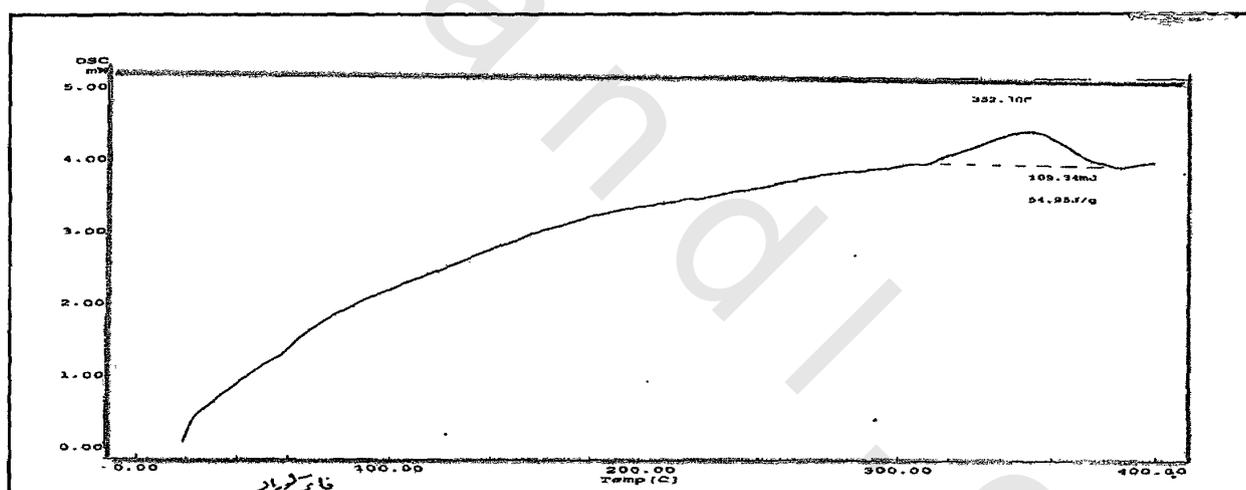
Fig (48): DSC for **Vulcanized Natural Rubber**

Results of Thermo-Gravimetric Analysis for the Prepared Samples

The data given in Table (34) and illustrated in Figs (49-53), show, that the modified rubber samples are thermally stable. The values of wt. loss % at different temperatures can be ordered as follows: 38.79% at 376.23 $^{\circ}$C for VNRBA$_{100-4}$, 48.47% at 377.41°C for VNRBA$_{50-3}$, 37.320 % at 372.79 $^{\circ}$C for VNRBA$_{50-2}$, 46.34% at 371.32 $^{\circ}$C for VNRBA$_{20}$, and 41.528% at 367.61 $^{\circ}$C for VNR.

Table (34): Thermo Gravimetric Analysis for the Prepared Samples

Samples	Temperature ^{o}C	Wt. Loss %
VNRBA$_{100-4}$	376.23	38.79
VNRBA$_{50-3}$	377.41	48.47
VNRBA$_{50-2}$	245.58 372.79	8.526 37.320
VNRBA$_{20}$	273.86 371.32	8.136 46.34
VNR	208 367.61	6.737 41.528

Fig (49a): TGA for Vulcanized Natural Rubber Modified with (100g Blown Asphalt+ 6.8 g Sulfur/100g NR (VNRBA$_{100-4}$)).

Fig (49b): TGA for Vulcanized Natural Rubber Modified with (100g Blown Asphalt+ 6.8 g Sulfur/100g NR (VNRBA$_{100-4}$)).

Fig (50a): TGA for Vulcanized Natural Rubber Modified with (50g Blown Asphalt+ 5.8 g Sulfur/100g NR (VNRBA$_{50-3}$)).
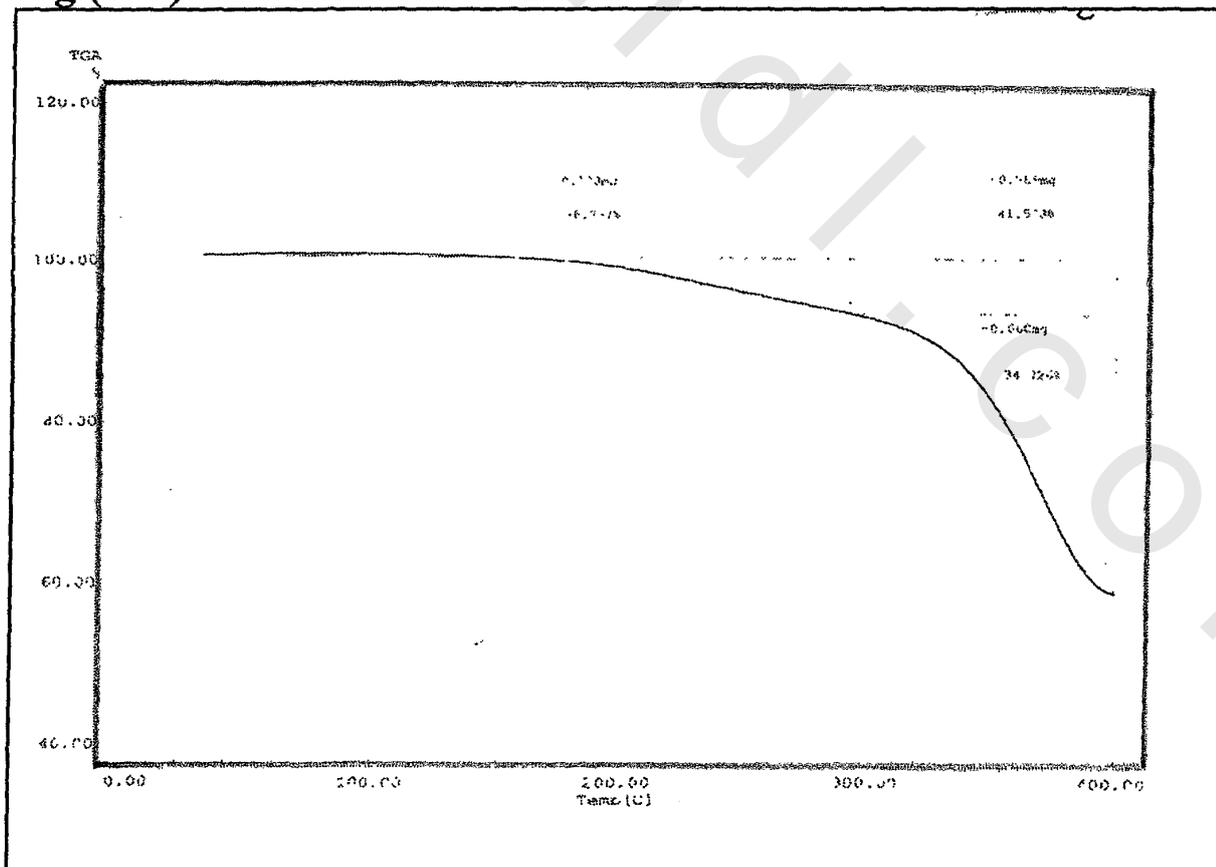

Fig (50b): TGA for Vulcanized Natural Rubber Modified with (50g Blown Asphalt+ 5.8 g Sulfur/100g NR (VNRBA$_{50-3}$)).

Fig (51a): TGA for Vulcanized Natural Rubber Modified with (50g Blown Asphalt+ 4.8 g Sulfur/100g NR (VNRBA$_{50-2}$)).

Fig (51b): TGA for Vulcanized Natural Rubber Modified with (50g Blown Asphalt+ 4.8 g Sulfur /100g NR (VNRBA$_{50-2}$)).

Fig (52a): TGA for Vulcanized Natural Rubber Modified with (5g Blown Asphalt+ 3.8 g Sulfur/100g NR (VNRBA$_{20}$)).

Fig (52b): TGA for Vulcanized Natural Rubber Modified with (5g Blown Asphalt+ 3.8 g Sulfur/100g NR (VNRBA$_{20}$)).

Fig (53a): TGA for Vulcanized Natural Rubber

Fig (53b): TGA for Vulcanized Natural Rubber

The Incorporation of Inorganic Nanoparticles into Vulcanized Elastomer Matrix.

The incorporation of inorganic nanoparticle into the modified elastomer matrix [Vulcanized Natural Rubber Modified with 50% Blown Asphalt and 5.8 g Sulfur (VNRBA$_{50-3}$)] leads to significant improvements in the mechanical properties of the elastomer [115]

Many researches have been focused on the polymer/clay nanocomposite. Actually, clay consisting of nanolayered silicate, many mineral oxides which have been widely used as fillers for rubber for many years [116, 117]

Recently the modification of rubber/ nanocomposites are greatly attractive and directs the attentions of scientists to apply the poly/ nanocomposites. Most of the developed rubber/nanocomposites exhibit much higher tensile strength than that of corresponding matrixes.

I-Carbon black in nano size (produced from Degussa AG Advanced Fillers and Pigment Germany) was used in different ratios of 5, 10, and 15 phr based on the carbon black content original which used, as shown in Table (35)

Table (35): Formulations of modified Vulcanized Natural Rubber (VNRBA$_{50-3}$).

Ingridents(phr)	VNRBA$_{50-3}$^{1}	VNRBA$_{50-3}$^{2}	VNRBA$_{50-3}$^{3}
NR	100	100	100
BA	50	50	50
S	5.8	5.8	5.8
ZnO	2.0	2.0	2.0
Stearic acid	1.0	1.0	1.0
TMTD	1.0	1.0	1.0
MBT	4.5	4.5	4.5
Original C.B	45	40	35
Nano C.B	5	10	15

In this work the nano carbon black is blended in different ratios relative to the original carbon black. The obtained vulcanized samples and their properties are investigated on the light of mechanical, thermal stability, resistance to external media, swelling values, and crosslinking values of the vulcanized samples, and Δtg.

Mechanical Properties
- Tensile Strength (Ts) kgf/mm^2, and Elongation at Break% (Eb)
Values of (T.S) and (Eb) are determined for the vulcanized samples based on different percentage (5, 10, and 15) g of nano carbon black to 45, 40, and 35) g respectively relative to original carbon black content. After post-curing for 0.25h at 155 °C. several tests were carried out using the Tension Machine Type M-10(HUNG-TA INSTRUMENT Co. LTD), to estimate the values of tensile strength (kg/mm^2) and elongation at break (%).

The data given in Table (36), and Figs (54, 55) show that the value of tensile strength for VNRBA$_{50-3}$^{3} (51.9 kgf/mm^2) the highest as compared with the tensile strength value for the other samples.

The value of elongation at break (1003.9%) for the same sample VNRBA$_{50\text{-}3}^{3}$ the highest as compared with the other samples. Such behavior is a result of increasing the crosslinking value.

Such mechanical behavior of rubber/carbon black nanocomposite seem to be strongly related to the interfacial interaction between nano-carbon black phase and soft rubber phase [116]. Moreover the values of tensile strength kgf/mm^2, and elongation at break % increased by increasing the percent of the nano carbon black. As result of increasing the surface area by decrease the diameter of particle size, the homogeneity and activity in the matrix can be achieved.

The obtained data show that the values of tensile strength kgf/mm^2 can be arranged according to the following order of vulcanized postcured rubber samples;

VNRBA$_{50\text{-}3}^{3}$; (51.9 kgf/mm^2)> VNRBA$_{50\text{-}3}^{2}$; (50.3 kgf/mm^2)> VNRBA$_{50\text{-}3}^{1}$; (49.7 kgf/mm^2)

The values of elongation at break (%), for the same samples proceed according to the following order of vulcanized postcured rubber samples; VNRBA$_{50\text{-}3}^{3}$; (1003.9%)> VNRBA$_{50\text{-}3}^{2}$; (987.8%)> VNRBA$_{50\text{-}3}^{1}$; (970.1%)

- Absorbed Energy (kgf/mm) During Deformation

Results of calculating the absorbed energy values for the above mentioned tested samples concerning tensile strength given in Table (36). show that the value of absorbed energy for the tested samples depends on the added quantity of nano carbon black. This indicates that the value of the absorbed energy increases with the effective particle size resulting from the quantity of nano carbon black.

- Young's Modulus, kgf/mm^2

Values of Young's modulus calculated for the above mentioned tested samples, show that the Young Moddules varies with the quantity of added nano carbon black.

Table (36): Mechanical Properties at Room Temperature for the Prepared Vulcanized Natural Rubber Modified with Blown Asphalt using Particle Carbon Black in Nano size.

Samples Mentioned in (Table35)	Tensile Strength (kgf/mm^2)	Elongation atBreak (%)	Absorbed Energy (kgf.mm)	Young's Modulus (kgf/mm^2)
VNRBA$_{50\text{-}3}$^{1}	49.7	970	0.531	10.6
VNRBA$_{50\text{-}3}$^{2}	50.3	987.8	0.557	10.9
VNRBA$_{50\text{-}3}$^{3}	51.9	1003.9	0.580	11.2

3^1 addition 5g Nano carbon black   3^2 addition 10g Nano carbon black   3^3 addition 15g Nano carbon black
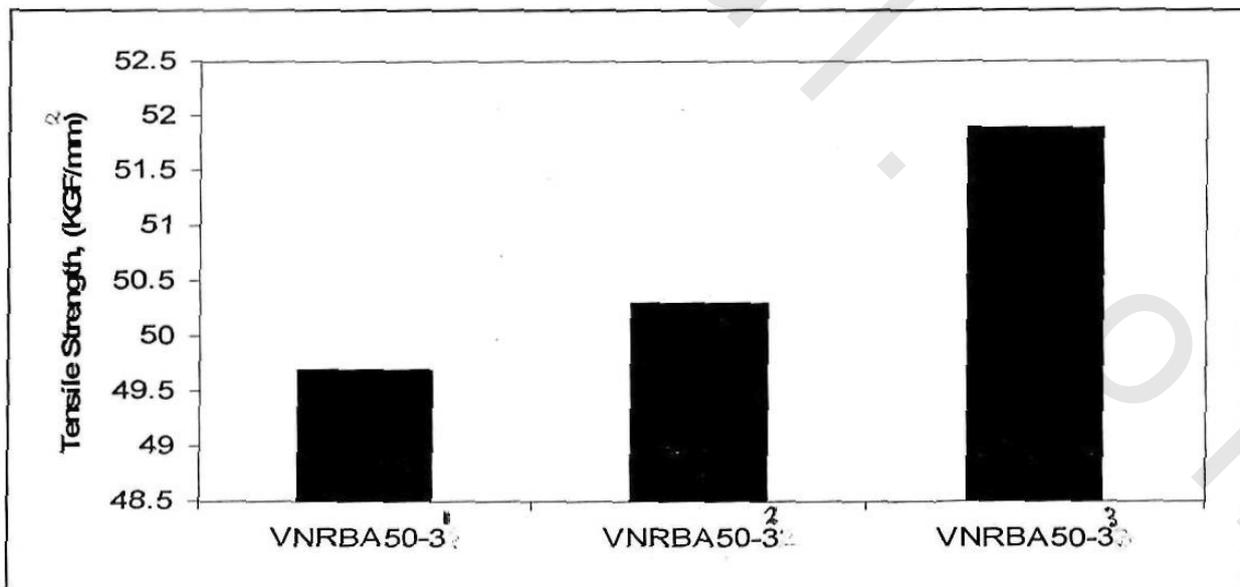
Fig (54): Tensile Strength, (Kgf/mm^2) for modified Vulcanized Natural Blown Asphalt with Nano Sized Carbon Black Particles.
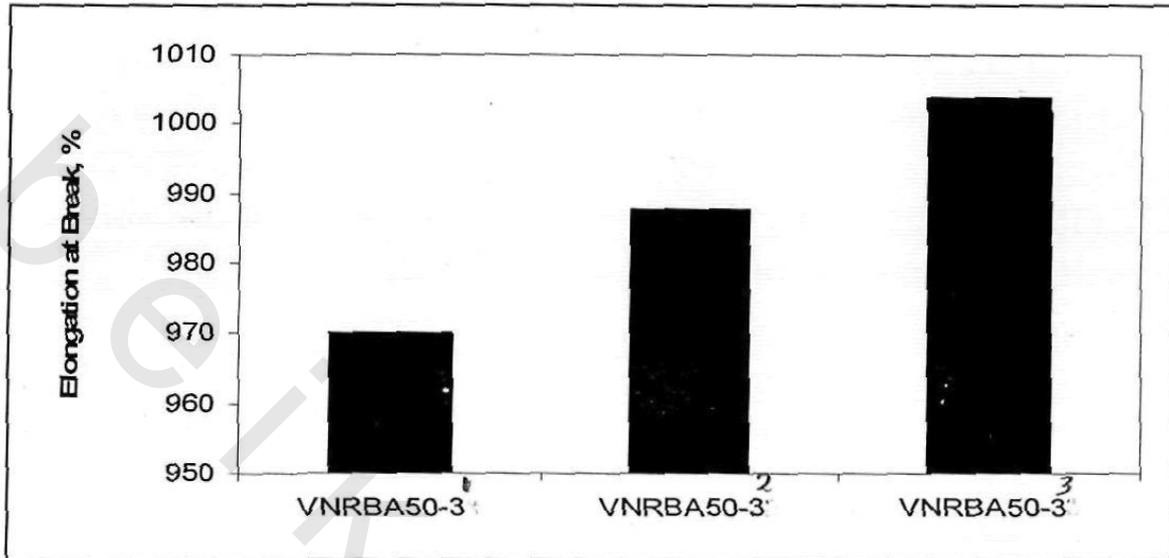
Fig (55): Elongation at Break, (%) for modified Vulcanized Natural Blown Asphalt with Nano Sized Carbon Black Particles.

Modification of vulcanized natural rubber – blown asphalt mixture with Local clay.

Locally clay has been used to modify the vulcanized natural rubber – blown asphalt mixture. Figure 56 (a) shows the scanning electron microscope for such composite. Which illustrates that the particle size is large and a squires wide distribution.

As is well known, reduction of the particle size and narrowing the distribution are very important factors for better properties of the nanocomposite. Therefore, the clay has been grinded by Ball Mill method to reduce the particle size. SEM (Fig 56 (b)) shows the sample after such grinding. By comparing both SEM (a) and (b), we can notice the big difference between both particle sizes. The reduction of particle size to the nano scale could probably lead to homogeneous distribution.

(a)   (b)
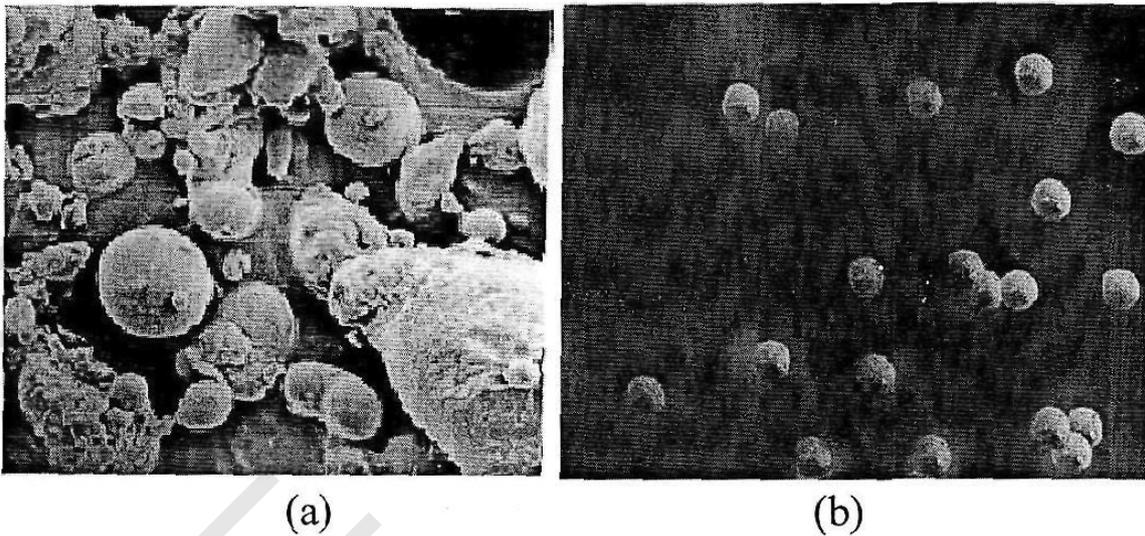
Fig (56): SEM for clay (a), (b) before and after crushing

Crushed clay nanocomposites was used after reduction of te particles size in different ratios of 5, 10, 15, and 20 phr based on natural rubber. Clay nanocomposites was also used in percentage of 15% to natural rubber + 10g nano carbon black +40g original carbon black with constant quantity of the other factors and without ZnO, as given in Table (37)

Table (37): Formulation of modified Vulcanized Natural Rubber (VNRBA$_{50-3}$) with Nanocomposites.

Ingrident (phr)	VNRBA$_{C1}$	VNRBA$_{C2}$	VNRBA$_{C3}$	VNRBA$_{C4}$	VNRBA$_{C5}$
NR	100	100	100	100	100
BA	50	50	50	50	50
S	5.8	5.8	5.8	5.8	5.8
ZnO	2.0	2.0	2.0	2.0	-
Stearic acid	1.0	1.0	1.0	1.0	1.0
TMTD	1.0	1.0	1.0	1.0	1.0
MBT	4.5	4.5	4.5	4.5	4.5
OriginalC.B	50	50	50	50	40
Nano C.B	-	-	-	-	10
NanoClay	5	10	15	20	15

In this work the clay nanocomposites were blend in different ratios with the natural rubber, to obtain the formulated vulcanized samples. The properties of the formulated vulcanized samples are then subjected to a series of studies, such as Tensile strength (T.S), elongation at break (Eb), thermal stability, Swelling, crosslinking values, and differential scaning calarometric.

Mechanical Properties
- Tensile Strength (Ts) kgf/mm^2, and Elongation at Break% (Eb)

Values of (T.S) and (Eb) were determined forthe vulcanized samples contaning on different percentages of clay (5, 10, 15, and 20)g natural rubber. Morever quantity of (15% nano clay + 10g nano carbon black +40g original carbon black) together with constant quantity of other factors and without ZnO . After post-curing time for 0.25h at 155 $^{\circ}$C, the tests were carried out using Tension Machine Type M-10(HUNG-TA INSTRUMENT Co. LTD), to estimate the values of tensile strength (kgf/mm^2) and elongation at break (%).

The data given in Table (38) , and Figs (57and 58), show that the value of tensile strength kgf/mm^2 can be arranged according to the following order:

$VNRBA_{50-3C1}$ (42.35 kg/mm^2) > $VNRBA_{50-3C2}$ (41.65 kg/mm^2) > $VNRBA_{50-3C5}$ (40.8 kg/mm^2) > $VNRBA_{50-3C3}$ (39.77 kg/mm^2) > $VNRBA_{50-3C4}$ (37.9 kg/mm^2),

The same samples can clear be arranged according to the values of elongation at break; as follows:
$VNRBA_{50-3C1}$ (850%) > $VNRBA_{50-3C2}$ (805%) > $VNRBA_{50-3C5}$ (780%) > $VNRBA_{50-3C3}$ (724%) > $VNRBA_{50-3C4}$ (640%)

The data shows that the tensile strength (kgf/mm^2) and elongation at break (%) decrease with further increased addition of clay nanocomposites. Several possible reasons are responsible for such decrease. One is the flaws existing in the nanocomposites, such as the weak boundaries between particles and the bubbles trapped during the sample preparation. Another possible reason is the inhomogeneous network density of the sample [118-120].

Another possible reason is that the poor compatibility between clay and natural rubber could lead to poor adhesion between the matrix and the reinforcing particles, thus no improvement of the tensile strength was achieved.

Such mechanical behavior of rubber/nanocomposites is strongly related to the interfacial interaction between the nanocomposites phase and the soft rubber phase [117]. On the other hand the values of tensile strength were observed as following, VNRBA$_{50-3C5}$ (40.8 kg/mm^2) > VNRBA$_{50-3C3}$ (39.77 kg/mm^2).

The elongation at break % of the VNRBA$_{50-3C5}$ `was (780%) was found greater than of the obtained VNRBA$_{50-3C3}$. The increase of value obtained could be attributed to the use of 10g of nano carbon black and 40g of original carbon black. The difference in the results is due to the increase of surface area which arises as a result of decrease of diameter of particle size. The modification of particle size lead to more homogenety and activity in the matrix.

Table (38): Mechanical Properties at Room Temperature for the Prepared Modified Vulcanized Samples.

Samples	Tensile Strength (kgf/mm^2)	Elongation At Break (%)
VNRBA$_{50-3C1}$	42.35	850
VNRBA$_{50-3C2}$	41.65	805
VNRBA$_{50-3C3}$	39.77	724
VNRBA$_{50-3C4}$	37.9	640
VNRBA$_{50-3C5}$	40.8	780

C1 addition 5% nanoclay,   C2 addition 10% nanoclay,   C3 addition15% nanoclay,
C4 addition 20% nanoclay,   C5 addition 15%nanoclay + 10g Nano carbon black without ZnO
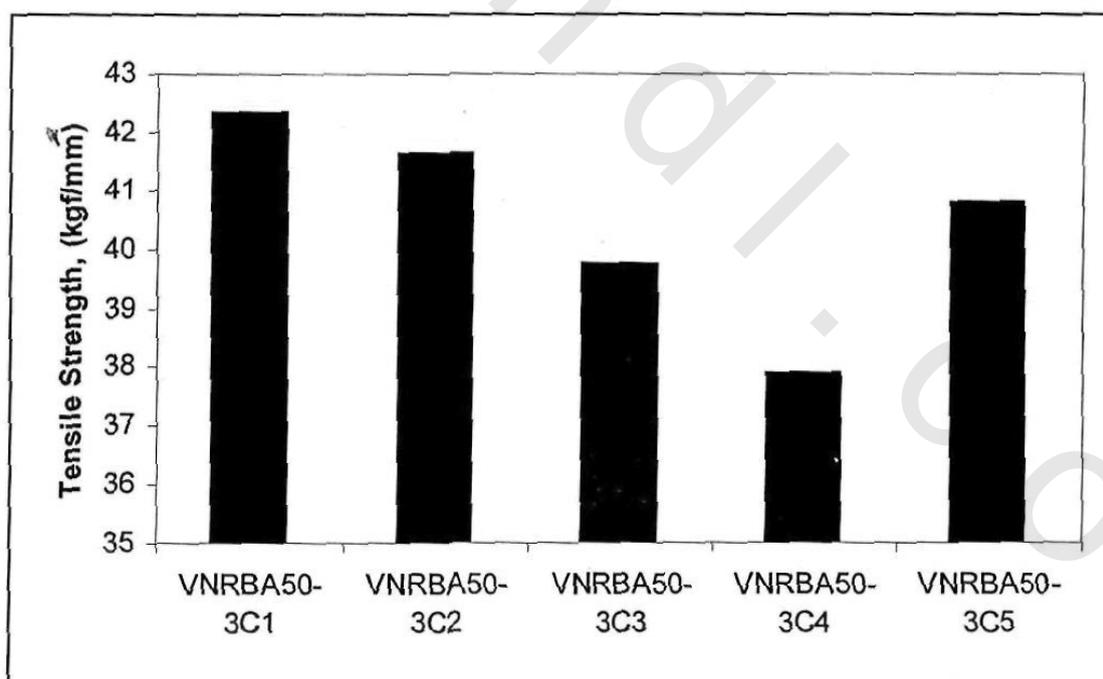
Fig (57): Tensile Strength, (Kgf/mm^2) for modified Vulcanized Natural Blown Asphalt with Nanocomposites
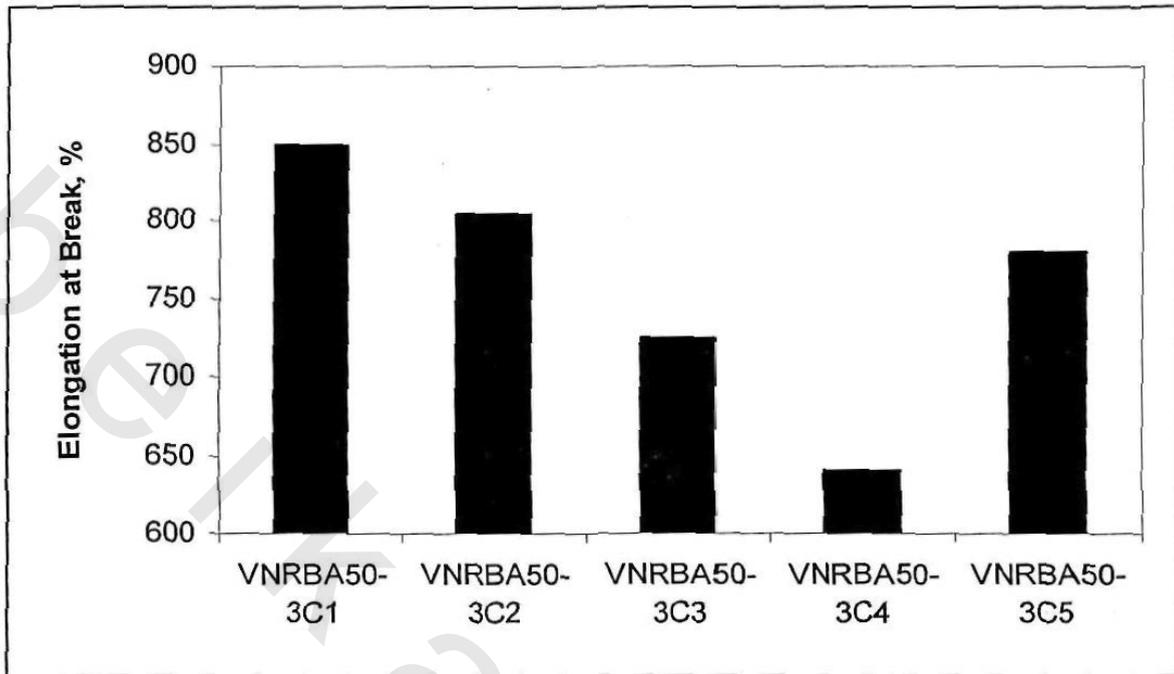
Fig (58): Elongation at Break, % for modified Vulcanized Natural Blown Asphalt with Nanocomposites.

-Thermal Stability

The studied samples were consisted of vulcanized rubber modified blown asphalt using carbon black in nano size in different percentage, three sample ($VNRBA_{50-3}{}^{1}$, $VNRBA_{50-3}{}^{2}$, $VNRBA_{50-3}{}^{3}$). The clay nanocomposites were used also in different ratios 5, 10, 15, and 20 phr based on the natural rubber. The clay nanocomposites was used as 15% in a large mixture of natural rubber + 10g nano carbon black +40g original carbon black with constant of another factors and without ZnO. Five samples ($VNRBA_{50-3C1}$, $VNRBA_{50-3C2}$, $VNRBA_{50-3C5}$, $VNRBA_{50-3C3}$, $VNRBA_{50-3C4}$)

The eight samples were placed in the furnace at 200 °C, and then withdrawn from the furnace after fixed time intervals; get cold at room temperature, weighed. The weight loss for the samples was recorded and shown in Table (39), and Fig (59).

The value of wt. loss decreased with increasing the percentage of nanocomposites. The eight samples gave thermal stability values ordered as :

$VNRBA_{50-3C5} > VNRBA_{50-3C4} > VNRBA_{50-3}^3 > VNRBA_{50-3C3} > VNRBA_{50-3}^2 > VNRBA_{50-3}^1 > VNRBA_{50-3C2} > VNRBA_{50-3C1}$.

It can be noticed that, from that the arrangement the addition of nano carbon black by 15phr is better than addition of 15% nanoclay, the addition of 10, and 5 phr of nano carbon black is gave better samples than the addition of 10, and 5 % of Nano clay, this phenomena may be due to the surface area of the carbon black is important and defines how much surface is available for interaction with other materials in the rubber components, generally, the small particle size of carbon black has a higher surface area.

Table (39): Thermal Stability (wt. loss, %) for Vulcanized of Different Formulations Modified with Nanocomposites, Heatead at 200 °C .

| Samples No.	Weight loss, % after curing time, hrs.						
	5	10	20	40	80	150	200
$VNRBA_{50-3}^1$	0.831	0.871	0.905	0.973	1.026	1.254	1.861
$VNRBA_{50-3}^2$	0.825	0.863	0.890	0.968	1.013	1.246	1.850
$VNRBA_{50-3}^3$	0.816	0.852	0.882	0.951	0.973	1.109	1.695
$VNRBA_{50-3C1}$	0.842	0.875	0.909	0.981	1.032	1.263	1.875
$VNRBA_{50-3C2}$	0.834	0.873	0.907	0.976	1.029	1.249	1.869
$VNRBA_{50-3C3}$	0.819	0.857	0.883	0.954	1.004	1.231	1.841
$VNRBA_{50-3C4}$	0.802	0.843	0.876	0.931	0.962	1.074	1.463
$VNRBA_{50-3C5}$	0.796	0.839	0.863	0.897	0.924	0.942	1.146
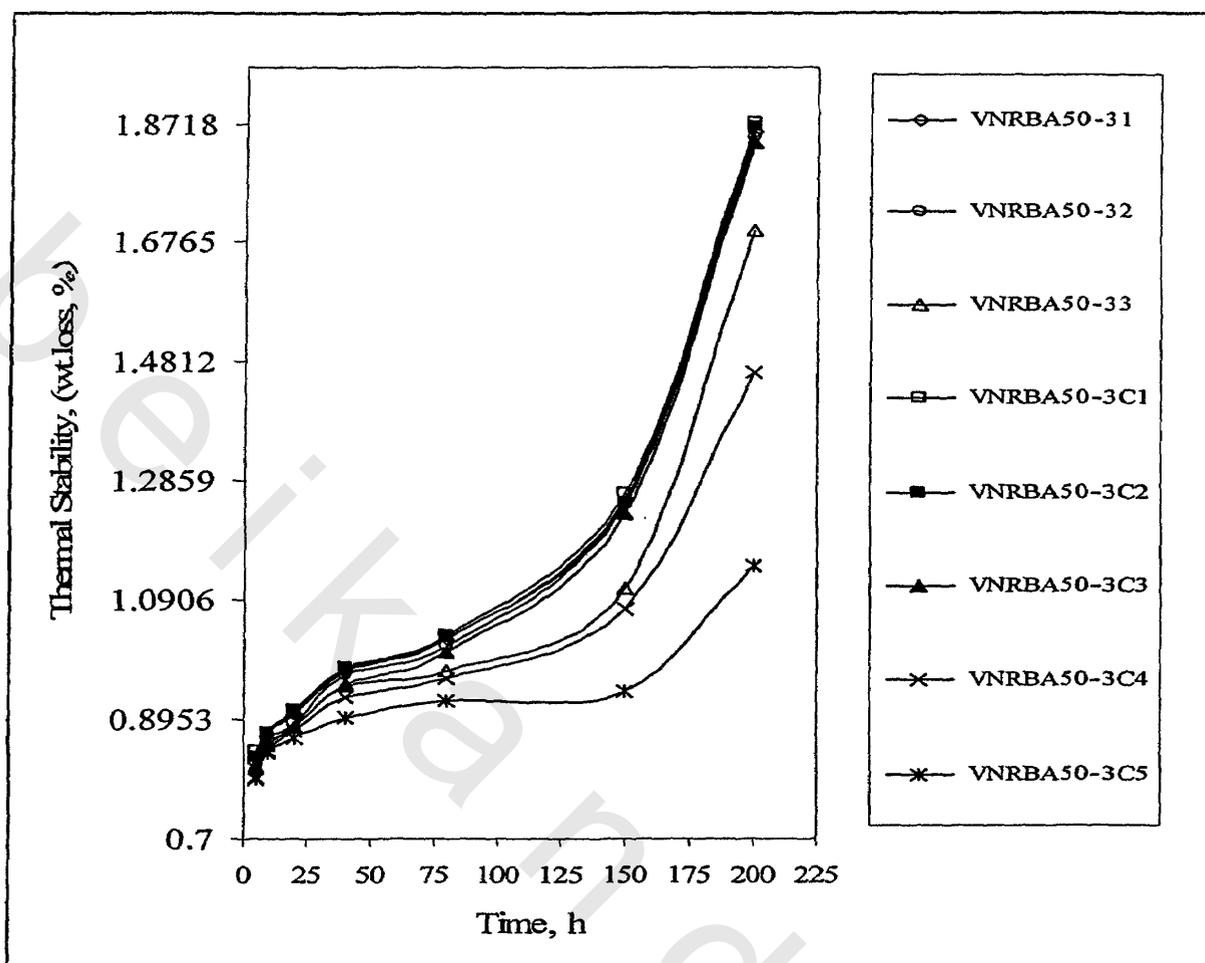
Fig (59): Thermal Stability (wt. Loss, %) for Vulcanized Different Formulation Samples modified with Nanocomposites Heated at 200°C.

The obtained results of heating show that the recorded values (wt. loss %) generally increases with increasing time of heating for all tested samples which based on themodified $VNRBA_{50-3}$. This finding may be due to increase the crosslinking value.

© **Swelling and Crosslinking Values**

The time dependence of swelling degree, % (Q%) of the eight nano-composit samples ($VNRBA_{50-3}^{1}$, $VNRBA_{50-3}^{2}$, $VNRBA_{50-3}^{3}$), ($VNRBA_{50-3C1}$,$VNRBA_{50-3C2}$, $VNRBA_{50-3C5}$, $VNRBA_{50-3C3}$, $VNRBA_{50-3C4}$) in benzene and kerosene is shown in Table (40) and illuterateed in Figs (60-63). The data were picked after 0.258h at 155°C).

The swelling values (Q%) and crosslinking values (1/Q) change with changing the volume of added (nano composites) g to the rubber in the process.

This means that the values of swelling (Q%) decreases with increasing the volume of added (nanocomposites) g to rubber in the process, and this is inversely proportional with the corresponding values of crosslinking (1/Q). This means that the values of crosslinking increases with increasing the added volume of (nano composites) as shown in Table (40), and Figs (60-63).

The swelling values, % (Q%) and crosslinking values (1/Q) depend on the time of sample immersion in thesolvents.

Generally the values of swelling increase with increasing the immersion time for the tested samples. The values of crosslinking 1/Q decreases with increasing the time of immersion. This means that increasing the immersion time gives more chances to the solvent to penetrate into the chain and the particle of the sample. This pentration probably destroys the physical bonds between the particles and chains in the sample. This character being the same in the case of kerosene.

The swelling values (Q), and crosslinking values (1/Q) are affected by the type of solvent. Generally all thestudied samples in benzene achieved high swelling values Q (%) and lower crosslinking values (1/Q) as compared with the corresponding samples studied in kerosene.

Table (40): Swelling Values (Q), and Crosslinking Values (1/Q) in Benzene, and Kerosene, at Room Temperature for Vulcanized Rubber Modified with Blown Asphalt, and Nanocomposies Samples After Post-Curing.

Sample	Time	Benzene		Kerosene	
		Q	1/Q	Q	1/Q
VNRBA$_{50-3}$[1]	0.5	0.284	3.521	0.269	3.717
	1.0	0.457	2.188	0.446	2.242
	6	0.878	1.139	0.869	1.150
	12	0.952	1.050	0.941	1.063
	24	0.993	1.007	0.981	1.019
VNRBA$_{50-3}$[2]	0.5	0.279	3.584	0.268	3.731
	1.0	0.448	2.232	0.436	2.293
	6	0.869	1.150	0.858	1.165
	12	0.948	1.054	0.937	1.067
	24	0.987	1.013	0.986	1.014
VNRBA$_{50-3}$[3]	0.5	0.271	3.690	0.259	3.861
	1.0	0.443	2.257	0.432	2.314
	6	0.858	1.165	0.846	1.182
	12	0.939	1.064	0.927	1.078
	24	0.976	1.034	0.964	1.037
VNRBA$_{50-3C1}$	0.5	0.268	3.731	0.256	3.906
	1.0	0.436	2.293	0.423	2.364
	6	0.850	1.176	0.841	1.189
	12	0.927	1.078	0.916	1.091
	24	0.971	1.029	0.963	1.038
VNRBA$_{50-3C2}$	0.5	0.261	3.831	0.254	3.937
	1.0	0.431	2.320	0.423	2.364
	6	0.848	1.179	0.839	1.191
	12	0.921	1.085	0.910	1.098
	24	0.964	1.037	0.953	1.049
VNRBA$_{50-3C3}$	0.5	0.254	3.937	0.242	4.132
	1.0	0.427	2.342	0.415	2.409
	6	0.842	1.187	0.831	1.203
	12	0.917	1.091	0.905	1.104
	24	0.959	1.042	0.948	1.054
VNRBA$_{50-3C4}$	0.5	0.249	4.010	0.237	4.219
	1.0	0.421	2.375	0.413	2.421
	6	0.837	1.195	0.826	1.210
	12	0.908	1.101	0.897	1.114
	24	0.951	1.052	0.938	1.060
VNRBA$_{50-3C5}$	0.5	0.246	4.065	0.235	4.255
	1.0	0.418	2.392	0.407	2.457
	6	0.832	1.202	0.821	1.218
	12	0.891	1.122	0.879	1.137
	24	0.940	1.064	0.928	1.077
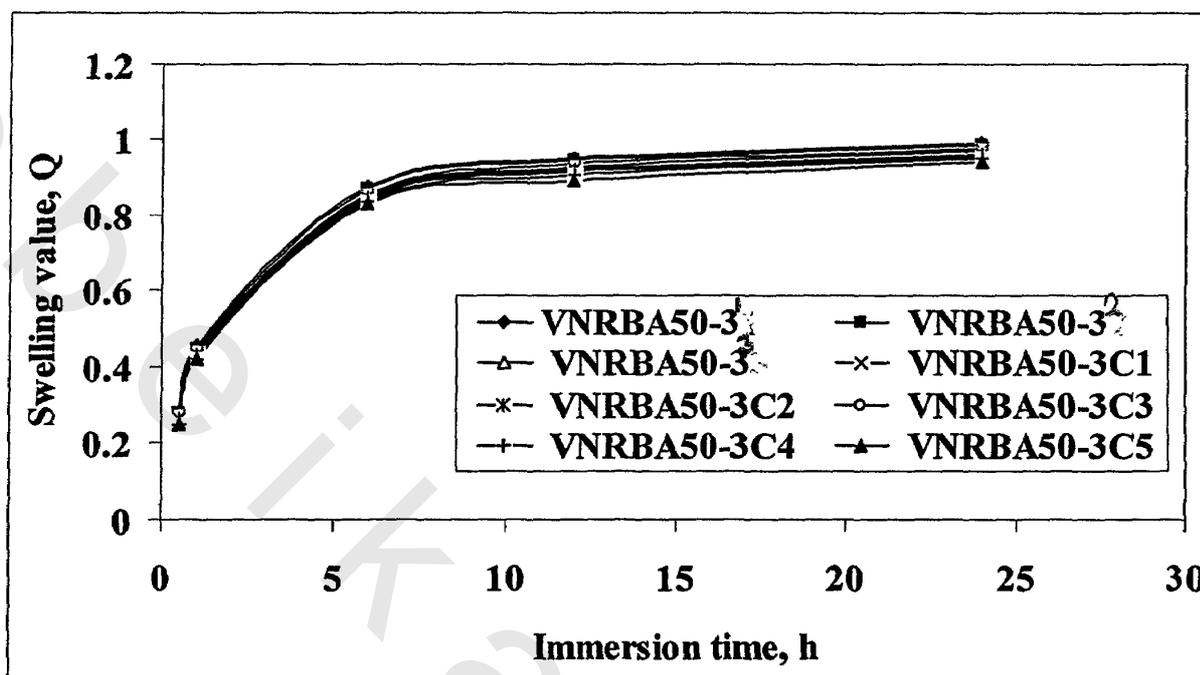
Fig (60): Swelling Value (Q%) in Benzene at Room Temperature for Vulcanized Modified Sample with Nanocomposites.
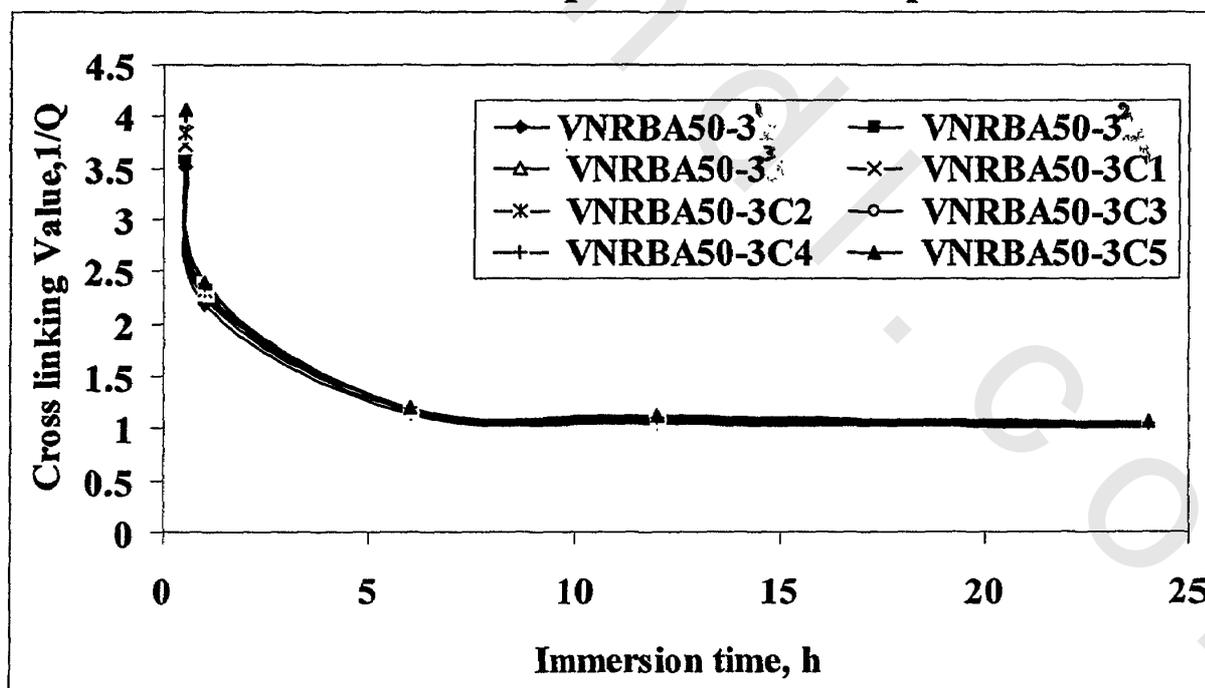

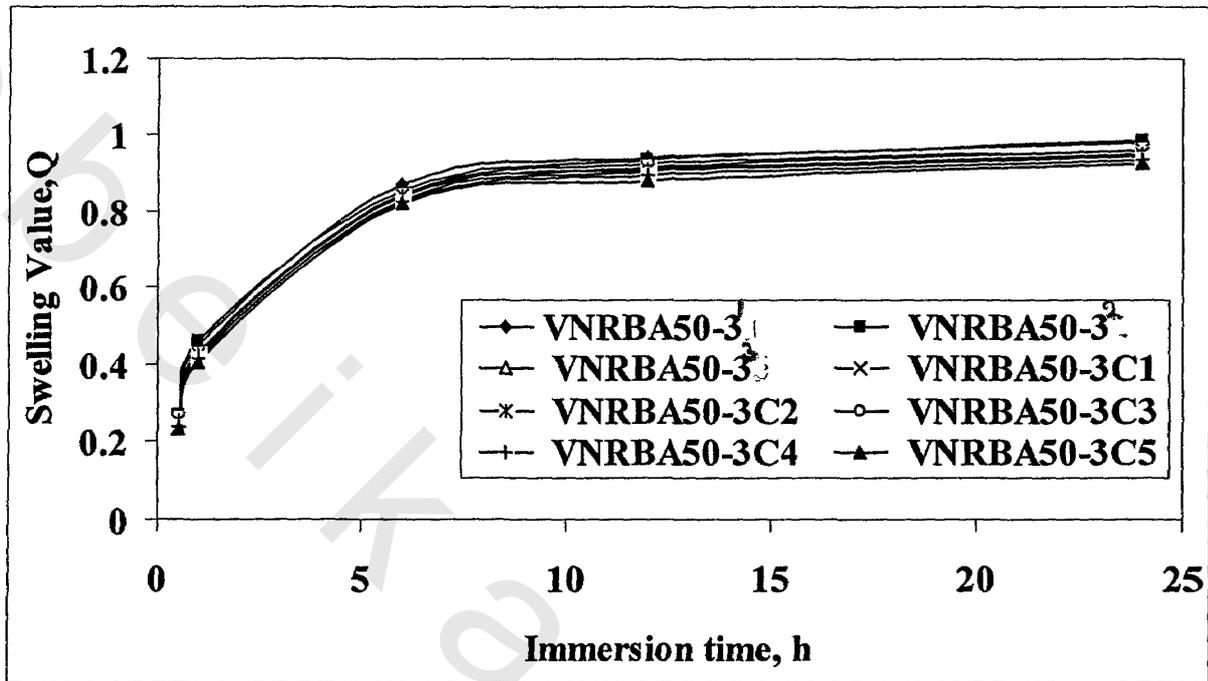**Fig (61): Crosslinking Value (1/Q%) in Benzene at Room Temperature for Vulcanized Modified Sample with Nanocomposites.**

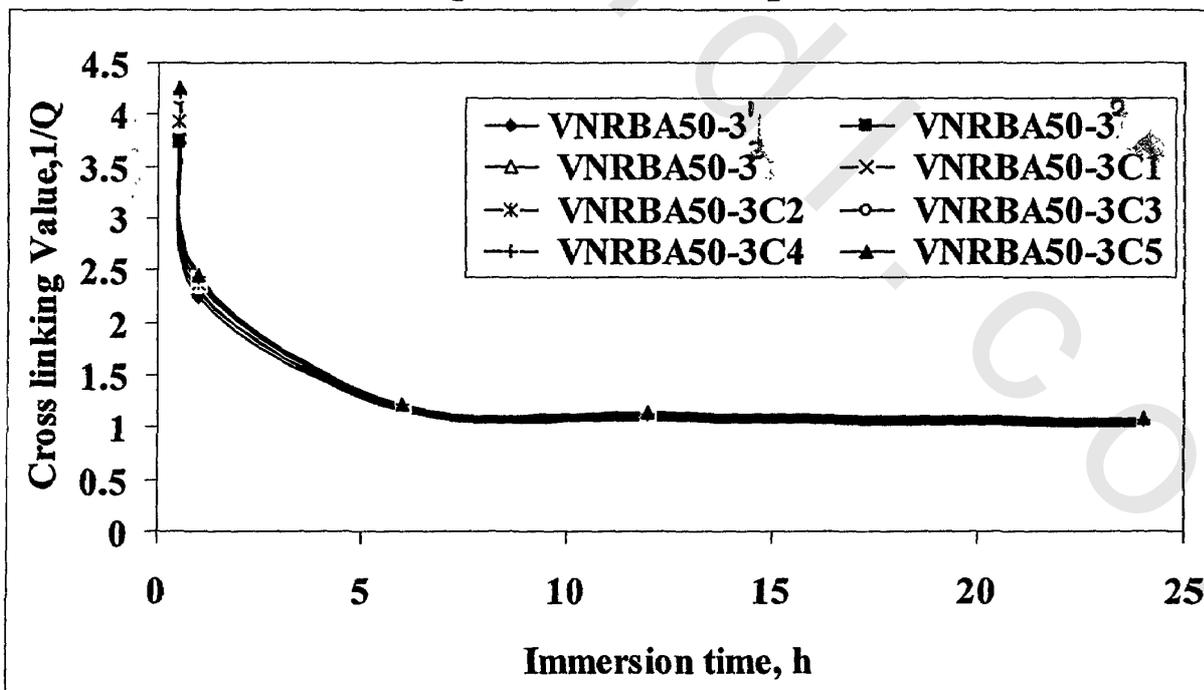**Fig (62): Swelling Value (Q%) in Kerosene at Room Temperature for Vulcanized Modified Sample with Nanocomposites.**

Fig (63): Crosslinking Value (1/Q%) in Kerosene at Room Temperature for Vulcanized Modified Sample with Nanocomposites.

- Differential Scanning Calorimetric Analysis (DSC) for Cured Sample.

DSC analysis of vulcanized rubber modified blown asphalt using nano carbon black (VNRBA$_{50-3}{}^{1}$, VNRBA$_{50-3}{}^{2}$, VNRBA$_{50-3}{}^{3}$), and clay nanocomposites used in different ratios 5, 10, 15, and 20 phr based on natural rubber, and clay nanocomposites 15% to natural rubber + 10g nano carbon black +40g original carbon black used with constant of another factors and without ZnO, (VNRBA$_{50-3C1}$,VNRBA$_{50-3C2}$, VNRBA$_{50-3C5}$, VNRBA$_{50-3C3}$, VNRBA$_{50-3C4}$). The obtained data were compared with vulcanized natural rubber (VNR), and Vulcanized natural rubber modified with blown asphalt (VNRBA$_{50-3}$).

After post-curing (for 0.25 h, at 155 °C), Δtg were listed in Table (41), and illustrated in Figs (64-73)

Table (41): Δtg for Modified Vulcanized Sample with Nanocomposites, VNR, and VNRBA$_{50-3}$

Samples No.	Δtg °C
VNRBA$_{50-3}{}^{1}$	0.71
VNRBA$_{50-3}{}^{2}$	0.68
VNRBA$_{50-3}{}^{3}$	0.5
VNRBA$_{50-3C1}$	1.24
VNRBA$_{50-3C2}$	0.99
VNRBA$_{50-3C3}$	-0.68
VNRBA$_{50-3C4}$	0.51
VNRBA$_{50-3C5}$	0.13
VNRBA$_{50-3}$	1.37
VNR	1.42
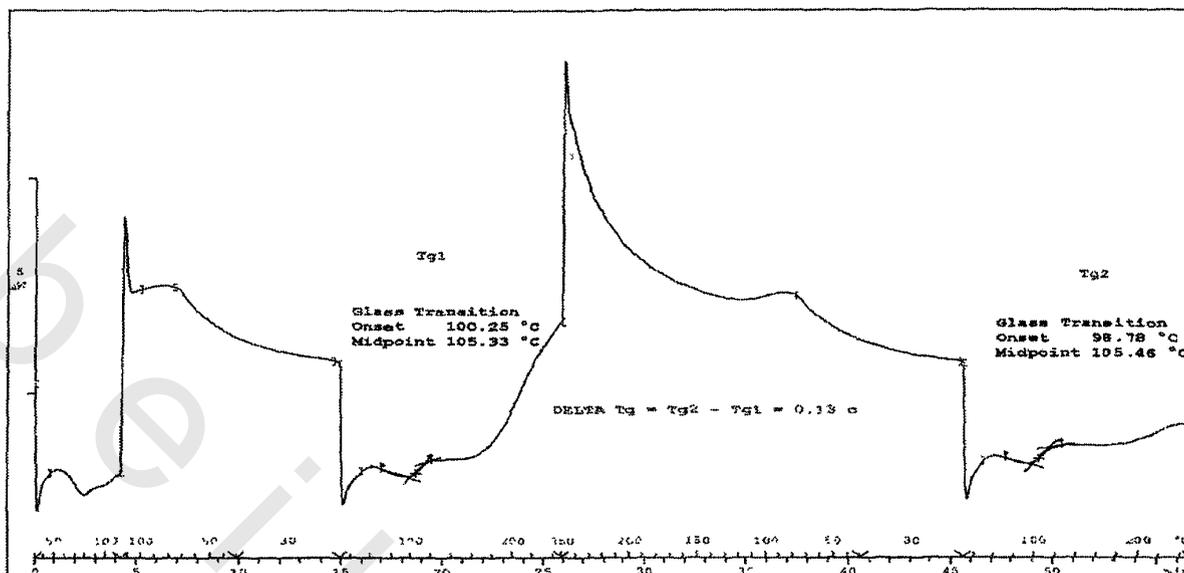
Fig (64): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 15%Nano Clay +10% Nano Carbon Black (VNRBA$_{50\text{-}3C5}$).
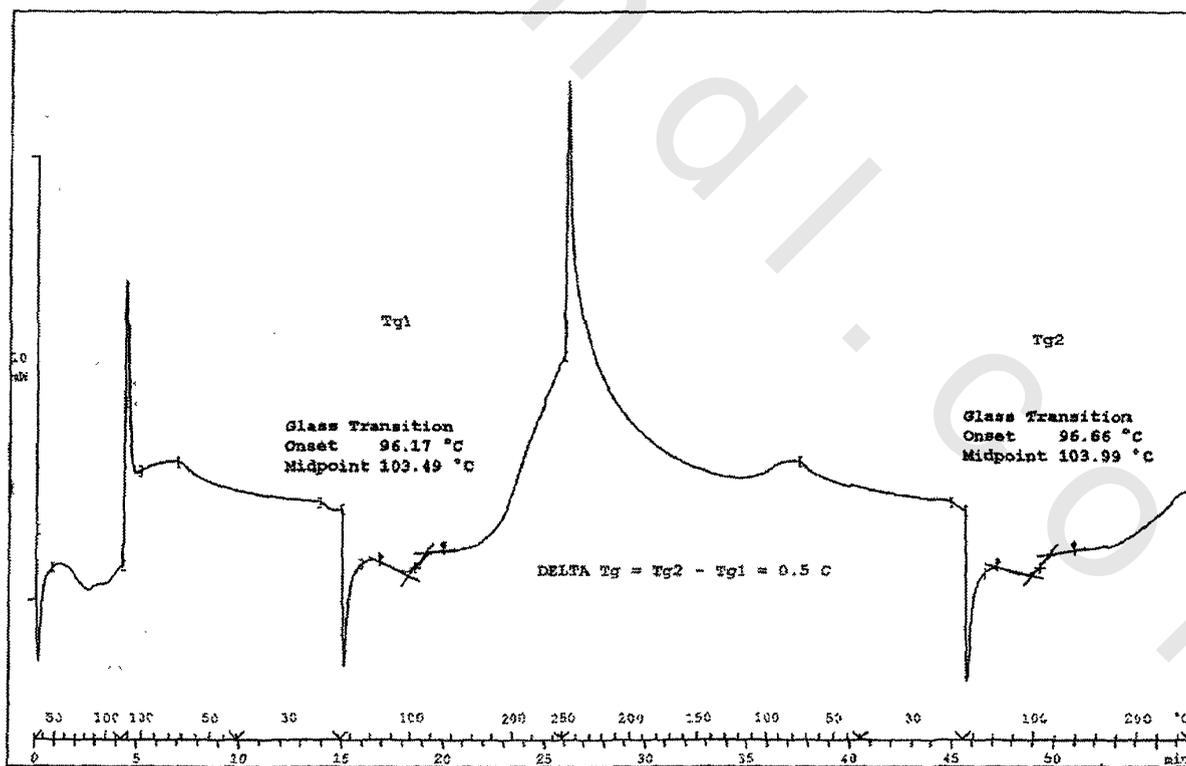
Fig (65): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 15% Nano Carbon Black (VNRBA$_{50\text{-}3}^{3}$)).
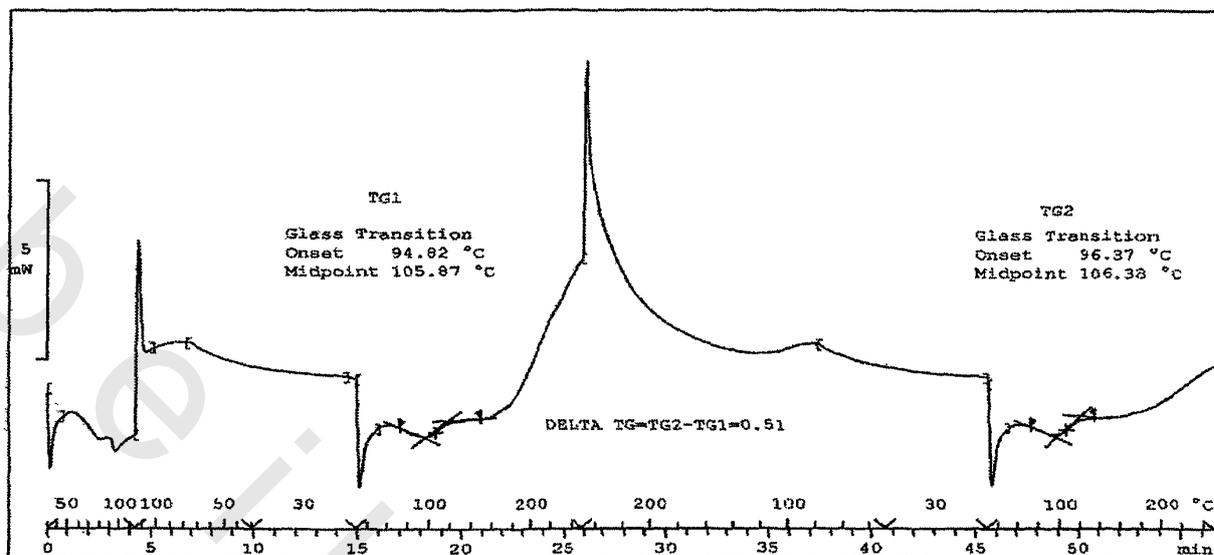
Fig (66): Δtg Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 20%Nano Clay (VNRBA$_{50-3C4}$)).
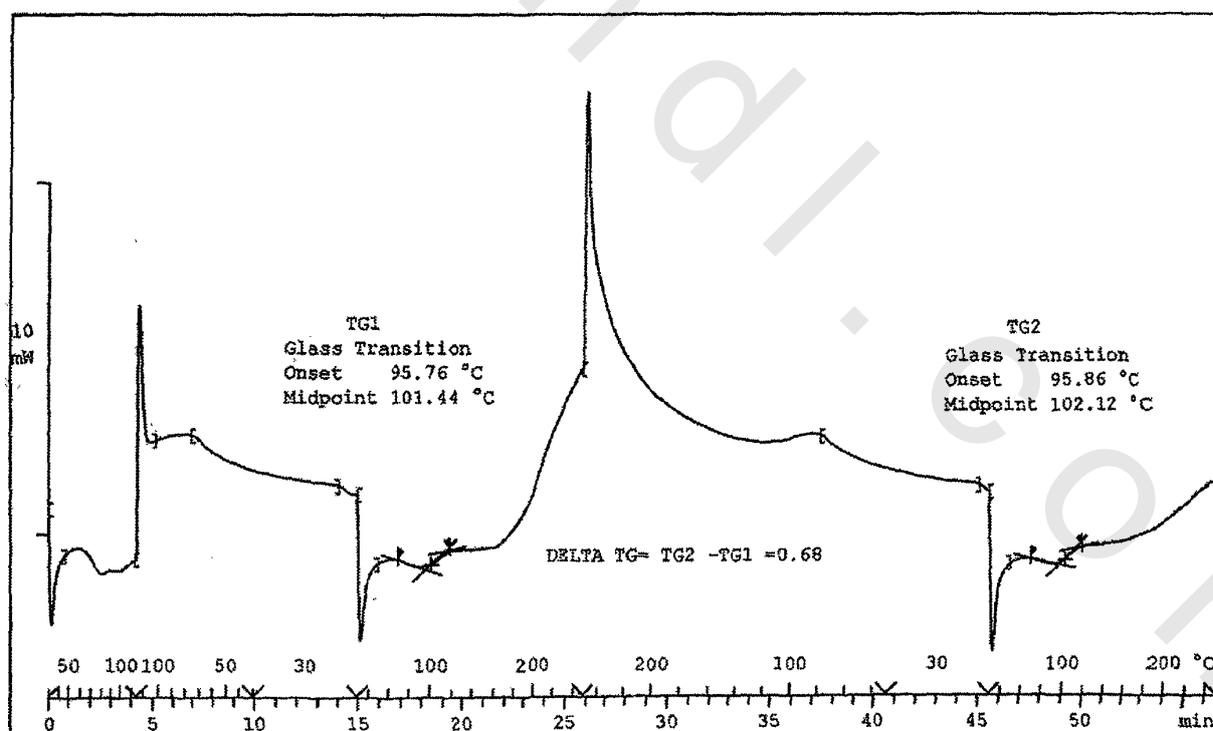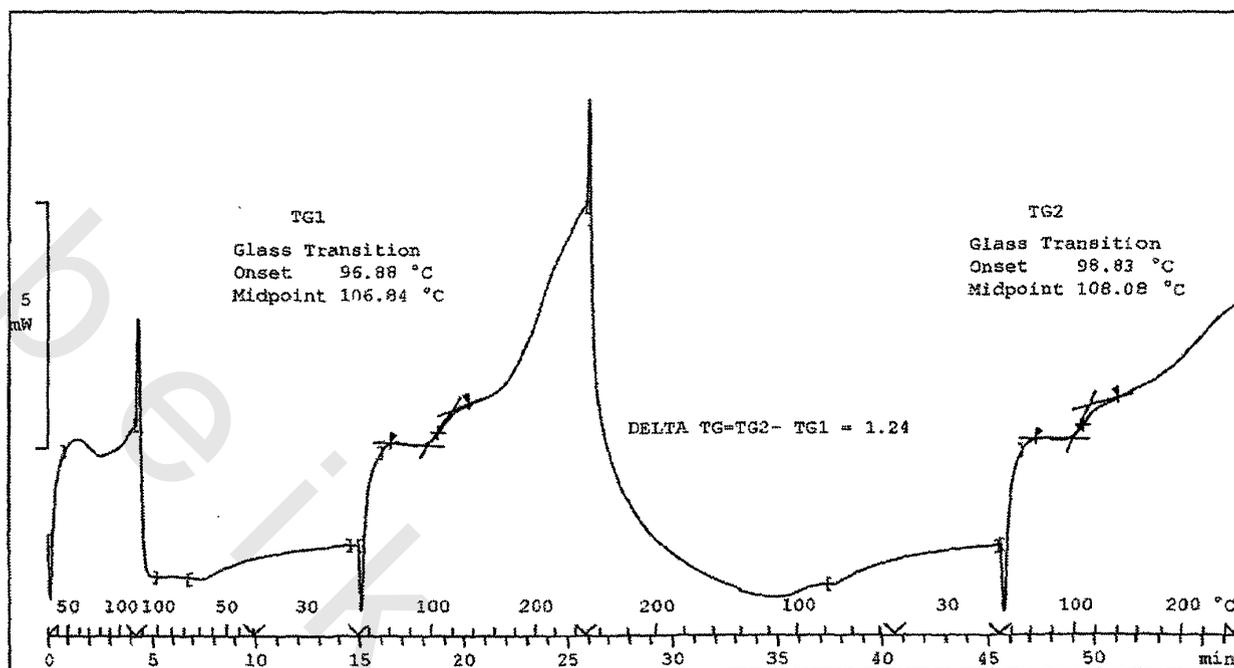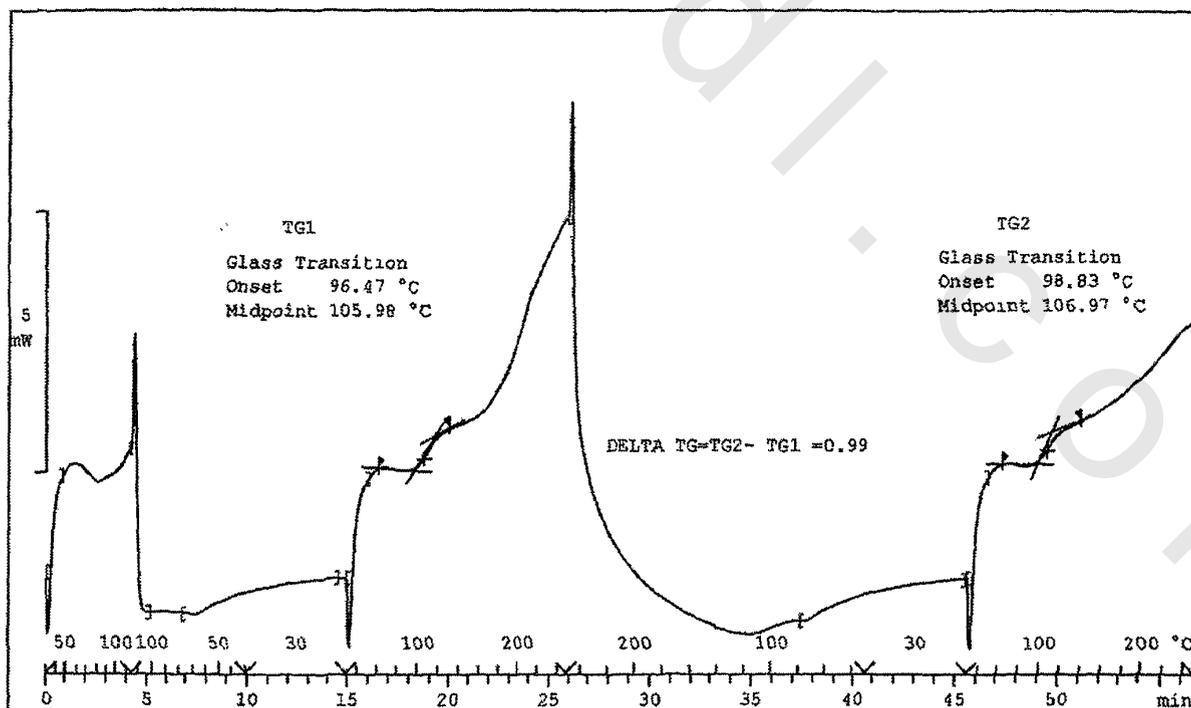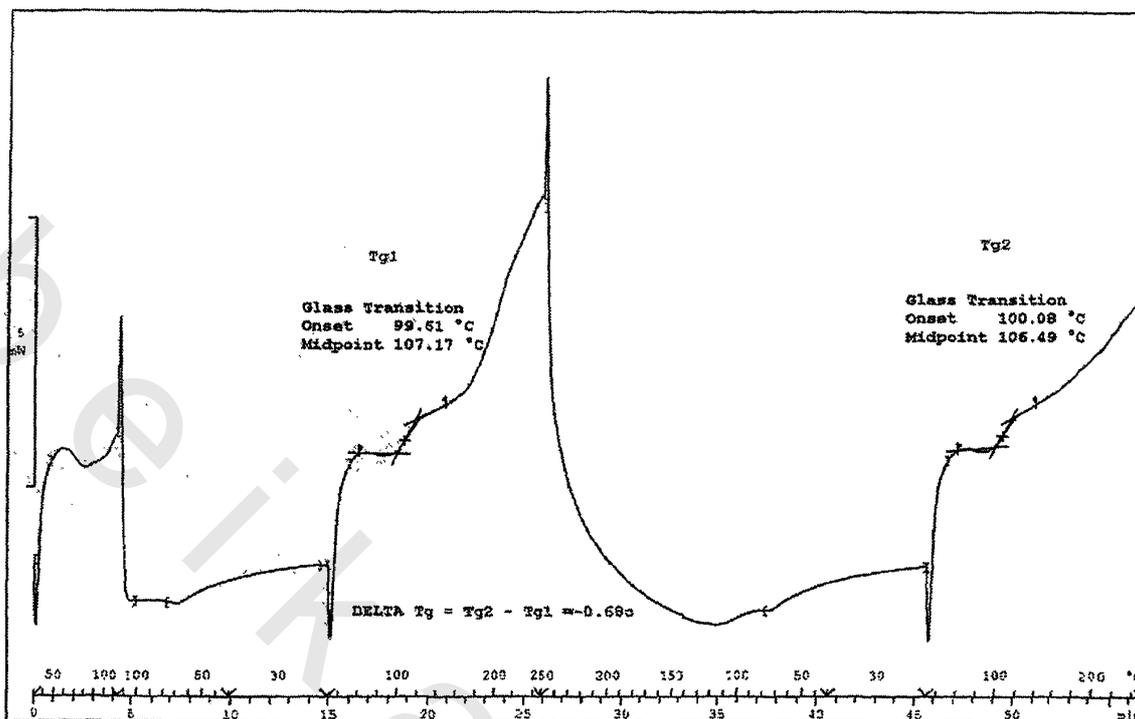

Fig (67): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 10%Nano Carbon Black (VNRBA$_{50-3}{}^{2}$).

Fig (68): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 5% Nano Clay (VNRBA$_{50-3C1}$).

Fig (69): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 5% Nano Clay (VNRBA$_{50-3C2}$)

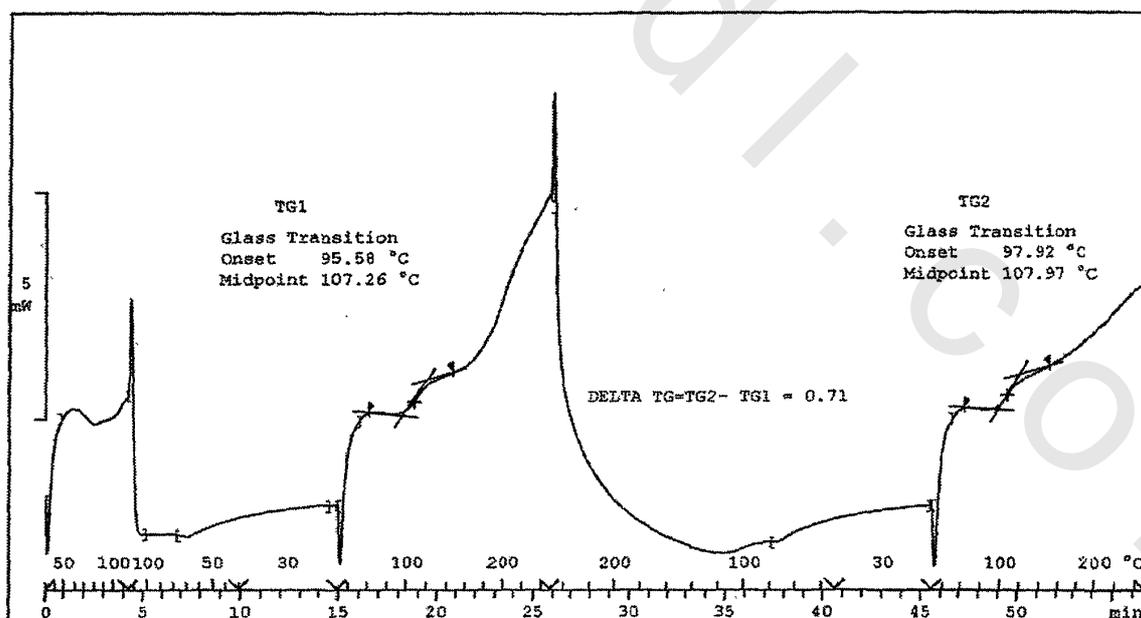**Fig (70): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+ 15% Nano Clay (VNRBA$_{50\text{-}3C3}$)**

Fig (71): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur+5%Nano Carbon Black (VNRBA$_{50\text{-}3}{}^{1}$).
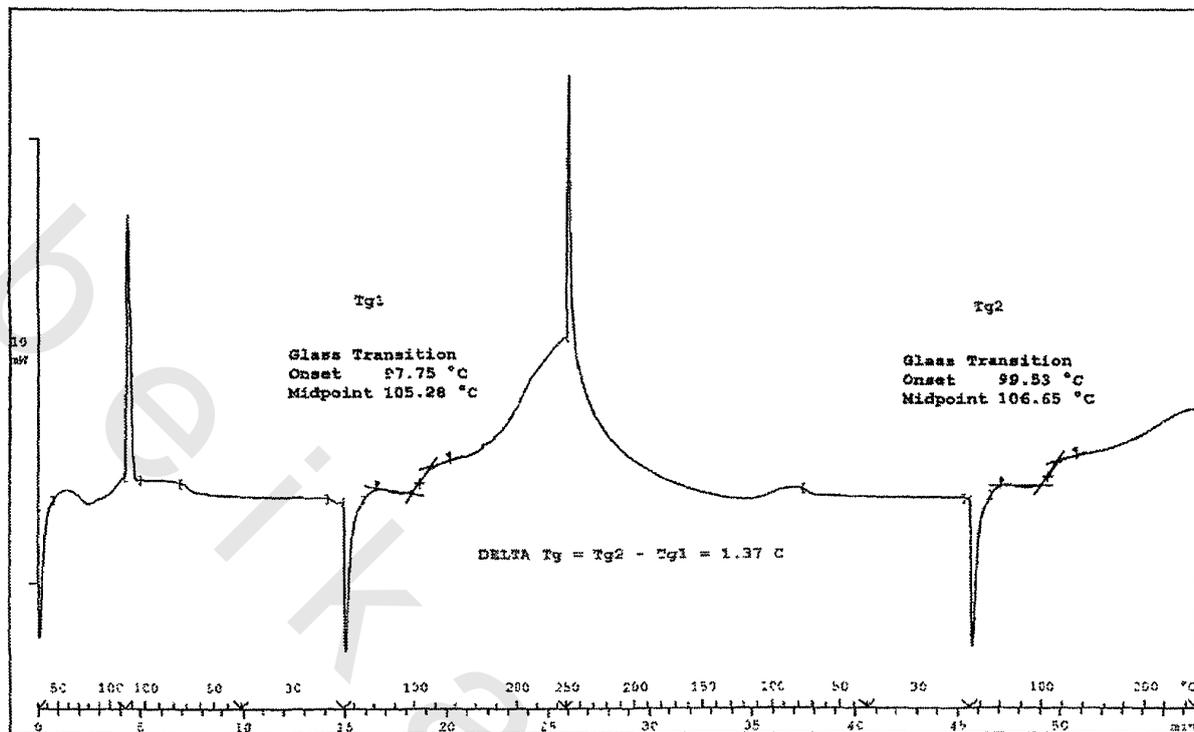
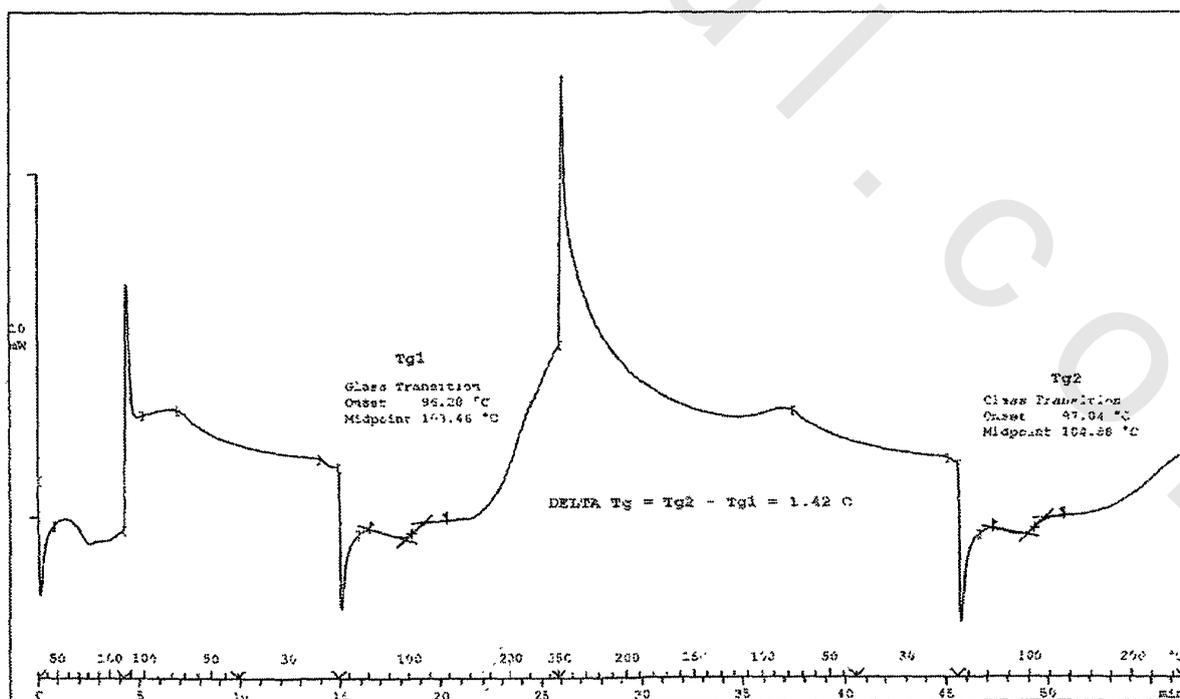**Fig (72): Δtg for Vulcanized Natural Rubber modified with 50g Blown Asphalt + 5.8g Sulfur (VNRBA$_{50-3}$).**

Fig (73): Δtg for Vulcanized Natural Rubber (VNR).