AIM OF THE WORK

AIM OF THE WORK

The aim of the present work was directed toward the synthesis of modified asphalt to be used in different applications.

Samples for pavement could be prepared by blending asphalt with epoxy resin to obtain paving mixtures with improved properties. The preparation of epoxy resin resembles considerable importance in being attached to renewable raw materials which exploit the synthetic capabilities of nature. Natural rubber is one of the most important biosynthesized polymers displays excellent chemical and physical properties, so that it finds widely application in various areas.

Bituminous-epoxy-aggregate mixtures were also well aimed for the preparation of paving samples, and subjected to physical mechanical tests. Their properties are compared with those of conventional paving mixtures.

Thus epoxy resin synthesized from natural rubber (ENR) was could be reacted with toluene-diisocyanate to obtain polyurethane, to be used as insulator synthesized from asphalt polyurethane foam using castor oil+ isocyanate and modified with polyurethane based on (ENR).

The introduction of asphalt in rubber industries as vulcanized mixture of natural rubber and blown asphalt using sulfur system by macromolecules could result in improving the mechanical properties by adding nano carbon black, and nano clay.

Dispersion of nano-size particles in rubberized asphalt is expected to yield materials with improved properties in several areas.

SUMMARY

SUMMARY

Improving of asphalt performance through some chemical reactions, and the effect of adding nano particles

The present work is concerned with the synthesis, characterization and physical properties of novel materials with specific desirable properties to be used in many applications, as pavement, insulation, and rubber industries (joints).

The raw materials are; natural rubber, styrene butadiene rubber, peracetic acid, Dolomite aggregates, limestone as filler, sand, local asphalt penetration grade 60/70which is modified with epoxy resin based on (epoxidized natural rubber, and epoxidized styrene butadiene rubber) is cured by curing agent (maliec anhydride) and evaluated, for application as paving materials.

Also asphalt penetration grade 60/70 is modified with castor oil + isocyanate to produce asphalt foam modified with polyurethane based on epoxidized natural rubber; the modified product can be used in insulation.

Finally blown asphalt is incorporated in rubbery materials together with macromolecules, and nano-molecules like nano carbon black, and nano clay for being used in rubber industries.
- The present thesis includes three main chapters;

1-The first chapter is concerned with the **introduction,** which deals with the subject of asphalt definition , asphalt types, chemistry of asphalt, asphalt composition, modification of asphalt, compatibility of the mixture's component, polymers, classification of polymers, rubbers, epoxy resin, manufacture of

epoxy resins, Epoxidation of Olefins, Epoxidation Processes, Epoxidation with Preformed Peracid Process, Properties of Epoxidized Rubber, Vulcanization, Casting, polyurethane, properties of urethane, polyurethane in asphalt, application, pavment asphalt, type of asphalt pavement, pavement maintenance and rehabilitation, properties and specifications for aggregates and asphalts, aggregates for asphalt mixtures, Marshall Test for hot mixtures, nanomaterial and nanotechnology, Why are we so fascinated with downsizing materials to a nano-scale?. Method of preparation.

II- The second chapter deals with the **experimental** part where the used chemicals, their specifications, used apparatus for chemical reaction, methods of epoxidation, polyurethanation, and the evaluation of the obtained products are explained. The specifications of selected locally produced asphalt samples in (ARE) are mentioned together with the necessity of improving qualities, are also mentioned.

The physical, chemical, and mechanical properties of asphalt penetration grades (60/70) using the above mentioned prepared epoxy pre-polymer, and polyurethane pre-polymer based on (epoxidized natural rubber) are evaluated.

Test specimens obtained from asphalt modified sample are evaluated for being used for paving and the values of optimum asphalt content for the determination of stability and flow are determined according to Marshall Test.

The study of vulcanization condition of natural rubber mixed with blown asphalt using macro, and nano filler, and evaluation of vulcanized sample by stress-strain measurements, elongation

at break, Δtg, determination of the degree of swelling, were carried out using both kerosene and benzene as solvents. The chemical resistance, in different media like distilled water, freshly prepared acid (H_2SO_4 3%), acetone, benzene, and kerosene is also estimated

Asphalt polyurethane foams from castor oil and isocyanate, to which is added polyurethane based on epoxidized natural rubber for modification are also prepared. Tests were also carried out on the prepared formulations such as sound proofing test, vibration damping test, thermal stability, differential scanning calorimetric (TGA, and DSC),

III- The third chapter is concerned with the **results and discussions** consists of three main parts.

In the first part the results of preliminary experiments illustrate the suitable epoxidation conditions for natural rubber, and styrene butadiene rubber using preformed peracetic acid (aqueous solution 59%),

The presence of OH and epoxy groups are confirmed by I.R. and (tg) glass transition temperature. This mixture was further used in the synthesis of epoxy, and polyurethane based on ENR. The obtained results are detemined using 59% peracetic acid concentration (38 g) added to 10g (NR, and SBR), followed by stirring for 4hrs, at 30 °C. The values of epoxy group content, for (epoxidized natural rubber =29%, and for epoxidized styrene butadiene rubber=26%). The hydroxyl value of epoxidized natural rubber = 26, hydroxyl value of epoxidized styrene butadiene rubber=19, iodine value of epoxidized natural rubber = 57, iodine value of epoxidized styrene butadiene rubber=80. The low values

in case of styrene-butadiene rubber can be attributed to the difficulty that the catalytically species has to reach the olefinic bond due to the presence of a phenyl ring.

The determined different parameters suitable for blending asphalt cement with epoxy resins, used for paving are, curing temperature of 150–170°C and curing time 20hrs. The suitable quantity of curing agent is 40% of the weight of epoxy resin.

Asphalt-aggregate mixtures for paving are obtained by mixing the unmodified asphalt with aggregate. The aggregates were at first evaluated through gradation by sieve analysis to determine the percent of each grade which should be included according the necessary specifications. Such aggregates were 50% dolmite as coarse aggregate + 45% sand as fine aggregate + 5% limestone powder as filler. The Marshall test was evaluated to estimate the effect of epoxy resin on the suitability of the prepared samples for road pavement. Thus the samples studied on the Marshall test are; sample based on asphalt 60/70 penetration grade (produced by Suez Co.) only; the sample contains of asphalt paving mixture modified with epoxidized natural rubber 5% (ENR + 40%MA) (second sample), (3rd sample)10% (ENR + 40%MA), (4th sample) 15 %(ENR + 40%MA) added to asphalt paving mixtures. The (fifth sample) it that which was used in hall no. 3 in international Egyptian air port, and the (sixth sample) contains of 15% (ESBR+ 40 %MA) to asphalt paving.

The suitability of mixtures subjected to Marshall Test were determined, using percentages of asphalt, and asphalt modified =5.5% relative to the asphalt paving mixtures. It was noticed that 15 %(ENR+40%MA) is the best ratio for achieving the highest stability (16632), and decreased air voids to 2.5% and value of

flow=2.9mm, the mineral voids=14.6%, Marshall quatant =3735n/mm, VFA=83.0%, and density =2.374g/cm^3.

Such above mentioned values are found to be satisfactory for the limitation of the surface layer, and satisfactory for the limits of international Egyptian air port project technical specifications.

Adding the same percentage of 15% (ESBR+40%MA) at the same conditions is found to increase the stability to 17222N, and air voids to 3.4%, 4.8mm flow. The properties of mixture composed of aggregate and asphalt 60/70 penetration grade (produced by Suez Co.), improved with 15% ESBR have been therefore proved to be the best.

The second part is concerned with the preparation and evaluation of Asphalt-polyurethane foam for different applications

Asphalt polyurethane foams were synthesized from the prepared polyurethane product based on dimethyl diphenyl diisocyanate (MDI) and castor oil, According to the OH group content of C.O (polyol) the amounts of C.O added were accurately calculated according to the desired NCO/OH ratio in asphalt emulsion. These products were modified with polyacrylic acid, water base, commercial [Addibond 65], and polyurethane based on epoxidized linseed oil at different NCO/OH ratios.

It is found that the ratio of NCO/OH = 1.2 (in case of asphalt foam) is the most suitable ratio for obtaining the sample which was chosen for economical point of view, and can be easily stirred especially in presence of additives to form different formulations.

The asphalt –polyurethane foam sample with 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 added during the preparation of asphalt polyurethane foams.

The ratio of NCO/OH=4 (in case of modified asphalt foam) is the most suitable ratio for obtaining the sample which can be easily stirred, and acquires the suitable curing properties with the asphalt polyurethane foam.

i- Results of sound Proofing Test carried out:

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; for foam sample modified with 3% polyacrylic acid (IL=59.0) > for foam samples modified with 3% { 1% addibond 65 + 2% polyacrylic acid (have IL= 56.5)}> for foam sample modified with 20%polyurethane (based on ENR + MDI) at NCO/OH =4 (have IL=50)

The vibration damping performance is generally represented by the velocity level (VL).

In case of unmodified foam sample, the value of loss factor proceeds according to 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 proceed in the following order of the used modifier for the foam samples having NCO/OH=1.2; such sequence is; 3%polyacrylic acid (29)> foam sample modified with 20% polyurethane at NCO/OH = 4 (22).

The decrease in the vibration of the specimens is a probably due to the increased viscoelastic behavior in the modified samples.

Water Absorption

Result of test method of the water absorption carried out for all prepared samples, show that, water absorption (water absorption rate wt. %) in case of samples having NCO/OH ratios = 1.2 are similar to this obtained for modified samples, as compared with the unmodified

Thermal Stability

Results of thermal stability of the prepared foams at 200 °C for 200hr show that, the addition of 3% polacrylic acid to 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.

Results of DSC analysis show that up till 291.79°C in case of NCO/OH=1.1 and 305.64°C in case of NCO/OH=1.2 no sign of physical changes are noticed in the morphology of the foamed samples. However physical changes are noticed at 320°C for

modified sample with 25% PU, at 367.35°C for modified sample with 20% PU, at 314°C for modified sample with 2%A+1%Addibond, at 287.05 °C for modified sample with 25% Addibond, at 302 °C for modified sample with 20%Addibond, and at 378.34 °C for modified sample with 3%Acrylic acid

Results of TGA, show thermally stability, as indicated from the values of wt. loss % at different temperatures; 41.13 % at 374.92 °C incase of modified sample with 25 % polyurethane, 37.618 % at 364 66 °C in case of modified sample with 20 % polyurethane, 39.074% at 368 °C in case of modified sample with 15 % polyurethane, 43.169% at 369.2 °C in case of modified sample with 2% A+ 1% Addibond 65.

The third part is concerned with vulcanization reaction between blown asphalt and natural rubber.

Blown asphalt was used in different ratios of 5, 10, 20, 50, and 100 phr based on natural rubber. The sulfur accelerated system consists of (S; 3.8) phr, ZnO; 2.0phr, Stearic acid; 1.0phr, TMTD; 1.0phr, MBT; 4.5phr, and carbon black; 50phr, based on natural rubber.

For samples containing high content of blown asphalt it is seen that it is important to increase processability of samples and increase curing process. For this purpose different ratios of sulfur (3.8, 4.8, 5.8, 6.8, and 7.8) phr were used with natural rubber, modified blown asphalt at ratios of 50, and 100 phr based on natural rubber.

Oxidized asphalt was blended with different ratios of natural rubber (NR), (individually formulated) for obtaining vulcanized

samples and their properties are studied and compared, vs. mechanical, thermal stability, resistance to external media, swelling values, and crosslinking values of the vulcanized samples, DSC, TGA were evaluated.

Values of tensile strength (T.S) and elongation at break (E.b) are determined for vulcanized natural rubber samples (VNR), and also for vulcanized samples based on the same natural rubber materials previously subjected to blown asphalt in different percentage (5, 10, 20, 50, and 100) relative to 100 phr from(NR). The overall studied samples are 14, used after post-curing for 0.25h at 155 °C, to estimate the values of tensile strength (kgf/mm^2) and elongation at break (%).

The obtained data show that the values of tensile strength kgf/mm^2 proceed according to 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 values of elongation at break (%), for the same samples proceed according to 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 values for $VNRBA_{50-3}$ (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). Depending upon the added volume of blown asphalt (BA). This indicates that the value of absorbed energy increases with the effect resulting from the quantity of blown asphalt.

The Vulcanized natural rubber modified with blown asphalt samples acquires wt. loss values; % lower than that for similar vulcanized natural rubber. For example after 200 h, $VNRBA_5$, the obtained wt. loss value 2.630% < the corresponding value for VNR, for which the wt. loss value 3.110%. This means that the modification of vulcanized natural rubber increases the thermal stability, i.e. decreases wt. loss value %.

In other words the thermal stability (determined by wt. loss; %) increases with increasing the added volume of BA g, and sulfur content to rubber. due to increasing the crosslinking value (1/Q).

SWELLING the variation of the degree of swelling, after different time values, for vulcanized rubbers (VNR), and vulcanized rubber modified blown asphalt ($VNRBA_5$, $VNRBA_{10}$, $VNRBA_{20}$, $VNRBA_{50-3}$, $VNRBA_{100-4}$). in solvents (benzene and kerosene), at room temperature show that:

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

The values of swelling, (Q%) in benzene after 24 h for samples after post-cure are; $VNRBA_{20}$ (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 volume of added (BA) g to rubber in the process, which is inversely

proportional to the corresponding values of crosslinking (1/Q) as follows; for samples $VNRBA_{20}$ (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 the quantity of (blown asphalt) g added.

Similar behavior was noticed with increasing the amount, of blown asphalt with increasing the S content. The swelling values in benzene after 24 h for samples after post curing decreases with increasing the quantity of added (sulfur) g to rubber in the process which is inverse with the corresponding values of crosslinking (1/Q) as follows; $VNRBA_{100\text{-}4}$(0.945%) < $VNRBA_{50\text{-}3}$(1.002%)

(ii) The swelling values, % (Q%) and the corresponding crosslinking values (1/Q) change with the time of immersion of the studied samples in solvents. Generally the values of swelling increase with increasing time of immersion for all tested samples, however the corresponding values of crosslinking 1/Q decrease with increasing the time of immersion. This means that increasing the immersion time gives more chance for solvent to penetrate into the studied samples and probably destroys the links between chains, this character is also clear in case of kerosene.

(iii) All studied samples in benzene acquire higher swelling values Q (%), and lower crosslinking values (1/Q) as compared with the corresponding samples studied in kerosene. This may be due to the high molecular weight of kerosene which is difficult to penetrate as compared with benzene.

The studied chemical resistance (wt. loss %) for vulcanized rubber samples, was compared with that for the vulcanized rubber samples modified with blown asphalt.

Vulcanized natural rubber modified with 50% blown asphalt + 5.8 g sulfur (relative to 100g NR) gave higher resistance toward all testing media. Generally all testing samples greatly resist all testing media and their chemical resistances (wt loss, %) depend on the chemical constitution of the sample used and their resistance toward media proceed in the following order as example, for the post cured samples immersed in 10% H_2SO_4, for 3 weeks; $VNRBA_{100-4}$, (wt. loss, 0.937%) < $VNRBA_{50-3}$, (wt. loss, 1.147%) >$VNRBA_{20}$, (wt. loss, 1.217%) < $VNRBA_5$, (wt. loss, 1.362%) < VNR, (wt. loss, 1.521%) .

The **DSC analysis** show no sign of physical changes in the morphology of the samples up to (365.37°C, 394.84 °C) for $VNRBA_{100-4}$, and 382.51°C for $VNRBA_{50-3}$, (187.03°C, 297.18 °C, 378.11 °C) for $VNRBA_{50-2}$, 356°C for $VNRBA_{20}$, 352.30°Cfor VNR, (as given in Figs 43-47, and Table 34), illustrating that they are thermally stable

The values of TGA show that the studied samples are thermally stable, as indicated from the obtained value of wt. loss, % at different temperature; 38.79% at 376.23 °C for $VNRBA_{100-4}$, 48.47% at 377.41°C for $VNRBA_{50-3}$, 37.320 % at 372.79 °C for $VNRBA_{50-2}$, 46.34% at 371.32 °C for $VNRBA_{20}$, 41.528% at 367.61 °C for VNR.

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 ($VNRBA_{50-3}$)), (100g of NR)

I- Carbon black in nano size was used in different ratios of 5, 10, and 15 phr based on original used carbon black.

Values of (T.S) and (E.b) are determined for vulcanized samples containing quantities (5, 10, and 15 g) of nano carbon black relative to 45, 40, and 35 g respectively of the original carbon black. The values of tensile strength (kg/mm^2) and elongation at break (%).$VNRBA_{50-3}^{3}$; (51.9 kgf/mm^2)> $VNRBA_{50-3}^{2}$; (50.3 kgf/mm^2)> $VNRBA_{50-3}^{1}$; (49.7 kgf/mm^2)

$VNRBA_{50-3}^{3}$; (1003.9%)> $VNRBA_{50-3}^{2}$; (987.8%)> $VNRBA_{50-3}^{1}$; (970.1%)

The values of tensile strength kgf/mm^2, and elongation at break % were increasing by increasing the percent resulting from the decrease of diameter of particle size, which yields more active size that appeared to make more homogeneity and activity in the matrix.

II- Clay nanocomposites were used in different ratios of 5, 10, 15, and 20 phr based on natural rubber. Clay nanocomposites was also used in quantity of 15% added to natural rubber + 10g nano carbon black +40g original carbon black together with constant quantities of the other constituents and without ZnO.

Values of (T.S) and (E.b) are determined for vulcanized samples containing different percentage of clay (5, 10, 15, and 20)g of natural rubber. 15% clay added to natural rubber + 10g nano carbon black +40g original carbon black with constant values of the other factors and without ZnO. The obtained values of tensile strength, kgf/mm^2 proceeds according to the following order of the studied samples:

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

The values of elongation at break for cured sample according to following order of the studied samples:
$VNRBA_{50\text{-}3C1}$ (850%) > $VNRBA_{50\text{-}3C2}$ (805%) > $VNRBA_{50\text{-}3C5}$ (780%) > $VNRBA_{50\text{-}3C3}$ (724%) > $VNRBA_{50\text{-}3C4}$ (640%)

Such data show that the tensile strength (kg/mm^2) and elongation at break (%) decrease with further increasing the percentage of clay nanocomposites. Possible reason is the poor compatibility between clay and natural rubber leading to poor adhesion between the matrix and the reinforcing particles, thus no improvement in tensile strength was observed.

On the other hand the values of tensile strength kgf/mm^2, for the samples $VNRBA_{50\text{-}3C5}$ (40.8 kg/mm^2) > $VNRBA_{50\text{-}3C3}$ (39.77 kg/mm^2), were increasing by using quantities of (10g) of nano carbon black together with40g original carbon black respectively without ZnO, which is clearly due to the increasing surface area together with decreasing the diameter of particle size, yielding more active size which appeared to impart more homogeneity and activity in the matrix.

Thermal Stability

The studied samples were ($VNRBA_{50\text{-}3}^{1}$, $VNRBA_{50\text{-}3}^{2}$, $VNRBA_{50\text{-}3}^{3}$), and ($VNRBA_{50\text{-}3C1}$,$VNRBA_{50\text{-}3C2}$, $VNRBA_{50\text{-}3C5}$, $VNRBA_{50\text{-}3C3}$, $VNRBA_{50\text{-}3C4}$)

The obtained results of heating the sample till 200°C show that the values of value wt. loss % generally decrease with increasing the percentage of nanocomposites, as noticed from the obtained data in the following order;

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

It is noticed from the above mentioned arrangement that the addition of carbon black by 15phr is better than addition of 15% nanoclay. The addition of 10 and 5 phr of nano carbon black is better from as compared with the addition of 10, and 5 % of Nano clay. Such phenomena could be due to the surface area of a carbon black which is important and defines how much surface is available for interaction with other materials present in a rubber component. Generally, small particle size of carbon black will acquire a higher surface area.

Swelling and Crosslinking Values

The time dependence of degree of swelling, for the specimens ($VNRBA_{50\text{-}3}^{1}$, $VNRBA_{50\text{-}3}^{2}$, $VNRBA_{50\text{-}3}^{3}$), and ($VNRBA_{50\text{-}3C1}$,$VNRBA_{50\text{-}3C2}$, $VNRBA_{50\text{-}3C5}$, $VNRBA_{50\text{-}3C3}$, $VNRBA_{50\text{-}3C4}$) in solvents (benzene and kerosene), at room temperature show that, the values of swelling (Q%) decreases with increasing the quantity of added (nanocomposites) g to rubber in the process, and this is inversely proportional to the corresponding values of crosslinking (1/Q) which increase .

ΔTg analysis for vulcanized rubber modified with blown asphalt using nano carbon black gave ΔTg values of ($VNRBA_{50\text{-}3}^{1}$= 0.71, $VNRBA50_{\text{-}3}^{2}$=0.68, $VNRBA_{50\text{-}3}^{3}$=0.5). Clay nanocomposites was used in different ratios of 5, 10, 15, and 20 phr based on natural rubber. Clay nanocomposites, was added in ratio of 15% to natural rubber + 10g nano carbon black +40g original carbon black relative to 100 parts of NR with constant values of the other factors without ZnO. ($VNRBA_{50\text{-}3C1}$ =1.24, $VNRBA_{50\text{-}3C2}$ =0.99, $VNRBA_{50\text{-}3C5}$ =0.-68, $VNRBA_{50\text{-}3C3}$ =0.51 $VNRBA_{50\text{-}3C4}$=.013), as compared with vulcanized natural rubber (VNR=1.42), and Vulcanized natural rubber modified with blown asphalt ($VNRBA_{50\text{-}3}$=1.37).