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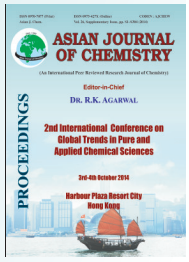

Synthesis of Vulcanization Retarder by Using Schiff Base with Maleic Anhydride

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The aim of this work to synthesize a compound plays as a retarder when use it in rubber vulcanization process, particularly in a blend of SBR/NR rubber. The compound was synthesized by using cyclo addition reaction of Schiff base and maleic anhydride. The products were characterized by FT-IR, ^{1}H NMR and elemental analysis.

Keywords: Vulcanization retarder, Schiff base, Rubber, Maleic anhydride.

INTRODUCTION

Rubber materials became a necessary and indispensable factor of industry and of daily life, the reason of this dignity is the most brilliant discovery and development of mankind, known as technology of vulcanization which means the changing of rubber material to a high deformable chemically cross-linked elastic solid instead of its original state (which was sticky when warm and brittle when cold). The rubber industry since that time was established and appeared vast progressive development over more than 100 years ago[1].

By vulcanization process the elasticity of rubber is increased while the plasticity decreased, this process in general occurred by formation of a cross linked molecular network between polymers chains[2].

To accomplish vulcanization several requirements needs, like vulcanizing agents (sulfur is the most famous agent used in this process, another agents are used such as peroxides, resin, metal oxides, *etc.*[3,4]) beside vulcanizing agent there is accelerators which minimized the time required for vulcanization, also there are activators antioxidant, fillers and reinforcing agents, process oils and there is retarders which represents the opposite work of accelerators, they help rubber to resist reversion especially in natural rubber compounds through increasing the scorch time in order to protect the products that may exposed to high temperatures which leads to scorching and more important aim the product service life when storing[2].

In this work 1,3-oxazepine-4,7-dione compound has been applied in vulcanization of rubber blend because oxazepine compounds represents a group which are the most important members in heterocyclic family, equally interesting with other hetero compounds for its theoretical implications, for the diversity of its synthetic procedures and for the physiological and industrial significance of these compounds[5].

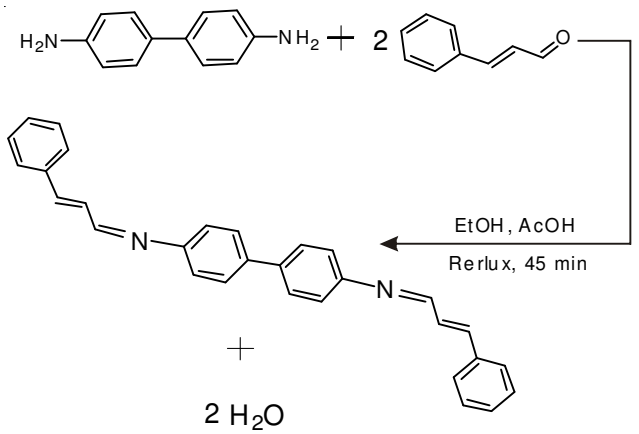
The results showed that the synthesized compound play as a retarder in this process by increasing scorch time and decreasing Torque and Mooney viscosity. The benefit of this behaviour is protecting the products from reversion, to guarantee reaching the batch into the mould (that contain grooves) uses before vulcanization occurred and canceling any deformation that can be happened through moulding process beside the long service time that could offer to the products.

EXPERIMENTAL

The chemicals employed in this work were from BDH, Scharlau, Fluka and Merck melting points were determined by using STUART-SMP 30 apparatus and they are uncorrected. The FT-IR spectrophotometer used was SHIMADZU-8400S using (KBr disc). ^{1}H NMR spectra acquired with Bruker Ultra Shield-400 MHz, the chemical shifts were referenced to TMS as an internal standard. Elemental analysis were performed by using Euro-EA-1106.

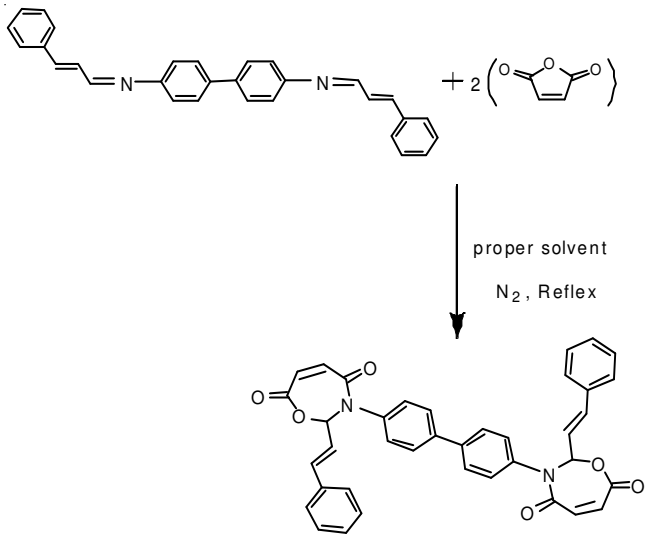
Synthesis of di-cinnamylidene benzidine (Schiff base A)[6]: Cinnamaldehyde compound (0.04 mol, 5.1 g) mixed with ethanol (98 %) and added to (0.02 mol, 3.7 g) of benzidine compound which also dissolved in ethanol, then 2-3 drops of glacial acetic acid have been added to the mixture. A refluxing process was starting with continuous stirring for (45 min) at 70-75 °C after end of reaction the mixture was cooled and deep yellow precipitate gained then this precipitate was filtered, washed by ethanol and recrystallized. The reaction monitored

by TLC test to check completion of reaction. The synthesis of Schiff base is illustrated in **Scheme-I**. Yield: 92.4 %, deep yellow precipitate, FT-IR (KBr, ν_{max}, cm^{-1}): 1627 (C=N), 1485-1579 (C=C aromatic), 3034 (C-H aromatic), 2870 (C-H aliphatic). ^1H NMR ($CDCl_3$)δ: 8.37 ppm (2H, HC=N), 6.77-7.68 ppm (Ar-H).



Scheme-I: Synthesis reaction of Schiff base (A)

Synthesis of compound B[7] (4,4′-(biphenyl-4,4′-diyl)*bis*-(2-styrenyl-5,6-diene-1,3-oxazepine-4,7-dione): Refluxing process of a mixture containing (0.001 mole, 0.41 g) of Imine (Schiff base A) and (0.002 mole, 0.20 g) of maleic anhydride (both were dissolved in dioxane) has been started and after 4 h. of reaction at 85 °C deep brown precipitate was gained, washed and recrystallized by using petroleum ether. The reaction mixture was followed by TLC test to check completion of reactions. The synthesis steps were summarized in **Scheme-II**. Yield: 58 %, deep brown precipitate. FT-IR (KBr, ν_{max}, cm^{-1}): 1597 (N-C=O), 1693 (-O-C=O)1390-1149 (C-O-C), 1510 (aromatic C=C), 1274 (C-N), 3100 (C-H oxazepine). ^1H NMR ($CDCl_3$)δ: 6.33 ppm (2H, N-C-O), 7.28-7.49 ppm (Ar-H).



Scheme-II: Synthesis reaction of oxazepine compound (B)

Materials and equipments of vulcanization process: The materials used in this work were applied from Al Kufa State Company for Tyre Industry. The tests carried out by using oscillating disc rheometer (ODR) to get the cure curves. Shore A apparatus was used to measure the hardness of sample and higher precision density tester GP-1205 was used to measured the specific gravity of sample.

Batch processing[8]: The batch compounding ingredients are illustrated in Table-1.

TABLE -1
COMPOSITION OF THE BATCH

Compounding ingredients	Ratio (pphr)
SBR	75
NR	25
Zinc oxide	5
Stearic acid	1
Oil	8
Carbon black	45
Sulfur	1.5
MBTs + oxazepine compound	2

The batch prepared according to ASTM D 3184. The using of oxazepine was in the step of adding the accelerator MBTs by adding oxazepine to the batch after the addition of MBTs in different percentage shown in Table-2.

TABLE-2
ADDITION PERCENTAGE OF
OXAZEPINE COMPOUND IN EACH RECIPE

Recipes	MBTs (pphr)	Oxazepine compound (pphr)
Recipe no. 1	2.0	0.0
Recipe no. 2	1.5	0.5
Recipe no. 3	1.0	1.0
Recipe no. 4	0.5	1.5

After the completion of processing the batches, the tests of rheology, hardness and specific gravity carried out.

Rheological tests: The test carried out by using oscillating disc rheometer. The sample was putted in the apparatus and test carry out at 180 °C for 6 min, a graph of Torque *vs*. vulcanized time was obtained and gave the following data: max torque, min torque (lb-in), scorch time TS_2 (s), cure time Tc 90 (s) and mooney viscosity the resulted curves shown in Figs. 1-3.

Hardness tests: In this test shore A apparatus was used to measure hardness of samples. This test carried out according to ASTM D1415 specifications, the results are shown in Fig. 4.

Specific gravity tests: The samples have been testing with higher precision density tester GP-1205 the result data are shown in Fig. 4.

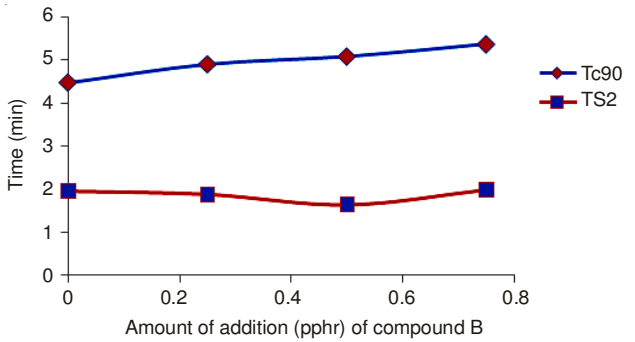


Fig. 1. Relation between the time of cure Tc 90 and scorch TS_2 with addition percentage of compound B

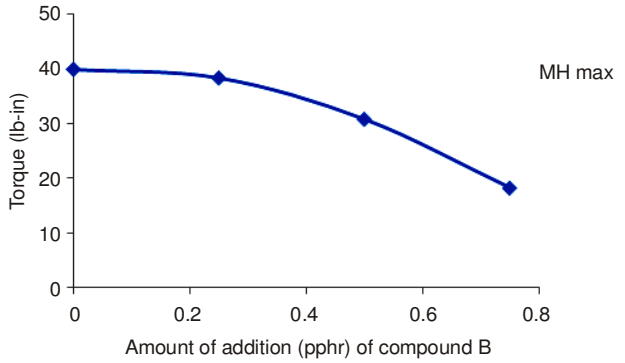


Fig. 2. Relation between the maximum torque with addition percentage of compound B

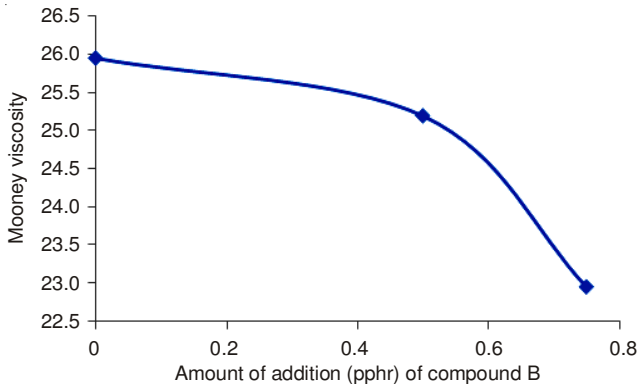


Fig. 3. Relation between the mooney viscosity with addition percentage of compound B

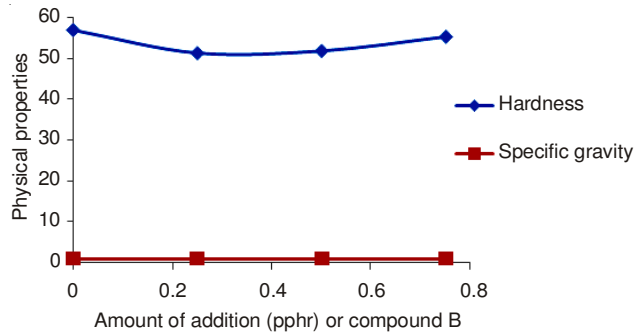


Fig. 4. Relation between the hardness and specific gravity with addition percentage of compound B

RESULTS AND DISCUSSION

For the synthesis of compound A which was a Schiff base, this compound has been prepared by condensation reaction of benzidine with cinnamaldehyde in presence of ethanol (98 %) as a solvent and few drops of glacial acetic acid. This compound characterized by using FT-IR spectra, the spectra shows the appearance of absorption band at 1627 cm^{-1} due to stretching vibration of the (C=N) imine group and disappearing the band of (symmetric, asymmetric) stretching vibration of the (-NH_2) group in the region of (3465-3250 cm^{-1}). ^{1}H NMR spectra using $CDCl_3$ as a solvent indicates the formation of imine group (C=N) through singlet peak at $\delta = 8.37$ ppm which belong to (2H, HC=N), the rest of the signals at $\delta = 6.77$-7.68 ppm refers to the aromatic protons with details.

The second step of work was using Schiff base A to generate seven membered ring oxazepine compound by 5+2 cycloaddition reaction with maleic anhydride in suitable solvent. The product of this reaction was 4,4′-(biphenyl-4,4′-diyl)*bis*(2-styrenyl-5,6-diene-1,3-oxazepine-4,7-dione), which characterized by FT-IR spectra the spectra shows disappearing of (C=N) band and appearance of absorption band at stretching frequency 1693 and 1597 cm^{-1} belongs to (-O-C=O, N-C=O), respectively, 1390-1149 cm^{-1} for (C-O-C) and 3100 cm^{-1} for (C-H, oxazepine). ^{1}H NMR spectra of this compound confirmed the generation of the compound through the peak at $\delta = 6.335$ ppm which belong to (2H, N-C-O) of oxazepine ring that formed besides peaks at δ = 7.28-7.49 ppm which relate to aromatic protons.

The third step of wok was application oxazepine compound in rubber vulcanization process specifically with SBR-NR blend. The results showed that oxazepine play as a retarder for vulcanization through delayed the action of the accelerator MBTs in order to prevent premature vulcanization through processing steps, this work done by increasing the scorch time from (4.47 to 5.37) beside decreasing in mooney viscosity from (25.9 to 22.9), in industry this behaviour making sure of preventing premature vulcanization upon processing especially when using molds that contains grooves or holes and through storing periods. Retarders having an importance rule in recent years because these retarders working on which is called schorching time of compounds that keeping goods from undesired vulcanizing process through storing them besides the important rule of increasing the shelf time of products.

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