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Functionalizing of Waste Tire Rubber with Active Functional Groups

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Abstract

In this study the waste tire rubber was converted to carboxylated rubber without needed to reclaimed the rubber. Active carboxylate moieties were incorporated to the rubber chains of the wasted tire directly. Three types of active materials were used for the reaction with the wasted rubber; maleic anhydride, N-(2,5-dimethoxyphenyl) maleimic acid and N-(3-carboxyphenyl) maleimic acid. The reaction was carried out by mixing the materials in closed system. The effect of feed ratio, time and the temperature of the reaction have been studied. It was noticed that increasing the time of reaction or the reaction increase the ratio of the reacted maleic anhydride or maleimic acid with the waste rubber. The optimum conditions for the reaction of maleic anhydride are more difficult than the reaction of maleimic acids. It was seen that period of time needed to get high reaction efficiency of maleic anhydride are 60min, at 220^0C, while maleimic acids are more efficient in reaction with the waste rubber

Key words: waste rubber, tiers, Maleic anhydride, maleimic acid

1. Introduction

The amount of the waste tires has been recently increased significantly. Because that the waste tires rubber is non- biodegradable [1]., It became a serious global environmental problem. The major problem of increasing the waste rubber as a piles is the formation of uncontrolled fires with emission of poisons gases [2]. When the tires are burned, they evolves a large amount of energy, therefore they can be used as a fuel [3]. There are several methods for recycling the waste tires for reuses, such as the recovery of the rubber for re-use; shredding the tiers into small pieces to be used in different civil engineering and automotive sectors, or heating tires under some controlled conditions to produce oil and carbon black in process called pyrolysis [4, 5]. It can be used as a partial replacement for coarse aggregates in concrete tile production [6]. The processing end- of- life tires form a critical and valuable resources of economy [7]. Recycling of the waste rubber is a big challenge for the researchers and industrialists. The difficulty of the recycling processes are generated from the three dimensional structure of the rubber by the effect of the vulcanization and the complex structure of the rubber products [8]. The reclaimed rubber that prepared from waste rubber and tires has been used as a substituted for virgin rubber and rubber modifications [9]. Many researchers study the using of end –of- life tiers in many fields, all the treated concern on the de devulcanizing steps before the use in the appropriate fields. The main constituents of the tiers are rubber (60-65%), carbon black (25-35%) and other industrial chemical additives needed for operation and processing [10]. Styrene – butadiene rubber (SBR) is the essential type of rubber used in tiers industries which can be reclaimed from the waste tiers. In order to modify the properties of the reclaimed rubber, many methods are employed. The most celebrated method is functionality with some polar materials like maleic anhydride [11] or acrylic acid [12], whereby the pure reclaimed rubber is inherently nonpolar [13]. The modified rubber is known as a carboxylated styrene butadiene rubber (XSBR). Many developed studies have been achieved on XSBR to be used in different advanced applications [14-18]. Within the frame of this work, a direct functionality process for waste rubber tiers was used without going to the hard process of devulcanizing. The introduced function moieties are maleic anhydride and the maleimic acid derivatives.

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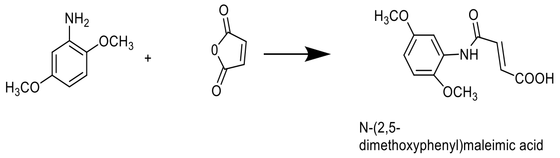
2. Experimental

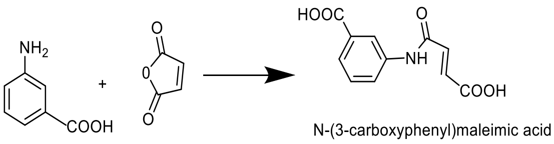
Maleic anhydride MAn, (fluka) was recrystallized from dried chloroform [19]. Powder waste rubber was supplied from Al- Diwaniyah company for rubber industries. All the reagents and solvent are supplied from Aldrich and used as received. The used solvents are dried by appropriate dryer before used [19].

Maleimic acid preparation: The maleimic acids of 2, 5- dimethoxy aniline and of 3-aminobenzoic acid are prepared by reaction of equimolar of MAn with the amine as follows:

N-(2,5-dimethxyphenyl)maleimic acid (MAdm): 1.02gm(0.01mole) of MAn dissolved in 10ml dry chloroform and solution of 3.829gm of 2,5-dimethoxyaniline dissolved in 10ml chloroform. The amine solution was added drop wise to MAn solution at (10°C) [20]. Mix for a period of 1hr., filter the produced maleimic acid and dried under vacuum.



N-(3-carboxyphenyl) maleimic acid (MAca): The same procedure was followed in preparation of maleimic acid from m-aminobenzoic acid and MAn by using dry acetone instead of chloroform as a solvent



Functionalizing the rubber with MAn:
A mixture of 1gm of powder waste rubber tires with different amount of MAn (0.01-0.2gm) and 0.01gm of the initiator benzoyl peroxide (BPO) was mixed thoroughly in closed stainless steel container at 120°C After complete the time of agitation the product was refluxed with water for a period of 0.5 hr., filtered and dried under vacuum. The filtrate was titrated with standard solution of potassium hydroxide to evaluate the amount of unreacted MAn. The time of the reaction time and temperature were studied as in table (1).

Functionalizing the rubber with maleimic acid:
The two types of maleimic acid (MAdm and MAca) were functionalized into the waste rubber. The same above procedure was followed to prepare the rubber function with maleimic acids. Whereby the maleimic acid was mixed with the powder of the waste rubber at 240°C for different period of time. Refluxing the product with water and filter, petroleum ether was added to the filtrate to detects any unreacted maleimic acid that will be precipitate. The time of reaction was studied to get the best conditions for higher functionality ratios, (table3).

3. Result and discussion

As the waste rubber of tiers contain about 60-65% styrene butadiene rubber [10], its reaction with MAn or maleimic acids will be available through free radical reaction process in the presence of the benzoyl peroxide as initiator. The product of this reaction can be considered as a carboxylated rubber.

MAn functionalized rubber:
Table (1) shows the effect of the reaction time, reaction temperature and the ratio of MAn on the efficiency of reaction (the ratio of MAn that can be reacted with the rubber). The results revealed that efficiency of reaction increased with increasing MAn feed ratio until the 0.1/ 1 (10% of MAn). Also, it was clearly notice that increasing the time of the reaction will increase the ratio of the reacted MAn with rubber until 60min. In the other hand, it was found that increasing the temperature of the reaction have a positive effect on the reaction proceeding. The best temperature of the reaction is at 220°C, whereby the rubber begins to melt. From table (2), the best condition for give higher yield of reaction of MAn with the rubber are at initial concentration of MAn 10% and a period of time 80 min. whereby the reaction temperature at 220°C. The product was characterized by infrared spectrum. In Comparison between the spectrum of the waste rubber (figure 1) with the spectrum of MAn functionalized the rubber (figure 2), it was clearly notice that the appearance of peaks at 1712cm-1 and at 1558cm-1 in figure 2 which are related to the frequency of the anhydride moiety. CHN elemental analysis (table 2) shows a decrease of the nitrogen and carbon elements ratios. This can be explained that adding of MAn to the sample with three oxygen atoms affected on the ratio of nitrogen and carbon negatively.

Maleimic acids functionalized rubber:
It was practically found that the reaction of the maleimic acid with the waste rubber did not occur until the temperature of the reaction is above the melting point of the maleimic acids. Also, it was found that the efficiency of functionalizing reaction increases with increasing the feed ratio of maleimic acid (tables 3 &4). Figures .3 and 4 indicates the infrared spectrum of N-(2, 5-dimethoxyphenyl) maleimic acid and N-(3-carboxyphenyl) maleimic acid functions the rubber respectively. The figures indicate the absorbance at 1699cm-1and at 1558cm-1 in figure 3 and at 1714cm-1 and at 1558cm-1 belong to the carbonyl group of the amide groups of the above respected compounds. CHN elemental analysis (table 2) shows an increase

in the nitrogen and a decrease in carbon ratios in according to waste rubber sample for both maleimic acids functionalized rubber samples.

Thermal analysis:

The TG curves of the waste rubber and its derivatives with MAn and maleimic acids are shown in figures (5-8) at a heating rate of 20^0C/min. the samples started to lose weight 300^0C. The DTA curves (fig.9-12) show two obvious peaks of weight $(300\text{-}450)^0$C. The pyrolysis of weight loss of about 53%, 46%, 48& and 47% for the pure waste rubber, the rubber functioned with MAn, rubber functioned with MAdm and rubber function with MAac respectively. The results reveal the functional groups can give an observed thermal stability to the rubber. This results confirm with previous studies that show the pyrolysis of the synthetic rubber ranged between 300-500^0C [21]. It was clearly notice from the DTA curves that the rate of pyrolysis increased at 300^0C from -0.03 1/min. for pure wasted rubber to -0.022, -0.018 and -0.022 1/min. for MAn, MAdm and MAac functionalized rubber respectively. In the other hand the rate at 400^oC was reduced from -0.054 to -0.06. -0.068 and 0.065 1/min. these results can be explained that at 300^oC, the function groups become to cyclized and lose the water molecule (the function group of MAn was open to succinic acid at the step of washing with water) whereby at 400^0C the lose processes of these function groups became very hard.

4. Conclusion

In this study the functionalizing of the rubber of the wasted tiers was functionalized. The incorporated functional groups are maleic anhydride and the maleimic acids derived from it. The operation was succeeded directly without the hard operation for extracting the rubber from its compounding. This process can open a new horizons for dealing with the wasted tiers in order to exploit the accumulated wasted tiers and convert it to a new type of materials can be used in different fields of industries.

Acknowledgment

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Table 1: Effect of time mole ratio and temperature on the ratio of reacted MAn with rubber

220^0C			180^0C			150^0C			120^0C						
60 min	45 min	30 min	60 min	45 min	30 min	60 min	45 min	30 min	60 min	45 min	30 min	BPO	MAn/	rubber	no
%95	%94	%63	%87	%74	%51	%63	%60	%50	%53	%48	%43	0.01	0.01	1g	1
%93	%95	%66	%86	%63	%55	%51	%53	%48	%48	%45	%45	0.01	0.03	1g	2
%92	%893	%55	%76	%63	%60	%50	%57	%52	%43	%40	%38	0.01	0.05	1g	3
%95	%89	%51	%73	%62	%52	%46	%39	%45	%43	%41	%40	0.01	0.06	1g	4
%92	%85	%44	%61	%43	%49	%57	%42	%43	%38	%32	%30	0.01	0.08	1g	5
%91	%88	%42	%63	%42	%37	%50	%44	%37	%31	%30	%28	0.01	0.1	1g	6
%87	%80	%53	%70	%56	%43	%51	%39	%33	%30	%31	%21	0.01	0.15	1g	7
%89	%80	40%	%62	%50	%32	%49	%42	%39	%27	%28	%22	0.01	0.2	1g	8

Table 2: CHNS elemental analysis of the prepared sample

sample	C%	H%	N%	S%
Waste rubber	73.87	5.356	0.875	1.965
MAn function rubber	64.16	3.879	0.481	1.395
MAdm function rubber	54.41	4.224	0.993	1.510
MAca function rubber	66.09	4.565	0.885	1.367

Table3: Effect of time and mole ratio on the reaction efficiency of MAdm with waste rubber at 240C.

60min.	45min.	30min.	MAdm	rubber	No.
100%	95%	92%	0.01	1g	1
100%	93%	90%	0.05	1g	2
100%	95%	88%	0.08	1g	3
99%	94%	88%	0.1	1g	4
98%	95%	89%	0.15	1g	5
98%	93%	89%	0.2	1g	6

Table 4: Effect of time and mole ratio on the reaction efficiency of MAac with waste rubber at 240C

60min.	45min.	30min.	MAac	rubber	No.
100%	96%	93%	0.01	1g	1
100%	95%	92%	0.05	1g	2
100%	95%	90%	0.08	1g	3
99%	94%	90%	0.1	1g	4
98%	93%	89%	0.15	1g	5
98%	93%	89%	0.2	1g	6

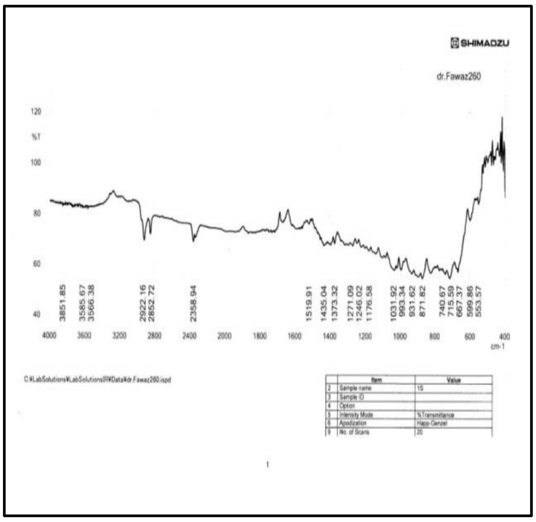

Fig.(1): IR spectrum of wasted rubber

Fig.(2): IR spectrum of MAn functionalized wasted rubber

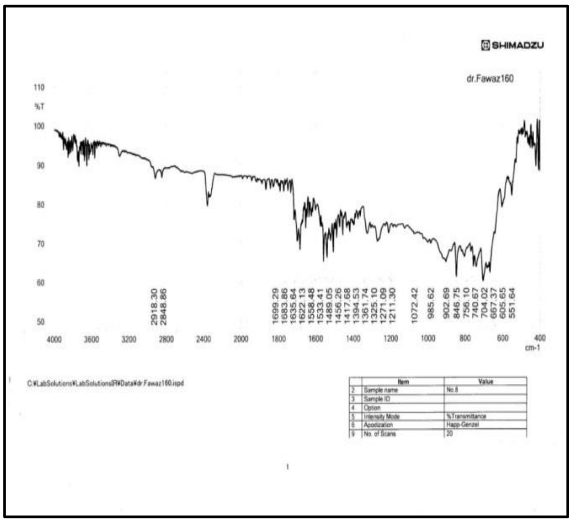

Fig.(3): IR spectrum of N-(2,5-dimethoxyphenyl) maleimic acid functionalized wasted rubber

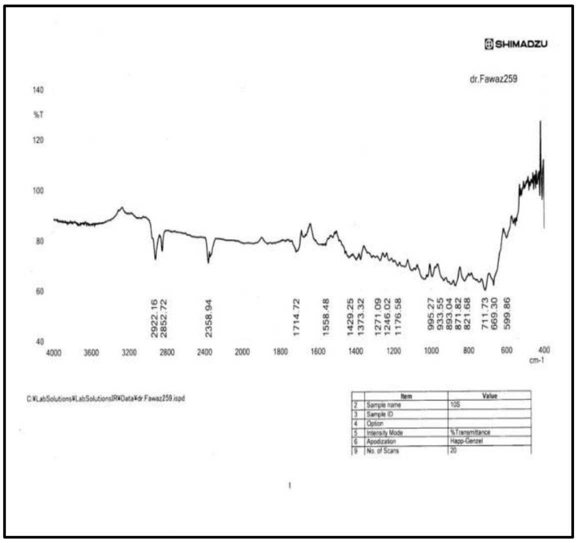

Fig.(4): IR spectrum of N-(3-carboxyphenyl) maleimic acid functionalized wasted rubber

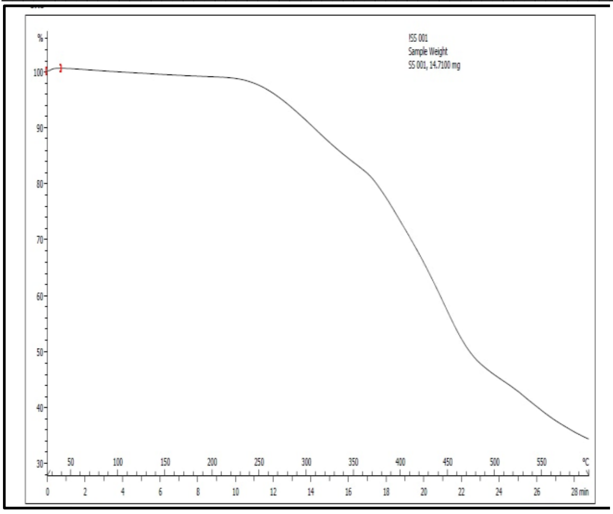

Fig.(5): TGA of wasted rubber

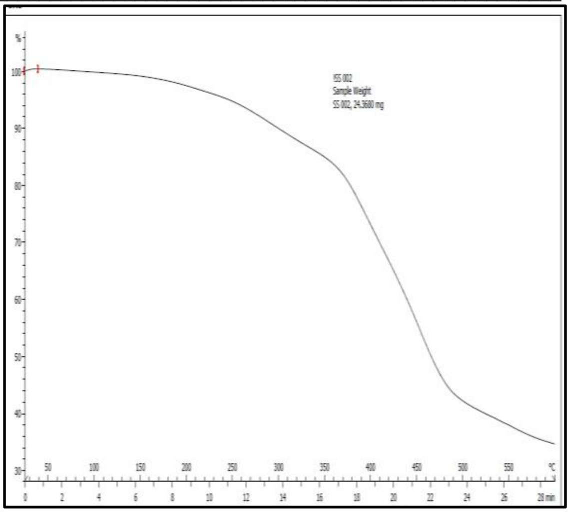

Fig.(8): TGA of N-(3-carboxyphenyl) maleimic acid functionalized wasted rubber

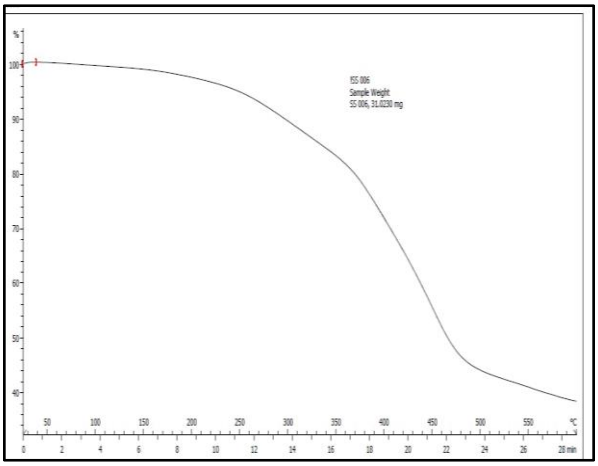

Fig.(6): TGA of MAn functionalized wasted rubber

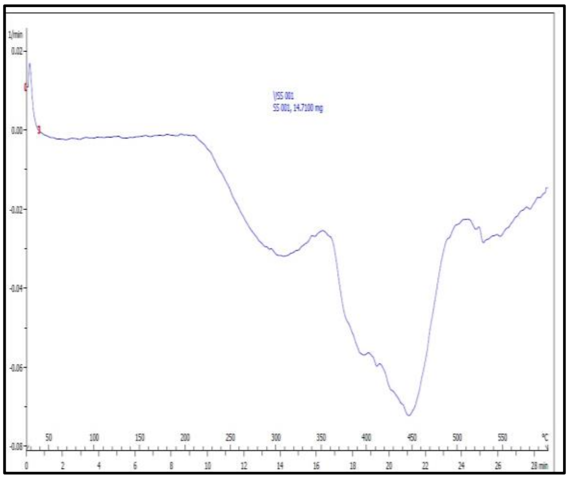

Fig.(9): DTA of wasted rubber

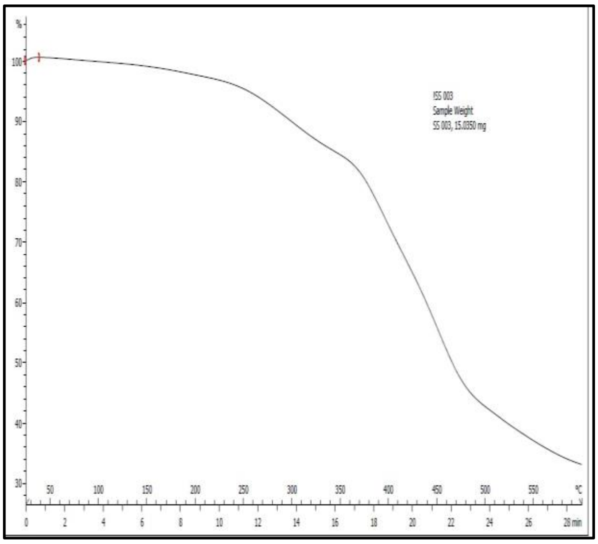

Fig.(7): TGA of N-(2,5-dimethoxyphenyl) maleimic acid functionalized wasted rubber

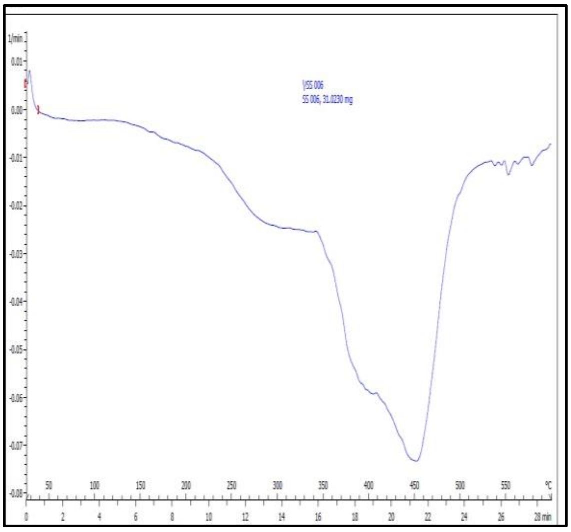

Fig.(10): DTA of MAn functionalized wasted rubber

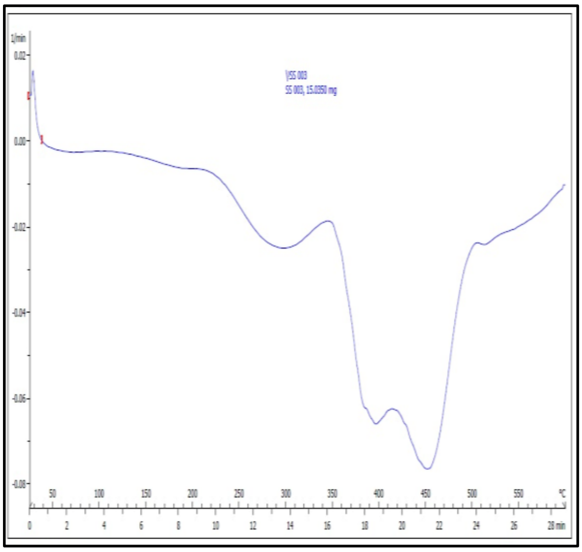

Fig.(11): DTA of N-(2,5-dimethoxyphenyl) maleimic acid functionalized wasted rubber

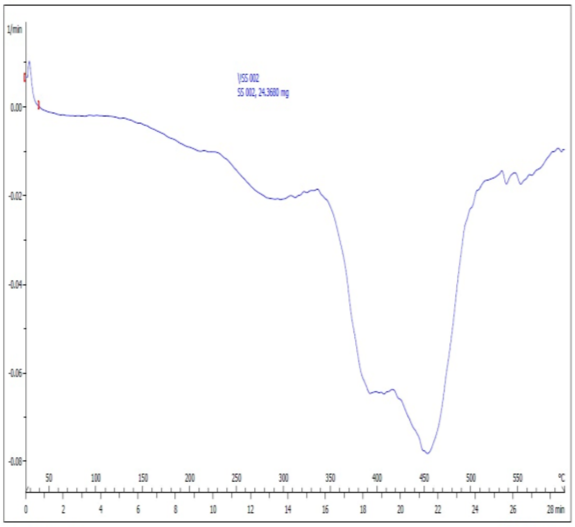

Fig.(12): DTA of N-(3-carboxyphenyl) maleimic acid functionalized wasted rubber

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