Effect of Mineral Fillers on Rice Straw Fiber/High Density Polyethylene Composites

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Abstract: Natural fibers are low cost, high specific properties and renewable nature and more useful to be used as reinforcement in thermoplastic materials .Mineral fillers such as calcium carbonate, talc are also used to improve the physico-mechanical properties . Tensile strength, flexural strength, impact strength, hardness and water absorption properties were evaluated. The results indicated that the mineral fillers loading had significant effects on the mechanical properties of the prepared composites. Thermogravimetric analysis (TGA) was investigated. 10% of calcium carbonate improves the tensile strength properties .Addition of calcium carbonate and talc to rice straw fibers (RSF)/HDPE composites was found to improve the flexural strength .The hardness of the composites was also improved when mineral fillers were added .5% of talc improves the impact strength of the prepared composites. Scanning electron microscopy was investigated to the prepared composites and revealed good interfacial adhesion due to the maleated polyethylene which was used as coupling agent.
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Keywords: Mineral Filler; Rice Straw Fiber; High Density Polyethylene

1. Introduction:

In recent years, natural fibers have been increasingly used as reinforcement in commercial thermoplastics due to providing several advantages such as low densities, low cost nonabrasive nature, high specific properties and renewable nature .It has advantages over traditional reinforcement materials such as glass fibers [1-4].Natural fibers are now considered as serious alternative to synthetic fibers used in various fields. The use of natural fibers as reinforcing materials in both thermoplastic and thermoset matrix composites provides positive environmental benefits with respect to ultimate disposability and best utilization of raw materials [5-8]. There are many factors that can influence the performance of natural fiber reinforced composites. Apart from the hydrophilic nature e of fiber, the properties of the natural fiber reinforced composites can also be influenced by fiber content amount of filler In general; high fiber content is required to achieve high performance of the composites. Therefore, the effect of fiber content on the properties of natural fiber reinforced composites is particularly significant. It is often observed that the increase in fiber loading leads to an increase in tensile properties [9]. Another important factor that significantly influences the properties and interfacial characteristics of the composites is the processing parameters used. Therefore suitable processing techniques and parameters must be carefully selected in order to yield the optimum composite products. In order to improve the similarity and adhesion between wood-flours and thermoplastic matrices, several chemicals have been employed with maleated coupling agents and were found to be the most suitable for organic filler filled thermoplastic composites [10-11]. Talc is a crystalline form of magnesium silicate which when pure has the formula Mg $(Si_4O_{10})(OH)_2$; talc has a platy structure that gives it reinforcing properties in polymers [12-13]. Mineral fillers such as talc and calcium carbonate increase the bending strength and heat distortion capacity of the wood-plastic composites (WPC) and decrease the creep under load. They may also improve the processing by working as a lubricating agent. Minerals may also work as flame retardants in the composites [14-15].

2. Materials

High Density Polyethylene (HDPE):was from Exxon Mobil Chemical with Density 0.964 gm/cm^3, melt Index 8.0g/10 min, melting temperature 134^{o}C. Rice Straw from Egypt agriculture field. Dicumyl Peroxide (DCP): was from Akzo Chemi, Netherlands, density: 0.98- 0.99 gm/cm³, processing temperature was 120^{o}C, suitable cross linking temperature: 150-170^{o}C. Maleic anhydride: was from Fluke. Calcium carbonate ($CaCO_3$): From Sigma-Aldrich Company. Talc: was from China.

2.1 Sample preparing

Rice straw was dried at 105°C for 24 h. The polyethylene and rice straw were then blended together in Barabender twin screw for 10 minutes to prepare the polymer composites. The temperature was 180 °C and the rotational speed was 60 rpm. The rice straw /HDPE composites were removed from the Brabender twin screw then pressed to sheet using the hydraulic press at 180°C for 5 minute.

2.2 Testing Methods:

The flexural and notched izod impact strength properties of the prepared composites were measured according ASTM standard D 790 and D 256 respectively. The morphology of prepared composites were observed by scanning electron microscopy (SEM) with a Joel JXA-840 A.

2.3 Water absorption:

Water absorptions of the composites were measured according to the ASTM D570 specification. The dried specimens were dipped in distilled water and maintained at 25 °C. All values of the water absorptions were calculated as the mean value of three samples. The water uptake was calculated as the following:

Water uptake % =(Ws -W_1)/W_1 ×100 ⟶ (1)

Where Ws is the weight of the water saturated specimen and W_1 is the weight of the oven dried speciment.

$TS_t = (T_t-T_0) / T_0 \times 100$ ⟶ (2)

Where Ts_t, is thickness swelling at time t (%), Tt and To are thicknesses at time t and dried condition (mm), respectively.

3. Result and Discussion:

3.1 Preparation of Maleated Polyethylene (MAPE):

Preparation of maleated polyethylene by grafting method of maleic anhydride on high density polyethylene in the presence of initiator; Dicumyl peroxide (DCP) [16]. That is prepared by melt mixing of HDPE with maleic anhydride in the presence of DCP; the melt mixing was carried out in a Barabender twin screw at 180°C and 60 rpm. Fourier transform infrared spectroscopy (FTIR) was used to measure the relative maleic anhydride (MA) grafting in polyethylene. Fig. (1), Fig. (2). Show the FTIR spectra of HDPE and HDPE-g-MA respectively; new peaks appeared at 1786 cm^{-1} due to asymmetric stretching modes of carbonyl (C=O) of saturated maleic anhydride[17-19]. The band at 1859 cm^{-1} and 1786 cm^{-1}, are characteristic of cyclic anhydride. The backbone molecule of polyethylene, had a strong peak of (-CH) at about 2917 cm^{-1} and 2848 cm^{-1}, and an attributed band to the rocking vibrations of -CH_2 bonds in HDPE was observed at 719 cm^{-1}.

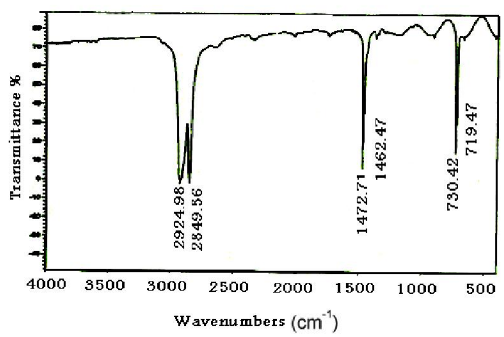


Fig (1) FTIR of virgin high density polyethylene (HDPE).

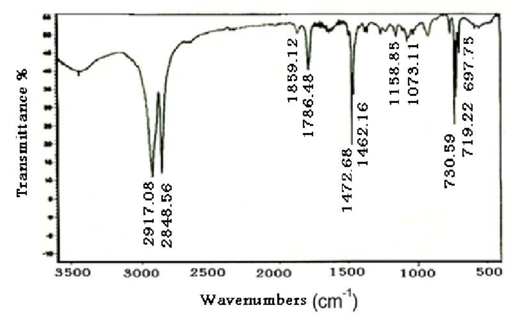
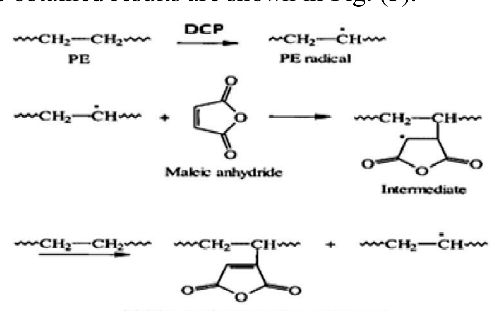


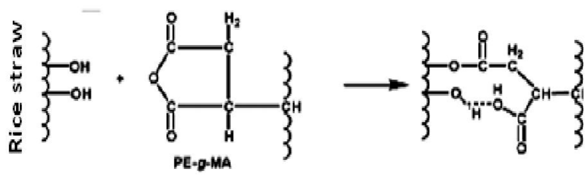
Fig (2): FTIR of Maleated high density polyethylene (MAPE).

3.2 Effect of Maleated Polyethylene amounts as a compatibilizer for the rice straw/HDPE composites.

Maleated polyethylene plays a vital role in the improvement of the mechanical properties such as tensile strength, flexural strength and hardness of the prepared polymer composites due to increasing the compatibility and interfacial bonding between rice straw and HDPE [20].In this study, we use different ratios of rice straw /HDPE composites in the presence of the coupling agent (maleated polyethylene); of different ratios: 1%, 3%, 5%, then study their effect. The obtained results are shown in Fig. (3).



Scheme 1: Reaction mechanism of maleic anhydride modification of PE. [21].



Scheme 2: Reaction mechanism interaction between rice straw and PE-g-MA.

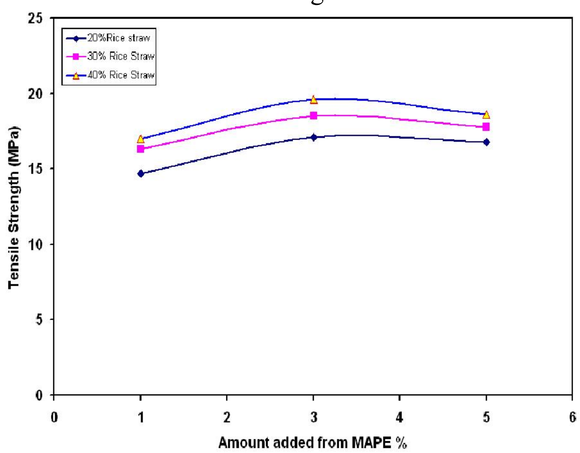


Fig (3) Represents the change in the Tensile strength with amounts of coupling agent (MAPE) at different Ratios of rice straw: HDPE (20 %, 30%, and 40%).

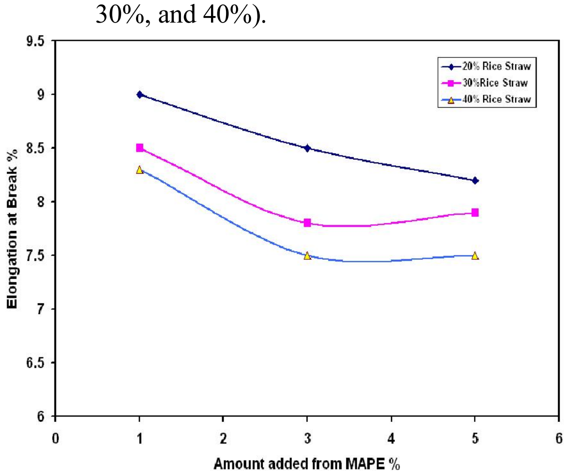


Fig (4): Represents the change in the Elongation % with amounts of coupling agent (MAPE) at different Ratios of rice straw: HDPE (20 %, 30%, 40%).

From Fig.(3).It was observed that, the addition of 3% of coupling agent is more effective than 1% and 5% which give slightly decreasing in tensile strength where increases from 14.7 to 17.1 MPa in case of 20% addition of rice straw and there is a slight decrease in case of 5% coupling agent to which amount 16.8MPa. This indicates that 3% better to improve the interfacial bonding on the prepared composites. From Fig (4) the elongation at break decreases as amount of rice straw loaded increases due to increasing the rigidity of the composites.

3.3 Effect of adding Calcium Carbonate and Talc during the preparation of RSF/HDPE composites:

In this study prepared composites from high density polyethylene/rice straw fiber /calcium carbonate composites and high density polyethylene/rice straw fiber/talc composites were studied with different composition as seen from Table (1).

Table (1): Composition of the studied formulations.

HDPE (wt%)	Coupling agent (wt%)	Rice straw flour (wt%)	$CaCO_3$ (wt%)	Talc (wt%)
37	3	55	5	-
37	3	50	10	-
37	3	40	20	-
37	3	55	-	5
37	3	50	-	10
37	3	40	-	20

From fig (5) it is clear to understand the effect of calcium carbonate content in the prepared composites .It was found that the added amount of calcium carbonate increases the tensile strength due to good interfacial dispersion of the prepared composites. The best amount which gives high tensile strength was at 10%, while increasing $CaCO_3$ up to 20% decreases the tensile strength, but elongation was found to decrease as amount of calcium carbonate increases as seen in Fig (6).

Also in Fig (7) it can be seen that, talc as a mineral filler added to RSF/HDPE to prepare the composites it also increases the tensile strength and elongation this is may be due to talc behave as a lubricant as seen in Fig (8).

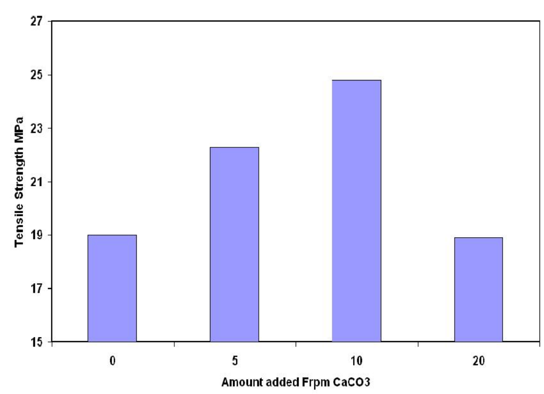


Fig. (5) Represents the relation between Tensile strength (MPa) with different amount of Calcium Carbonate.

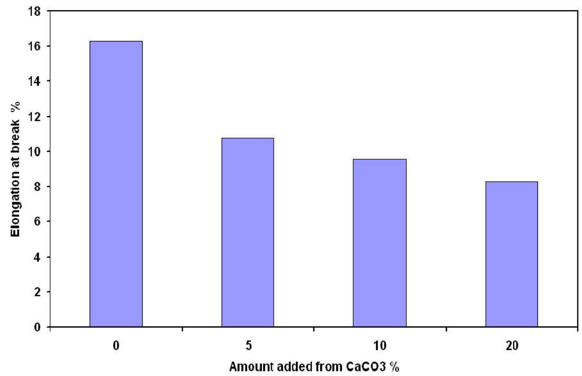


Fig (6) Represents the relation between Elongation at break % with different amount of Calcium Carbonate.

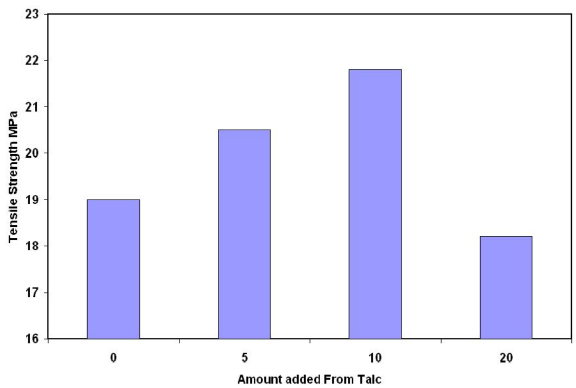


Fig (7) Represents the relation between Tensile strength (MPa) with different amounts of Talc

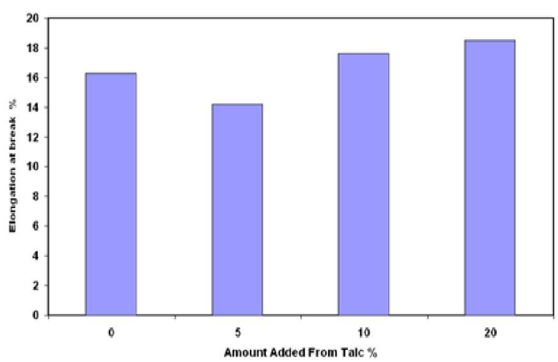


Fig (8) Represents the relation between Elongation at break % with different amounts of Talc.

3.4 Flexural test

From Fig (9) addition of calcium carbonate as a mineral filler to RSF/HDPE composites improves the mechanical properties such as flexural strength, where it increased from 39.48 N/mm^2 to 58.95 N/mm^2 at 5, 10% of $CaCO_3$ loaded respectively .It was observed also that the flexural strength decreases at 20% of $CaCO_3$ and we can conclude that 10% of $CaCO_3$ is more useful in application for obtaining high flexural strength. In case of using mineral filler like talc in Fig (10) it was found that the flexural strength increases up to 10% but it decreases to 44.11 N/mm^2 at 20% it is nearly the same as the result of 5% addition. The increased flexural strength may result from the fact that the stiffness of the rice straw fiber is higher than that of the HDPE matrix and the reinforcement introduced by the rice straw fiber enables stress to be transferred from the matrix to the rice straw fiber [22].

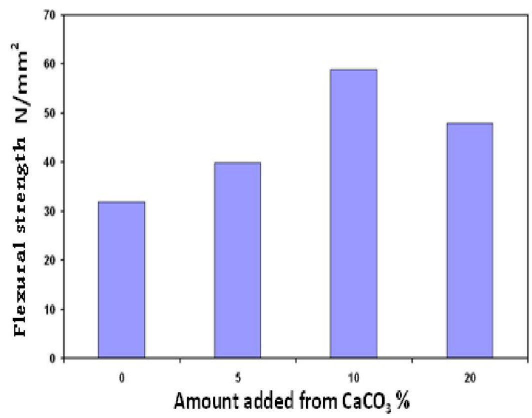


Fig (9) Represents the relation between Flexural strength N/mm^2 with different amount of Calcium carbonate%

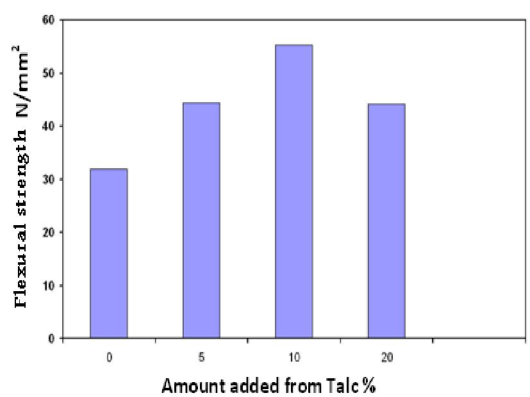


Fig (10) Represents the relation between Flexural strength N/mm^2 with different amount of Talc%.

3.5. Charpy impact test

Effect of calcium carbonate content on rice straw fiber and high density polyethylene composites were studied and the obtained results are shown in Fig (11). For impact strength (notched) it was observed that, presence of 5% $CaCO_3$ increases the impact strength then decrease as calcium carbonate increases .This could be due to the effect of brittle calcium carbonate content, which resulted in a lower strength. This result shows that calcium carbonate content significantly affected the impact properties [23]. In Fig (12) it was found that, Charpy notched impact strength at 5% increases then decrease at 10% and 20% of loaded talc.

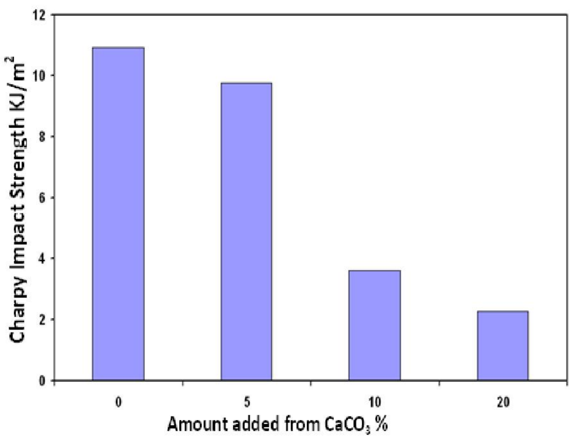


Fig (11) Represents the relation between Charpy impact strength KJ/m^2 with different amounts of Calcium carbonate.

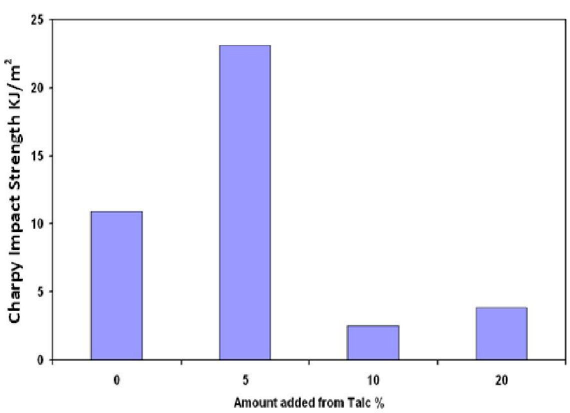


Fig (12) Represents the relation between Charpy impact strength KJ/m^2 with different amounts of Talc.

3.6 Hardness

Hardness is an important test for different application of rice straw /high density polyethylene composites, it was found that figure (13) which represents the effect of added amount of calcium carbonate on hardness, as increase of $CaCO_3$ amount increases the hardness .Also it was found that the hardness increases as talc amount increases till 10% but when reaching the talc to 20% the hardness of the composites decreases .The minerals had a remarkable effect on the mechanical properties of the RSF/HDPE composites. Both the tensile strength and hardness of the composites increased compared with the reference composite without adding any filler mineral [24].

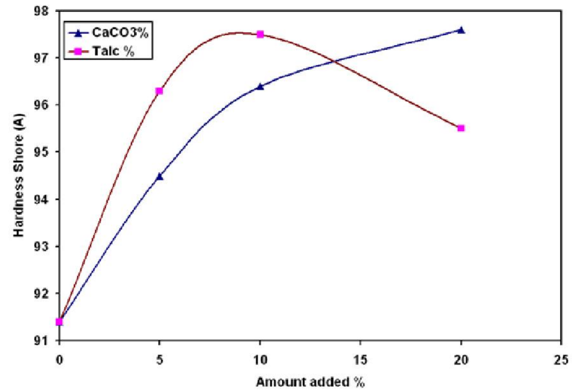


Fig (13) Represent the relation between hardness Shore (A) with different amounts of mineral filler added.

3.7. Water sorption characteristics

Water absorption and thickness swelling values of the composites were determined utilizing five samples with a dimension of 5 cm×5 cm. Thickness swellings of samples was calculated from the thickness measurements at five different points before and after samples submerged in distilled water for 24, 48 and 72 h . In the case of water absorption calculations, the weight of the samples before and after submerging in distilled water was determined detailed description of test procedures was given by Wechsler and Hiziroglu [25]. Water absorption in cellulose fibers is caused by hydrogen bonding between free hydroxyl groups of cellulose, and the water molecules; maleic anhydride groups on MAPE form hydrogen or covalent bonds with some of free hydroxyl groups of cellulose decreasing the water absorption capacity of cellulose. But the most frequently inserted method is employment of coupling agents. It was mentioned that coupling agents increase interfacial adhesion between fiber and matrix by chemical or physical interaction. Fig (14) represents the effect of time on the amounts of water absorption (%); water uptake was affected by calcium carbonate content. The water absorption of composites increased with increase of mineral $CaCO_3$ loading. This is due to the presence of hydrogen bond sites in natural fibers. The absorption of water by non- polar polymers, which contain fillers, depends on the nature of the fillers. For calcium carbonate, which is of hydrophilic sites, an increase in water sorption can be expected [26-29]. Addition of calcium carbonate to the prepared composites improves water uptake behavior than rice straw fiber. Also Fig (15) shows thickness swelling with immersion time which indicates dimension stability for the prepared composites.

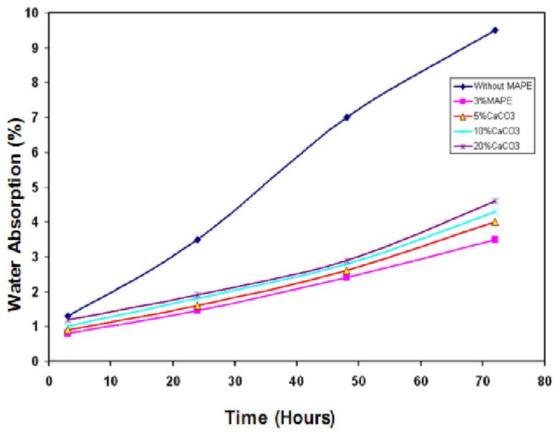


Fig (14) Represents the relation between Water uptake % with different immersion times.

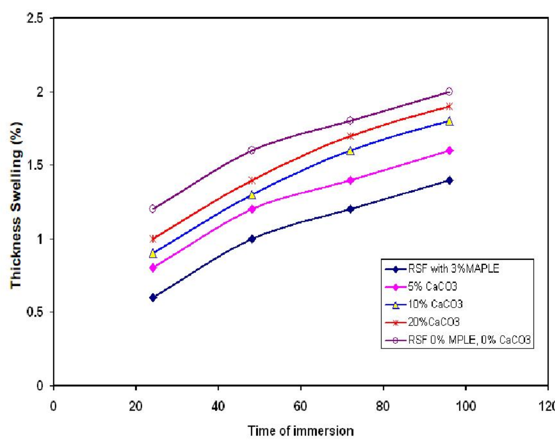


Fig (15) Represents the relation between thickness swelling (%) at different times of immersion.

3.8 Thermogravimetric analysis (TGA):

For studying the thermal stability of the prepared polymer composites, the Thermogravimetric analysis (TGA) was carried. The obtained results for the weight loss% changed with temperature was recorded and the obtained results are shown in Fig(16).From the figure it can be detected that at lower temperature until 200°C there is no large difference between the prepared composites formed from RSF/HDPE in presence of MAPE as compatibilizer and that with adding 10%$CaCO_3$, or 10% Talc, compared with pure PE. Thermogravimetric study showed that, the thermal stability of pure PE is higher than that of any other types of prepared polymer composites up to the high temperature (above 220°C) but at normal temperatures for using of polymer composites without rice straw (up to 220°C) there is no difference between Pure PE and the prepared RSF/HDPE composites.

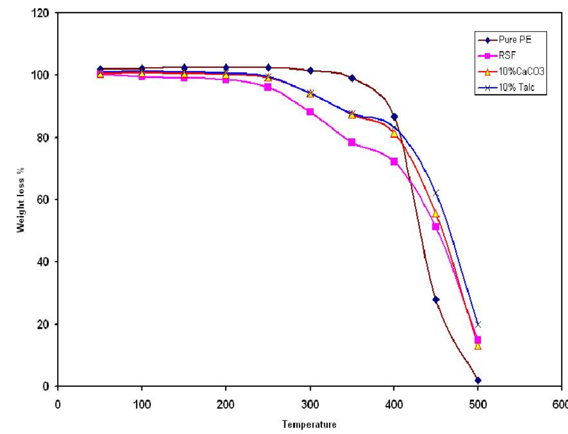
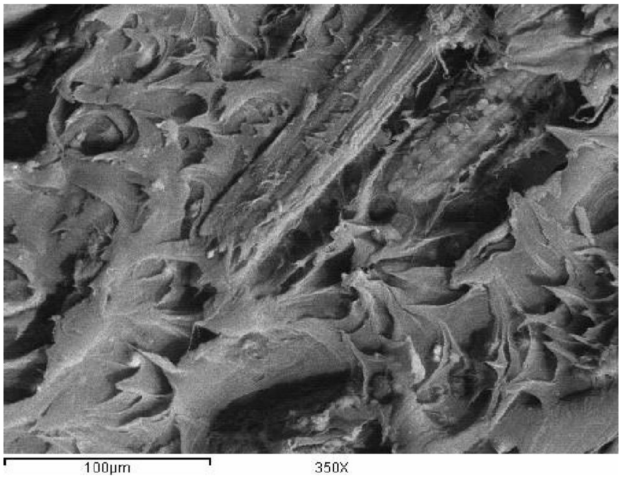


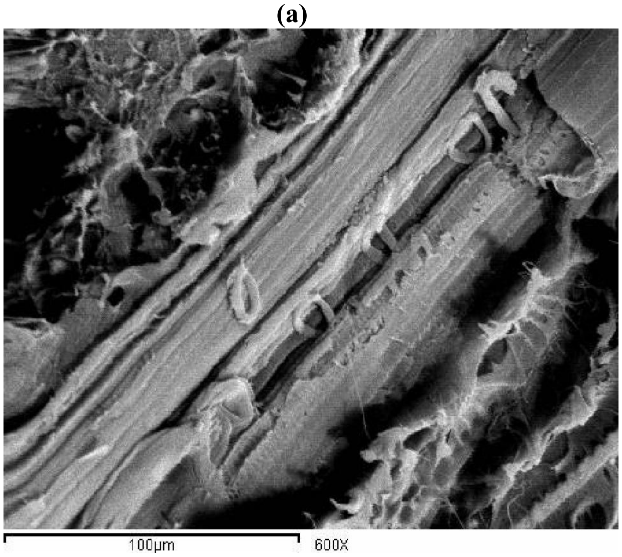
Fig (16) Represents the relation between Weight loss % at different Temperature.

3.9 Scanning electron microscopy (SEM):

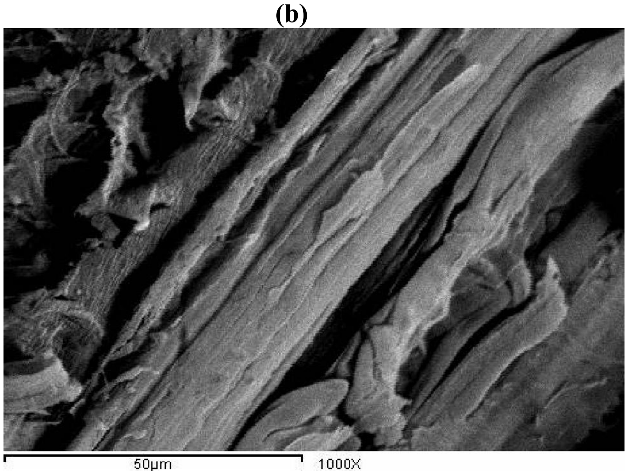
Samples were immersed in liquid nitrogen and fractured to ensure that the microstructure remained intact. Then samples were sputter coated by gold using a sputter-coater to avoid charging under the electron beam. [Fig (17)]. Represents the cross section of the specimens of RSF/HDPE/10% $CaCO_3$, RSF/HDPE/10% Talc composite respectively. It was found that the $CaCO_3$added to rice straw fibers/HDPE composite improves dispersiability, compatibility and interfacial bonding between rice straw fiber and HDPE as seen from figure (17 a,b,c) fiber coated with polymer. Fiber bundles embedded in the matrices due to good adhesion and compatibility between high density polyethylene and rice straw fibers. Bonding between the filler and the matrix polymer is strong, and the fracture did not occur at the interface but at the filler itself. This characteristic of the composite with compatibilizing agent (MAPE) and. Improved interfacial bonding leads to improved tensile property, which is reflected in the increased strength [Fig (17 d,e)] effect of Talc in homogeneity of composites and good dispersion is reflected on the physico-mechanical properties.



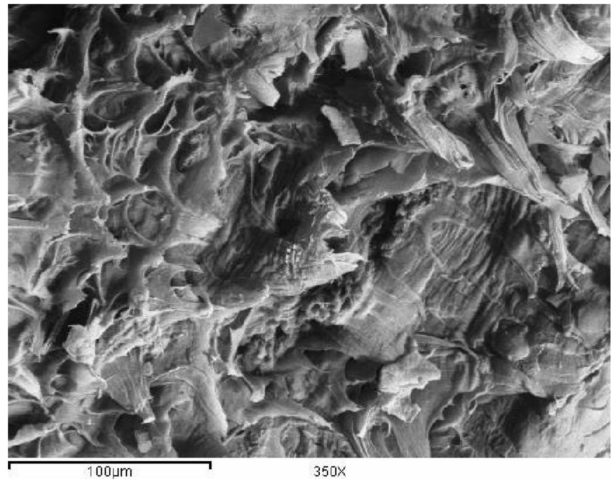
(a)



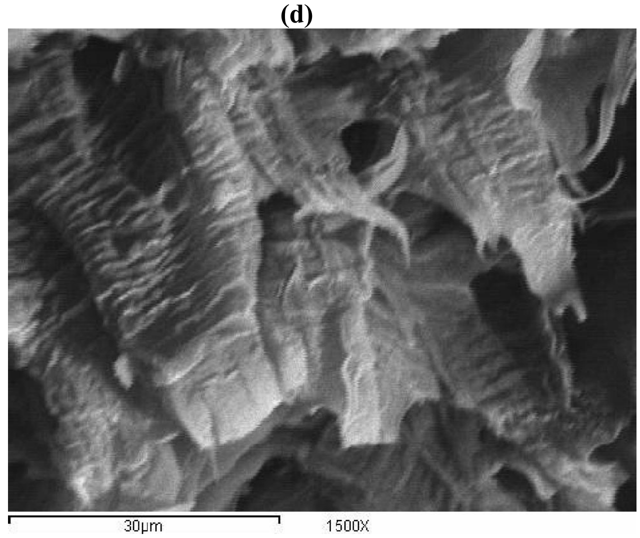
(b)



(c)



(d)



(e)

Figure (17) SEM observations of the composites (a)RSF/HDPE/10% $CaCO_3$ Composites with magnification 350x (b) RSF/HDPE/10% $CaCO_3$ Composites with magnification 600x (c) RSF/HDPE/10% $CaCO_3$ Composites with magnification 1000x (d) RSF/HDPE/10% Talc Composites with magnification 350x (e) RSF/HDPE/10% Talc Composites with magnification 1500x.

Conclusion

The following conclusions could be drawn from the results of the present study:

- Maleated polyethylene (MAPE) has a good effect on dispersiability of the prepared composites.
-Calcium carbonate and talc increase tensile strength and flexural strength till 10% added amount.
-Hardness increases as the amount added of $CaCO_3$ and talc increase.-
-Water absorption of the prepared composites of RSF/HDPE/$CaCO_3$ increases as amount of $CaCO_3$ added increases.
- The best amount which gives high impact strength was at 5%, but higher than this amount impact strength decreases as mineral filler loading increases.
-TGA indicates that there is no difference between the prepared composites and virgin polyethylene till 200^0C.
-Scanning electron microscopy was investigated to the prepared composites and revealed good interfacial adhesion.

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