International Journal of Environment & Water
ISSN 2052-3408

Utilization of Stone cutting waste powder as a compounding filler for polyethylene

Hassan Sawalha[1, 2*], Shadi Sawalha[1], Tahreer Yousof[1], Wala' Abu-Saa[1], Hiba Al-Sheikh[1],

[1] Chemical Engineering Department, An-Najah National University, P.O. Box 7, Nablus, Palestine
[2] Environmental Technology Engineering Department, Palestine Polytechnic University, Hebron, Palestine

Abstract

The present study aims at studying the possibility of compounding polyethylene using stone cutting solid waste (lime stone powder). Stone cutting waste powder (SCWP) mainly consists of calcium carbonate is usually disposed in open fields, roadside, sewage and agricultural land leading to several environmental and health problems. Samples of SCWP were collected and screened into different sizes. Polyethylene was compounded with the SCWP using an extruder and the compounded product was thermally pressed into sheets using thermal press machine. The mechanical and thermal properties of the resulting sheets were tested.

The results showed that the melt flow index of the composite sheets increases with decreasing the SCWP size, whereas it decreases with increasing the SCWP content. The elastic modules of the composites increased with increasing the SCWP content whereas the tensile strength decreased. The elastic modulus decreases dramatically with increasing the particle size of the SCWP up to a certain particle size (0.6 mm) after which it starts increasing with increasing the particle size. The addition of the SCWP improved crystallinity of the composites, however very high SCWP content disrupted the crystalline structure of polymer. The maximum value of melt flow index (4.1 g/min), tensile strength (11 MPa) and degree of crystallinity (53%) were obtained with the sample prepared with 30% w/w of 0.15 mm SCWP particles. On the other hand, the maximum elastic modulus value of (490 MPa) was obtained with the sample prepared with 60% w/w of 0.15 mm SCWP.

The main conclusion of the current study is that SCWP can be successfully utilized in improving the mechanical and thermal properties of polyethylene which helps in reducing the environmental impact of SCWP.

Introduction:

Polyethylene is the most common type of plastic that is extensively used in different applications due to its unique combination of properties, flexibility and cost. More than 70% of the total plastics market is polyethylene [1]. For instance, polyethylene based plastics are relatively cheap, chemically inert, very durable and has a good mechanical and thermal characteristics [2]. The polymer is, therefore, largely used in making variety of products including packaging material, shampoo bottles, milk container, toys, grocery bags, and gas and water pipes [3].

Polyethylene plastics are commonly compounded with fillers and additives to improve their mechanical and physical properties, durability, aesthetic appeal and process-ability, rigidity, dimensional stability, hiding power as well as reducing the costs of the raw materials. In general, the mechanical properties of the filled polymer composites depend strongly on the concentration, size, shape and distribution of filler particles within the polymer matrix [4-7]. Several studies showed that as the filler loading increases, the flexural strength, flexural modulus and tensile strength increases [4-7]. The flexural strength, flexural modulus and tensile strength increases, however, with decreasing the particle size. Calcium carbonate ($CaCO_3$) is one of the most popular mineral fillers used in the plastics industry [8]. Compounding plastics with $CaCO_3$ offers several advantages. For instance, its high chemical purity eliminates the negative catalytic effect on the aging process of the polymers, and its high whiteness and low refractive index reduces the consumption of expensive abrasive pigments such as titanium dioxide. Besides, the low abrasiveness of $CaCO_3$ reduces the wearing of the screws and cylinders of the extruder during processing [9]. Calcium carbonate is normally obtained from stone mines, but stone cutting industry produces large amount of slurry with high calcium carbonate content.

In Palestine, stone cutting industry is largest industrial sector that significantly contributes to the GDP of the country. Large rock blocks from local quarries are cut into the desired shape and size and used in constructing and decorating houses and buildings. Water is used during stone cutting process for cooling and lubricating the saws of the cutting machines and collecting the resulting dust. The resulted wastewater which is mainly contaminated with fine stone particles is collected and treated through sedimentation process to separate the stone particles form water [10]. The treated water is then recycled to the stone cutting plant and stone cutting sludge is disposed in open fields, roadside, sewage, agricultural lands and valleys which dries over time and stone cutting waste powder (SCWP) is produced (see figure 1) [10]. The Palestinian stone cutting plants annually produces about one million tons of SCWP and disposal of SCWP in agricultural land and other open area causes several environmental problems to the surface and ground water, air quality, soil, flora and fauna [11,12]. For instance, the high SCWP content in the soil increases pH of the soil lowers the fertility which adversely affects the plant growth. Moreover, lime cemented hard pans are formed as a result of the accumulation of calcium carbonate from SCWP on the soil surface which limits infiltration of water and root penetration into the soil layer. In addition, dumping the SCWP into the sewage systems creates blockages and damages the pumping stations [11, 12].

The aim of the current project is to study the possibility of compounding polyethylene with SCWP which mainly consists of $CaCO_3$. SCWP will be collected from local plants and screened into different sizes. The polyethylene will be then compounded with SCWP using an extruder and the compounded product is then pressed into thin sheets using thermal press machine. The mechanical, thermal and melt flow properties of the resulting compounded sheets will be tested.

Figure 1: photographs of stone cutting waste sludge

2. Experimental

2.1 Materials

Linear low density polyethylene (LLDPE), (Sabic, Saudi Arabia) was obtained from Palestine Plastic Industries Company LTD (Nablus, Palestine) and used as polymer. Its melt flow index, density, tensile strength at yield and flexural modulus as reported by the manufacture were 5 g/10min, 0.935 g/cm^3, 18 MPa and 724 MPa, respectively. Clean and not chemically treated SCWP was collected from local stone cutting plants located in Tulkarm, Palestine.

2.2 Screening

The SCWP was screened into different sizes using mechanical sieve shaker (Test Sieve Shaker, Endecotts LTD, London, UK). About 500g of the SCWP was placed onto the top sieves with the nest is covered, and then shacked by the mechanical sieve shaker until particles are fractionated. The particles retained from the top of the sieves of mesh sizes of 0.15 mm, 0.3mm, 0.6mm 2.36 were collected in separate bottles.

2.3. Preparation of compounded LLDPE-SCWP samples.

LLDPE-SCWP samples with different SCWP weight fractions (30%, 40%, 50% and 60%) of different particle sizes (0.15, 0.3 0.6 and 2.36 mm) were firstly mixed and tumbled to obtain homogenous dry mixtures. The LLDPE-SCWP mixtures were then compounded together using single screw extruder at 200 °C to produce composites in a form of rods. The compounded rods were extruded for the second time to insure uniform distribution of the SCWP particles within the polymer matrix. The extruded rods were then crushed using a crushing machine and the crushed compound were thermally pressed at 180 °C for 30 min using a thermal press machine and then cooled down to room temperature using water to form molded sheets.

2.4. Melt flow index (MFI)

Melt flow index measurements of the composites were carried out using MFI device (XH-408B Melt Flow Index Device, China) at 190˚C and under 2.16 kg weight. A small amount of the crushed composite (about 5g) was preheated for some time to reach the predetermined temperature on the plunger to extrude the melt through the capillary die. After a steady flow was reached (almost after 10 min) a sample of the melt was taken and accurately weighed. The samples were tested in triplicate.

2.6. Mechanical properties

The mechanical properties (ultimate strength and elastic modules) of the molded sheets were determined using (Testing Machine ST series, Sinowon, China). The composite sheets were cut into dog-bone like shape with a gage length of 40(mm) and a minimum width of 10mm. The tensile tests were performed at a constant cross-head of 4(mm/min) with a fixed gauge length of 39.91(mm). The ultimate tensile strength and elasticity modulus were determined for all samples.

2.7. Thermal properties

The differential scanning calorimeter (DSC model pyrix-6, Perkin Elmer, corporation U.K) was used to study the thermal properties of the LLDPE-SCWP composite. Samples of (4-6 mg) were cut from the sheets and placed in stainless steel pans. Sample were scanned through heating from 25˚C to 200˚C and then cooling down to 25 ˚Cat rate of 10˚C/min. The melting temperature and enthalpies of melting of the samples were then determined from the DSC thermographs. The degree of crystallinity (Xc) of the composite was determined from the DSC data using the following equation:

$$\left(\frac{\Delta H_f/(1-x)}{\Delta H_{f^o}}\right) * 100\%$$

Where ΔH_f is the heat of fusion of the sample, ΔH_f^o is the heat of fusion of 100% crystalline LLDPE which taken from literature as (293J/g) [13] and x is weight fraction of the SCWP in the sample.

3. Results and discussion

3.1 Melt flow index

The MFI properties of polymers highly affects their process-ability and ease of flow during fabrication and should be maintained within a certain range depending on the type of polymer. The effects of concentration and particle size of SCWP on MFI of the LLDPE-SCWP composites was investigated. Figure 2 shows the effect of the SCWP concentration on the MFI of the LLDPE-SCWP composites having same particle size of 0.15 mm. It is clear from the figure that the MFI decreases with increasing the SCWP concentration, indicating that the presence of SCWP within the polymer matrix increases the viscosity of the molten polymer which hinders the flow of polymer upon processing. It is worth mentioning here that with SCWP content up 40% the MFI of the composites was close to that of neat LLDPE sample. The MFI of the composites, however, increases with decreasing the particle size of the SCWP as shown in figure 3, indicating that the smaller the size of the SCWP, the better the compounding and adhesion with the LLDPE matrix and the lower the viscosity of the melt.

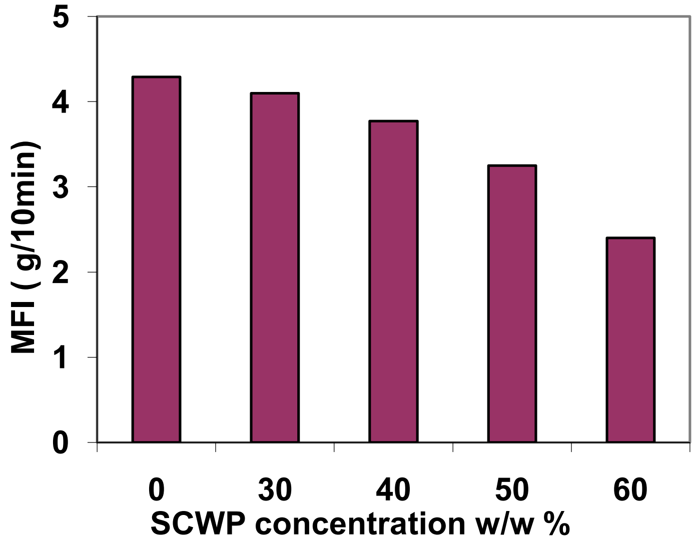

Figure 2: Effect of SCWP concentration on the MFI of LLDPE-SCWP composites. The average SCWP particle size is 0.15 mm.

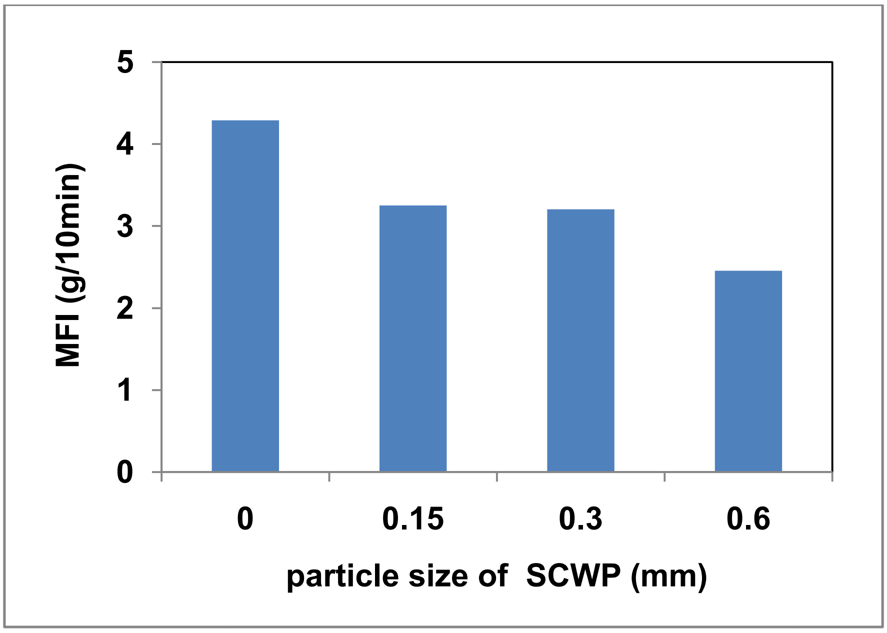

Figure 3: Effect of SCWP particle size on the MFI of LLDPE-SCWP composites. The concentration of SCWP is kept at 50% w/w.

3.2 Mechanical properties

The effect of SCWP concentration and particle size on the mechanical properties (Ultimate tensile strength and elastic modulus) of LLDPE-SCWP composites was studied. Figure 4 shows the ultimate tensile strength and elastic modulus as a function of the concentration and particle size of the SCWP. Figure 4a shows that the tensile strength of the composites decreases with increasing SCWP content, whereas an increase in the elastic modulus with the SCWP content was observed (see figure 4b). The increase in the elastic modulus of the composite suggests a strong interaction between LLDPE and SCWP filler due to the large interfacial area. On the other hand, the increase in the SCWP content seems to induce agglomeration and nucleation of the filler particles within the polymer matrix which reduces the size of crystalline spherulites of the polymer and consequently decreases the maximum strength of the composites. The effect SCWP on the mechanical properties of the composite was further studied through varying the particle size of the SCWP keeping the SCWP content constant at 50%. Figure 5 shows the effect of the size of the SCWP particles on the maximum strength (figure 5a) and elastic modulus (figure 5b) of the composites. The changes of the tensile strength with varying the SCWP content was not significant whereas the elastic modulus was strongly dependent on the filler's particle size. The elastic modulus decreases dramatically with increasing the particle size of the SCWP up to a certain particle size (0.6 mm) after which it starts increasing with increasing the particle size. For instance, the elastic modulus decreased from approximately 420 MPa to 200 MPa when increasing the particle size from 0.15 mm to 0.6 mm, respectively, then it increased to 330 MPa with increasing the particle size to 2.36 mm. The dispersion of the filler's particles within the polymer matrix determines to a great extent their mechanical performance; the better the dispersion the better the reinforcement of the composite and the dispersion of the particles depends on their size. The dispersion of small particles within the polymer matrix is better than the large ones, but one should keep in mind for the same filler content, the number of small particles is larger than that large particles giving the chance for small particles to agglomerate more than the large ones. This suggests that there is an optimum (size/number) ratio of the reinforcing particles that highly determines the mechanical performance of the composite. For better understanding of the mechanical properties of the composite, the thermal properties and crystallinity of the composites were studied and the results are discussed in the following section.

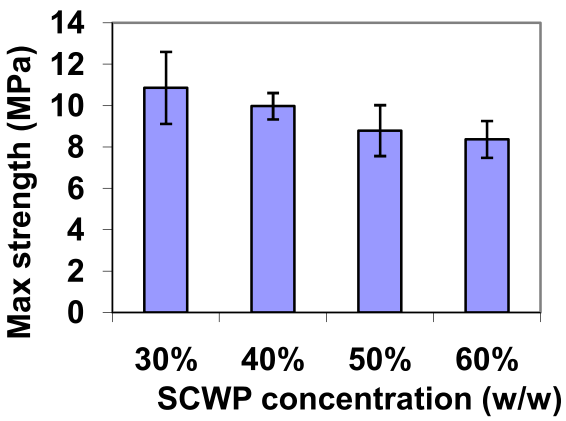

Figure 4a: Effect of SCWP concentration on the maximum strength of LLDPE-SCWP Composites. The average SCWP particle size is 0.15 mm.

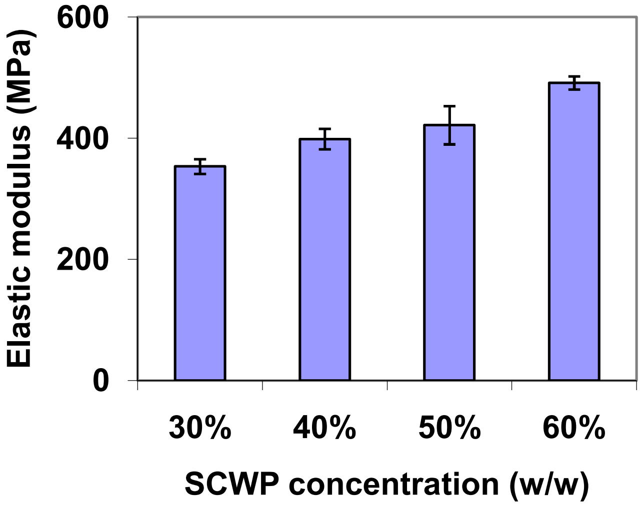

Figure 4b: Effect of SCWP concentration on the elastic modulus of LLDPE-SCWP Composites. The average SCWP particle size is 0.15 mm.

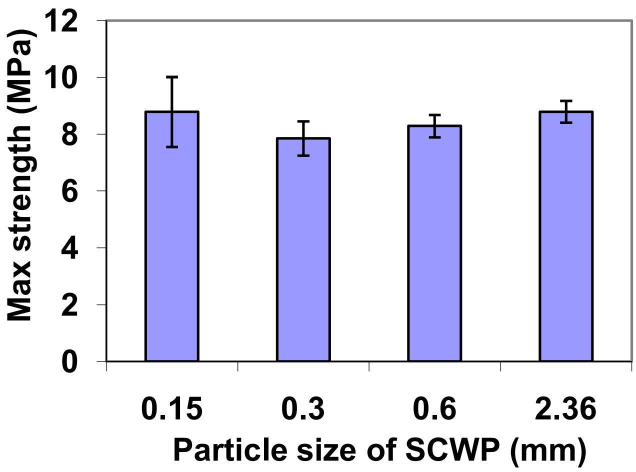

Figure 5a: Effect of SCWP particle size on the ultimate of LLDPE-SCWP composites. The concentration of SCWP is 50% w/w.

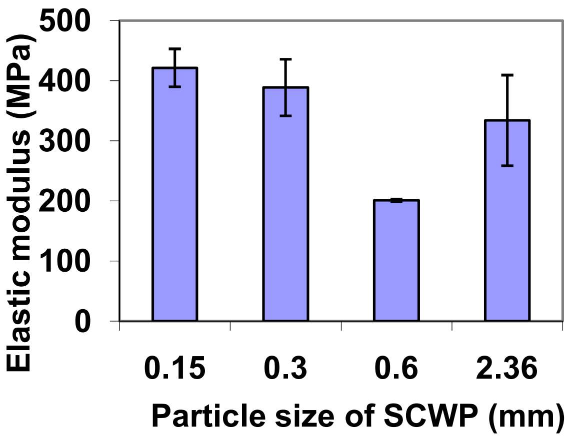

Figure 5b: Effect of SCWP particle size on the elastic modulus of LLDPE-SCWP composites. The concentration of SCWP is 50% w/w.

3.3 Thermal properties:

The effect of the SCWP concentration on the thermal properties of the composites was investigated using DSC technique. Three samples with different SCWP content of 0, 30 and 60% w/w of 0.15 mm particles were tested. Typical DSC heating and cooling curves of the LLDPE-SCWP composite are shown in figure 6 and summary of the results is given in Table 1. The DSC heating curves showed endothermic melting peaks with close melting temperatures ranging between 112 ˚C and 115˚C, but no cold crystallization peaks were observed. The degree of crystallinity of the composites was higher than that of pure LLDPE sample (see Table 1). However, the sample prepared with 60 % SCWP showed crystallinity degree (~40%) lower than that of 30% SCWP (~ 53%). The presence of high filler content within the composite seem to interrupt the crystalline structure and reduce the size of crystalline spherulites of the polymer, yielding to the formation amorphous structures. This supports the findings of the reduction in the tensile strength with increasing the filler content (see figure 3a).

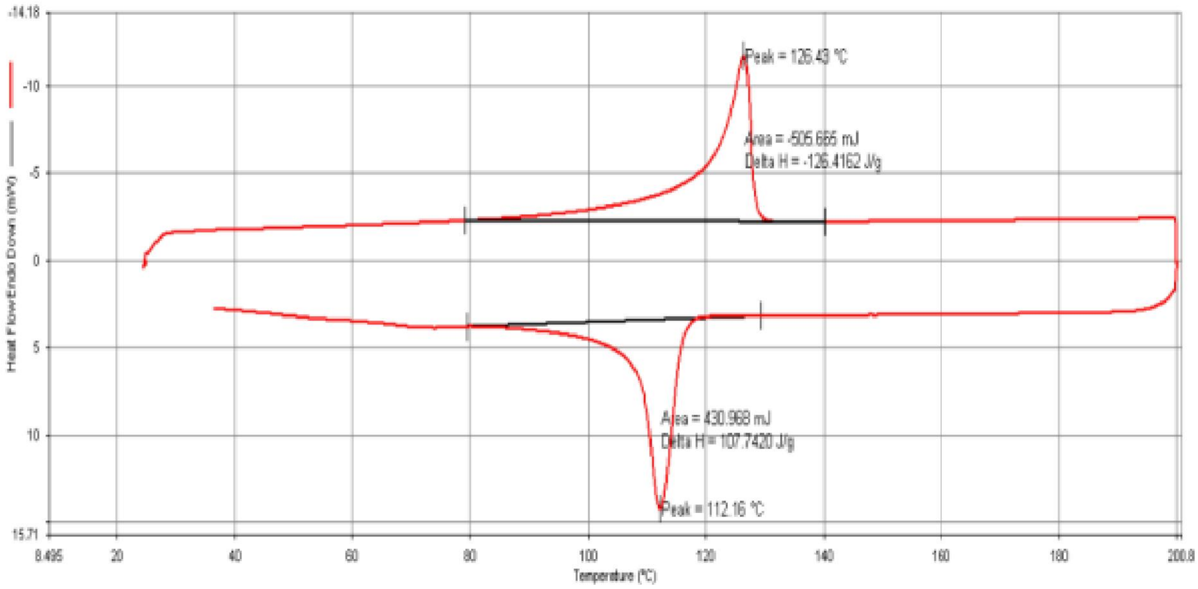

Figure 6: DSC heating and cooling curves of LLDPE-SCWP composite prepared with 60% w/w of 0.15 mm SCWP particles.

Table 1: Thermal characteristics of LLDPE-SCWP composites prepared with different SCWP content of 0, 30 and 60% w/w of 0.15 mm particles .

SCWP content x (w/w)	Tm [˚C]	ΔHm [J/g]	Xc %
Pure LLDPE	112.33	107.86	37
0.3	112.16	107.74	53
0.6	114.95	46.23	39

4. Conclusions:

In this study, the SCWP which poses real threats to the local environment in Palestine, was successfully utilized as compounding filler for polyethylene plastics. The elastic modules of the polymer-SCWP composites increased with increasing the SCWP content whereas the tensile strength decreased. The composites prepared with small SCWP particle size showed better mechanical performance than the large ones up to a certain critical size. The addition of the SCWP improved crystallinity of the composites, however very high SCWP content disrupted the crystalline structure of polymer. The MFI of the composites decreased with increasing the filler content, however it increases with decreasing the filler's particle size.

References

1. H.Raghu, S. Bose and P.Mahanwar, Effect of Particle Size of Filler on Coloration and Properties of High Density Polyethylene. Journal of Minerals & Materials Characterization & Engineering, 2006.5(1).

2. A.Pusz, k.Michalik; Fractografic Study of High Density Polyethylene Gas Pipe Following Small Scale Steady State Test. Journal of Achievements in Materials and Manufacturing Engineering, 2010.38 (2).

3. **B. Kowalska, D. Kowalski, M. Kwietniewski, A. Musz**, Influence of Polyethylene Pipe on the Quality of Water in a Water Distribution System. Journal of Sustainable Development, 2013.6 (2).

4. V.Betingyte , K. Zukiene, V.Jankauskaite, D.Milasiene, K.Mickus, A.Gulbiniene, Influence of calcium carbonate fillers on th properties of recycled poly (ε-caprolactone) based thermoplastic polyurethane, Materials science (Medziagotyra),2012.18 (3)

5. R. Deanin, Additives in Plastics. Environmental Health Perspectives, 1975.11: P.35-39.

6. A.Olad, A.Rashidzadeh, preparation and characterization polyaniline/$CaCO_3$ composite and its Application as Anticorrosive Coating on Iron, Iranian Journal of Chemical Engineering, 2008.5 (2)

7. M. Kulkarni, P.Mahanwar, Effect of Methyl Methacrylate– Acrylonitrile -Butadiene–Styrene (MABS) on the Mechanical and Thermal Properties of Poly (Methyl Methacrylate)(PMMA)-Fly Ash Cenospheres (FAC) Filled Composites, Journal of Minerals and materials characterization and engineering, 2012.11(4)

8. X. Huang, J.Y. Hwang, and J.M. Gillis, Processed Low NOx Fly Ash as a Filler in Plastics. Journal of Minerals & Materials Characterization & Engineering,2003.2 (1).

9. C.Armitt, Additives Feature Filler, Compounding World 2010.

10. M. Aljabari and H. Sawalha, "Treating Stone cutting Waste by Flocculation-Sedimentation", 28th WEDC Conference Sustainable Environmental Sanitation & Water Services, Kolkata (Calcutta) India, 18-22 November 2002.

11. N. Al-Joulani, Soil Contamination in Hebron DistrictDue to Stone Cutting Industry. Jordan Journal of Applied Science, 2008. 10 (1).

12. K.Alzboon, K.Mahasneh, Effect of Using Stone Cutting Waste on the Compression Strength and Slump Characteristics of Concrete. International Journal of Civil and Environmental Engineering, 2009.4(1).

13. B. Wunderlich, C.M. Cormier, Heat of Fusion of Polyethylene. Journal of Polymer Science: Part B Polymer Physics, 1967. 5