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# EFFECT OF SEA CRAB (CALLINECTES AMNICOLA) SHELL PARTICLES REINFORCEMENT ON HIGH DENSITY POLYETHYLENE COMPOSITE

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## ABSTRACT
*The use of environmental friendly materials that are renewable play valuable roles in reinforcements as natural fillers. This study examined the effect of using sea crab shell particles as reinforcing material in high-density polyethylene (HDPE). The composites were produced by varying the sea crab shell particles at 10, 20 and 30 wt.%. The elemental composition of the sea crab shell was determined using X-ray fluorescence spectrometry (XRF). The results of the XRF analysis showed that pulverized sea crab shell particles contains Ca, Al, Si and Fe as the major constituents while Mg, $P_2$, Ti, $K_2$, and $Na_2$ were present in traces. The physical and mechanical properties of the reinforced HDPE were also determined. As the particle content increased from 10 to 30%, the density of the composite was observed to increase from 0.95 to 1.1091g/cm$^3$.The tensile strength obtained increased from 15.36 to 17.91 MPa at 10% particle loading. The Young's modulus increased in proportion to increase in particle loading while the percentage elongation decreased. The impact strength also decreased with particles content. Furthermore, the flexural strength increased though the best result was obtained at 20%. The obtained results of the developed composites showed that sea crab shell particles is a viable reinforcement for polymer- matrix composite.*
***Keywords**: Sea crab shell, HDPE, X-ray fluorescence, reinforcement.*

## INTRODUCTION
Materials engineering and technological advancement currently require the application of functional composite materials with uncommon combination of properties. A composite material is developed by the combination of two or more materials. It is efficiently developed to exhibit high standard properties that cannot be exhibited if the individual materials had worked alone. The material with the higher percentage in a composite is called a matrix with other additional materials called reinforcements. These reinforcements may be fibrous or particulate whereby the distribution and geometry is structured to enhance one or more property (Smith and Yeomans, 1995).

Usually, the term composite is mostly used to refer to multiphase systems artificially made or deliberately tailored to meet specific applications. Polymer-based composite materials are being used in a wide range of structural applications and are made by the combination of polymers with organic or inorganic additives (one common additive material mostly used is glass fibre). Polymer-matrix composite materials applications range from small sail boats and domestic products to high performance carbon fibre epoxy systems utilized in military aircraft and spacecraft. In the automobile industry, polymer composite materials offer the possibility of reducing vehicle weight, thus increasing fuel efficiency and reducing $CO_2$ emissions (Aigbodion *et al.*, 2013). Additives for polymer composites have been variously classified as reinforcements, fillers or reinforcing fillers (Shnean, 2012; Callister, 2007; Griskey, 2008). These reinforcements are usually stiffer and stronger than polymers and as such enhance properties such as modulus and strength. Reinforced polymer composites offer some remarkable advantages, such as a high strength to weight o, enhanced corrosion resistance, and longer fatigue life in application as compared to metallic alloys (Misra *et al.*, 2008).

Polyethylene is a widely used thermoplastic generally grouped as high density polyethylene (HDPE) and low density polyethylene (LDPE), depending on the polymerization method applied during synthesis of ethylene (Lin *et al.*, 2005; Yasim and Daniel, 2004; Kalpakjian and Schmid, 2008; Masuelli, 2013; Riham, 2014; Taj *et al.*, 2007). A variety of additives in the form of fillers and reinforcements are added to polyethylene to meet various engineering requirements. Natural reinforcement is favoured over synthetic reinforcement due to positive environmental benefits such as utilization of agro waste leading to a sustainable environment (Maleque *et al.*, 2012; Bobelmann *et al.*, 2007; Abdel-Kader and Darweesh, 2010). They also have added advantages of being in abundance, renewable, cheap and biodegradable (Darweesh and Abo El-Suoud, 2014).

These achievable advantages prompted several researches into polymer composites made with natural reinforcements (Singha and Rana, 2012). Al-Sultani (2010) reported an experimental study on the mechanical behaviour of high density polyethylene (HDPE) using wheat straw composites. The results revealed that increasing wheat straw rate to 30 % in both fine and coarse forms, improved the tensile strength, hardness, flexural and impact strength values of the composite. Kumar *et al.* (2013) studied the effect of banana fibre reinforced high density polyethylene (HDPE)/polyamide (PA)-66. The work of Aigbodion *et al.* (2013) prepared composites of orange peels particles (un-carbonized and carbonized) as a reinforcing material with high-density polyethylene (HDPE). The results obtained showed that orange peel waste could be used as

biodegradable eco-friendly reinforcement. Danladi and Shu'aib (2014) fabricated and examined the properties of pineapple fibre reinforced HDPE. The results obtained for the impact strength, hardness , tensile strength and elongation of the composites were all found to decrease with increase in the reinforcement (Adnan *et al.*, 2015).

Sea crab (*callinectesamnicola)* shell is an agricultural waste found in all oceans or fresh water of the world. They are usually harvested in the coastal region of Nigeria, most especially in Lagos state, where the shell exists in abundance as waste product. Crab shell is primarily composed of calcium carbonate (Darweesh and Abo El-Suoud, 2014) and it also contains chitin. Both of which are eco-friendly compounds with many industrial applications. There is currently no available information in literature on the use of sea crab shell as reinforcing material for high density polyethylene (HDPE). Hence, this study is aimed at investigating the effect of sea crab shell particles on high density polyethylene composite. It is imperative for natural organic materials to find use in industrial and manufacturing applications. Also, there is the need to improve the mechanical properties of HDPE. This composite is expected to find applications in car bumpers, phone protective coverings, and in the aerospace industry.

## MATERIALS AND METHODS

### Materials and Equipment

Sea crab (*callinectesamnicola)* shell was used as the reinforcing material in the formulation of the composite samples. The sea crab shells were obtained from Oyingbo market, Lagos state and the high density polymer was obtained from a Chemical supply vendor.

### Material Preparation

The sea crab shells collected were sun dried for 4 weeks and ground into powder using a hammer mill. It was subsequently sieved with different apertures ranging from 75 – 425 µm. The finest particles (75µm) were used asshown in Figure 1.

Figure 1: Sieved sea crab shell particles (75 µm)

### Mixing and Moulding

The mixing and moulding of the materials were carried out on a two roll mill. The rolls were preheated to the processing temperature of HDPE ($135^0C \pm 5^0C$).On attainment of this temperature; the HDPE was squashed until a liquid melt was obtained. The Crab Shell Particles (CSP) were then added and mixed with the liquid melt until homogeneity was obtained. The resulting mix was placed in a mould and compounded into a flat sheet using a compression moulding machine. The above procedure was repeated with the crab shell particles concentration varied according to Table 1. Figure 2 shows the produced composite samples.

Table 1: Sample formulation

| Material | Control (%) | Sample 1 (%) | Sample 2 (%) | Sample 3 (%) |
|---|---|---|---|---|
| *Sea Crab Shell* | 0 | 10 | 20 | 30 |
| *HDPE* | 100 | 90 | 80 | 70 |
| *Total* | 100 | 100 | 100 | 100 |

Figure 2: Formulated composite samples

### Characterization and Analysis of Formulated Composite Samples

#### X-ray fluorescence spectrometry (XRF) analysis

The XRF analysis was carried out on Sea crab (*callinectesamnicola)* shell using an X Supreme 8000 oxford instrument in compliance with ASTM D 4294. The pulverized sea crab shell was prepared and loaded on the machine tray and analyzed using the X-ray fluorescence spectrometry (XRF).

#### Density test

The density of the composite samples was determined using Archimedes principle. The mass of the samples in air was measured and recorded and its effective mass when submerged in water was also recorded. Then the density was calculated using the formula in Equation (1):

$$Density(\rho) = \frac{mass(M)}{volume(V)} \quad (1)$$

#### Tensile test

Hounsfield tensometer was used to carry out the tensile test with maximum load of 1.2 kN. Sample with dimension $40\times 8\times 5\ mm$ was mounted on the clamps of the Tensometer. The distance between the clamps was gradually increased until failure. The applied force that initiated the failure and the change in length of the specimen were measured by the tensometer.

#### Hardness test

Hardness test was carried out using a durometer in accordance with ASTM D 2240. The sample was placed on the sample holder and the indenter knob was pressed on it and the hardness value was read as displayed on the pointer at three indentations, taking the average value as the hardness value in IRHD (International Rubber Hardness Degree).

**Impact test**

The test was achieved using ResilImpactor test instrument. The test sample was positioned on the test machine and firmly held and the total energy absorbed during impact was recorded. The calculation for the impact strength was thus calculated using Equation 2 [21].

$$\text{Impact strength} = U/A \quad (J/m^2) \tag{2}$$

Where U denotes the impact value of the specimen as displayed, (A) represents the area of the specimen.

$$A = l \times b \tag{3}$$

$l$ and b depict the length and breadth of the specimen, respectively.

**Flexural test**

The dimension of the specimen used for the flexural strength test was 30×100×8 mm. The test was administered at a constant support span of 80 mm and the load was applied via a hand pump. Values of the applied load and deflection were recorded from the extensometer digital readout. The flexural strength was calculated using Equation (4).

$$\text{Flexural strength } (F.S) = \frac{3FL}{2bd^2} \tag{4}$$

Where F denotes the load at a specified point of fracture in newton, L represents the gauge length of the support span in millimetres, b is the width of the sample in millimetres and d connotes the specimen thickness in millimetres.

**RESULTS AND DISCUSSION**

**XRF Analysis of Sea Crab Shell particles**

The result obtained from the X-Ray Fluorescence (XRF) analysis is shown in Table 2. Calcium has the highest concentration in its oxide form (63%). The analysis also showed traces of few metallic and non-metallic oxides. This result corresponds with previous works on the composition analysis of sea crab shell particles. Noureddine *et al.* (2014) while studying the crystalline structure of crab shell particles (CSP) using X-ray diffraction observed that the diffraction intensity of calcite was very strong indicating a large percentage of calcium in CSP. Arulvel *et al*. (2017) also characterized CSP using Energy Dispersive X-ray Spectroscopy (EDS) and Fourier transform infra-red spectroscopy (FTIR). The EDS gave the elemental analysis (Figure 3) indicating a high percentage of calcium and oxygen while the FTIR showed the presence of carbonate ions.

| Element | Net Counts | Weight % | Atom % |
|---|---|---|---|
| O | 14602 | 57.51 | 76.26 |
| Mg | 2529 | 2.45 | 2.14 |
| Al | 235 | 0.22 | 0.18 |
| Si | 87 | 0.08 | 0.06 |
| P | 2191 | 2.13 | 1.46 |
| K | 264 | 0.32 | 0.17 |
| K | 0 | - | - |
| Ca | 24302 | 37.29 | 19.74 |
| Ca | 0 | - | - |
| Zn | 0 | 0.00 | 0.00 |
| Zn | 603 | - | - |
| Total | | 100.00 | 100.00 |

Figure 3: Elemental composition of CSP (Arulvel *et al.*, 2017)

The high percentage of calcium and carbonate ions in CSP indicates that CSP can serve as a good source of calcium carbonate thereby making it a reinforcing agent in composites as calcium carbonate is being widely used in industrial applications due to it good mechanical properties. Also, the difference in the type and composition of the metal oxides form the previous works can be attributed to locational differences in the CSP analyzed.

Table 2: Composition of sea crab shell

| Element | Concentration (wt %) |
|---|---|
| $Na_2O$ | 0.00 |
| MgO | 2.41 |
| $Al_2O_3$ | 20.42 |
| $SiO_2$ | 10.88 |
| $P_2O_5$ | 7.06 |
| $K_2O$ | 0.73 |
| CaO | 63.03 |
| $TiO_2$ | 0.60 |
| $Fe_2O_3$ | 6.60 |

**Density**

The values of the calculated density for the various composition of produced composite are shown in Figure 4. There is appreciable change in the density of the Pure HDPE compared to the composite. The density increased with increasing particle content. Even though the increase in density is minimal it limits the use of the composite in applications where very low density (below 1 g/cm$^3$) is required.

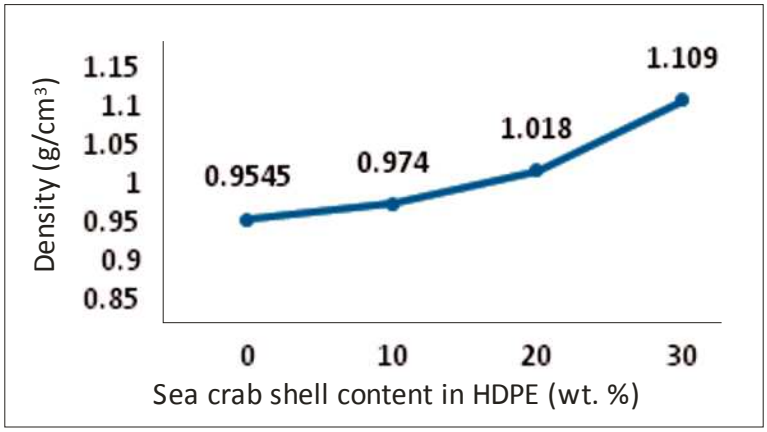


Figure 4: Density of composite with various compositions of sea crab shell particles

**Tensile Strength**

The result for the tensile test of the various compositions is presented in Figure 6. The tensile strength increased with weight fraction of sea crab shell particles in the composite to 10 wt. % and subsequently decreased. A similar observation was reported by Aigbodion *et al.* (2013) and Akanbi *et al.* (2015). Ku *et al*. (2011) also reported the same trend for the tensile strength of natural fiber reinforced composites. The subsequent decrease in tensile strength can be attributed to the decrease in the interfacial area as particles content increased. It can also be seen from Figure 5 that the percentage elongation and tensile strength took the same format. This is because the particles tend to restrict the movement of the HDPE. The percentage elongation and Young's modulus (modulus of elasticity or stiffness) show an inverse relationship i.e. as the percentage elongation decreases with increasing particles content, the modulus of elasticity increases. Thus, an increase in the particle content resulted in a corresponding increase in the value for Young's modulus. For the composition with 30 wt. % of crab shell particle material, the deviation in the trend for percentage elongation and value for Young's modulus can be attributed to uneven distribution of the particles in HDPE. It may also be due to the poor interfacial bonding between the polymer and the reinforcement.

**Hardness**

The hardness value for the various composites is shown in Figure 7. The hardness values of the composite samples show a general increase as the percentage of sea crab shell particles increased in the HDPE matrix. There was an initial decrease at 10 wt. % of the particles and then a subsequent increase. It is thus seen that the addition of sea crab shell particles increases the general hardness of the composite. The increase in the hardness indicates that CSP-HDPE interactions offered a large indentation resistance.

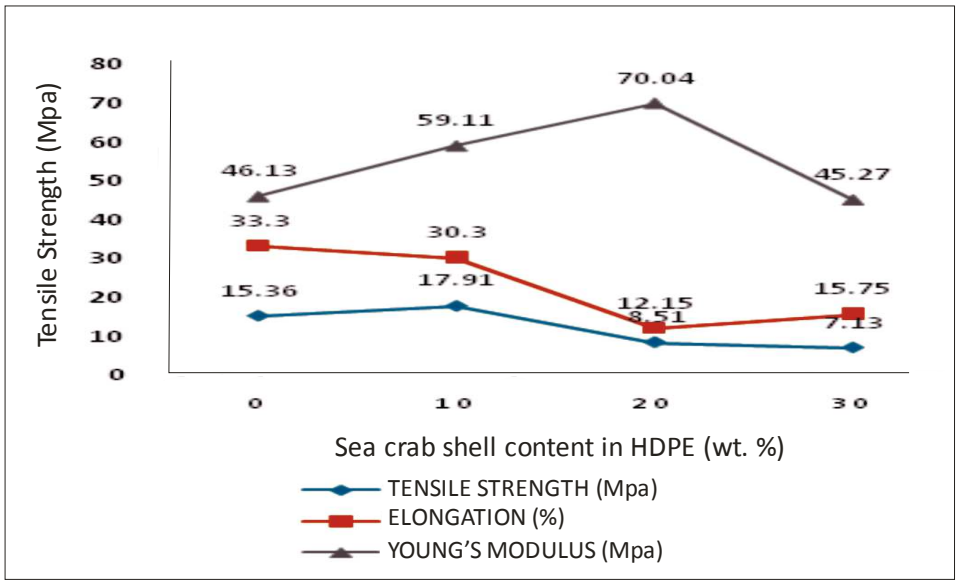


Figure 5: Variation of the tensile strength, percentage elongation and young's modulus with percentage weight of sea crab shell particles

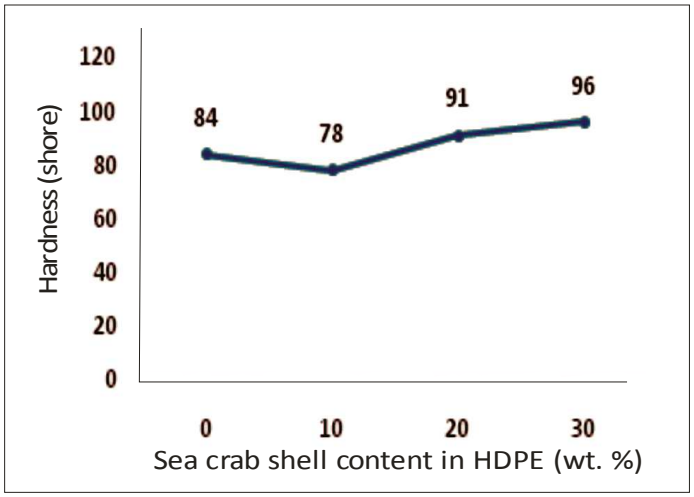


Figure 6: Variation of hardness with percentage by weight of sea crab shell particles

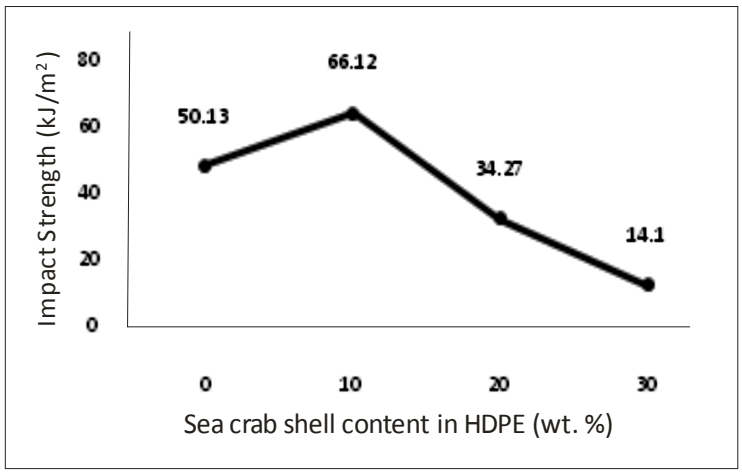


Figure 7: Variation of impact strength with increasing wt. % of sea crab shell particles

**Impact Strength**

From the result of impact strength shown in Figure 8, it was observed that there was a general decrease of the impact strength with increasing particles content. At 10 wt. % of particles content, t he impact strength rose considerably before dropping with increasing particle content. The impact strength is a me asure of a materials ability to absorb sudden application of load. The poor impact strength property shown by the composite can be attributed to the poor dispersion of the crab shell particles in the composite. Ununiformed dispersion of particles in a matrix causes spots of aggregates in the composite. These spots serve as stress concentrations thereby allowing the quick and easy propagation of cracks (Tanniru and Misra, 2015).

**Flexural Strength**

The result obtained shows an increase in flexural strength as the percentage weight of sea crab shell increase, as seen in Figure 8. There was a decline in flexural strength at 30 wt % of the particles. The introduction of sea crab shell particles enables the composite to restrict the movement of polymer chains thus reducing the elasticity of composites and increasing the stiffness. This accounted for the overall increase in flexural strength. The decrease in flexural strength at 30 wt % of sea crab shell is due to the poor interaction between the particles and polymer. Herrera-Franco and Valadez-Gonzalez (2005) also reported that the flexural property of a composite strongly depend on the adhesion between the matrix and reinforcement.

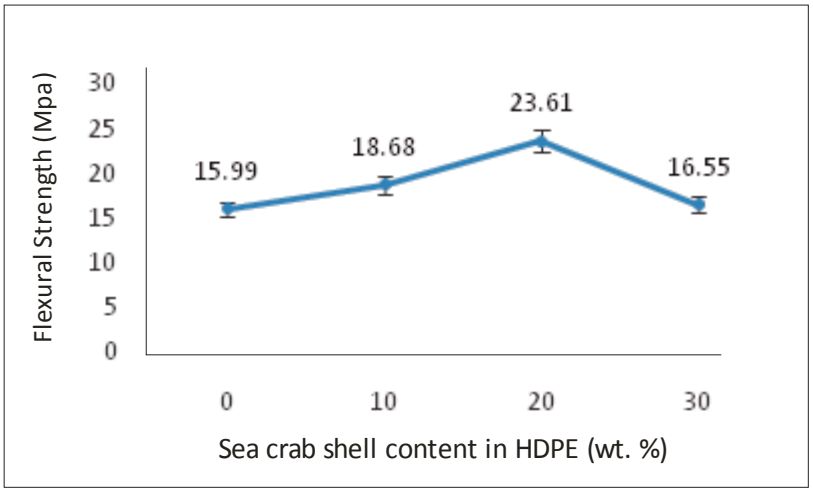


Figure 8: Variation of flexural strength with increasing percentage weight of sea crab shell

## CONCLUSIONS

The XRF analysis showed the major constituent of the sea crab (Callinectes Amnicola) shell to include oxides of calcium with traces of other metallic and non-metallic oxides.The density of the composites showed a reasonable minimal difference compared with the 100 wt% HDPE. The decrease in the impact strength further confirms the importance of homogenousdistribution of reinforcement material in the production of composites.

The increase in flexural strength, hardness and modulus of elasticity of the produced composite with an increase in percentage of sea crab shell particles showed a good viability of CSP as a good reinforcing agent in composite materials.

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## REFERENCES

Abdel-Kader, A. H. and Darweesh, H. H. M. (2010) Setting and hardening of Agro/cement composites, Bio Resources, 4 (1), 43-54.

Adnan, N. A, Fahan, M. M., Fadhil, M. M. (2015) Mechanical Properties of TiO2 Reinforced Polystyrene-Modified Unsaturated Polyester, Chemistry and Materials Research. 7(5), ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online).

Aigbodion, V., Atuanya, C. U.,Igogori, E., and Ihom, P. (2013) Development of High Density Polyethylene/ Orange Peels Particulate Bio-Composites,Gazi University Journal of Science, 26(1), 107-117.

Akanbi, M. N., Onuoha, F. N., Elele, I. N., Nwogu, S. C. (2015) Effect of carbonized saw dust on the mechanical properties of polyolefins plastics, journal of scientific research and reports, Science domain international, 6(6): 461-467, ISSN 2320-0227.

Al-SultaniK. F. (2010) Mechanical Properties Investigation of HDPE Matrix Composites Reinforced with Wheat Straw Fibres, The Iraqi Journal for Mechanical and Material Engineering, 10 (1).

Arulvel, S., Elayaperumal A, Jagatheeshwaran, M. S. (2017) Electroless nickel – phosphorus coating on crab shell particles and its characterization, Journal of Solid State Chemistry, 248, 87-95.

Bobelmann, F., Romano, P., Fabritius, H., Raabe, D. and Epple, M. (2007). The Composition of the exoskeleton of two crustaceans: The America Lobster Homerusamericanas and the edible crab, Thermochemica Acta, 463 (1-2): 65-68.

Callister, W. D. (2007) Material Science and Engineering-an introduction. John Wiley and Sons Inc, New York, 8th ed., 647.

Danladi, A. and Shu'aib, J. (2014). Fabrication and Properties of Pineapple Fibre / High Density Polyethylene Composites. American Journal of Materials Science, 4 (3): 139-143 DOI:10.5923/j.materials.20140403.04.

Darweesh, H. H. M. and Abo El-Suoud, M. R. (2014) Setting, hardening and mechanical properties of some cement agrowaste composites - Part I,Amer. J. Mining and Metallurgy, 2(2), 32-40.

Griskey, R. G. (2008) Polymer,Microsoft student, Redmond, W.A. Microsoft Corporation.

Herrera-Franco, P. J., Valadez-González, A. (2005). A study of the mechanical properties of short natural-fiber reinforced composites, Composites Part B: Engineering, 36(8), 597-608.

Kalpakjian, S., Schmid, S. R. (2008). Manufacturing Processes for Engineering Materials, 5th ed. Pearson Education ISBN No. 0-13-227271-7.

Ku H., Wang, H., Pattarachaiyakoop, N., Trada, M. (2011). A review on the tensile properties of natural fiber reinforced polymer composites, Composites Part B: Engineering,42 (4),856-873.

Kumar, M., Singh, R. K., Shekhar, H. and Poomalai, P. (2013). Studies on banana fibre reinforced high density polyethylene (HDPE)/polyamide (PA)-66 blend composites,Wudpecker Journal of Food Technology,1 (4), 062 – 073.

Lin, Y., W. Du., D.tu, Zhong and Q., DU. (2005). Space charge distribution and crystalline structure in low density polyethylene (LDPE) blended with high density polyethylene (HDPE), Polym.int, 54, 465-470.

Maleque, M. A., Atiqah, A., Talib, R. J., and Zahurin, H. (2012). New Natural Fibre Reinforced Aluminium Composite for Automotive Brake Pad,International Journal of Mechanical and Materials Engineering (IJMME), 7(2), 166-170.

Masuelli, M. A. (2013). Introduction of Fibre-Reinforced Polymers – Polymers and Composites: Concepts, Properties and Processes. Retrieved from http://dx.doi.org/10.5772/54629.

Misra, K. R., Kumar, S. and Misra, A. (2008). Dynamic Analysis of Banana Fibre Reinforced High Density Polyethylene/Poly (e-Caprolactone) Composites, Journal of Mechanics of Materials and Structures, 3 (1).

NoureddineRamdani, Jun Wang., Xuan-yu He, Tian-tian Feng., Xiao-dong, Xu., Wen-bin Liu, Xin-sheng Zheng (2014). Effect of crab shell particles on the thermomechanical and thermal properties of polybenzoxazine matrix, Materials and Design,61,2014,1-7.

Riham, A. M. (2014). Investigation of Reinforced Polystyrene Foam Waste with Natural or Synthetic Fibres. M. Eng thesis report. The American University, Cairo.

Shnean, Z. Y. (2012). Mechanical and Physical Properties of High Density Polyethylene Filled with Carbon Black and Titanium Dioxide. Diyala Journal of Engineering Sciences, 5(1), 147-159.

Singha, A. S. and Rana, R. K. (2012). Natural fibre reinforced polystyrene composites: Effect of fibre loading, fibre dimensions and surface modification on mechanical properties. Materials and Design, 41, 289–297.

Smith, P. A. and Yeomans, J. A. (1995). Benefits of Fibre and Particulate Reinforcements. Material science and Engineering, 2.

Taj, S., Munawar, A. M. and Khan, U.S. (2007). Natural Fibre-Reinforced Polymer Composites, nProc. Pakistan Acad. Sci, 44 (2), 129-144.

Tanniru, M. and Misra, R.D.K. (2005). On enhanced impact strength of calcium carbonate-reinforced high-density polyethylene composites, Materials Science and Engineering: A, 405 (1–2), 178-193.

Yasim, A. and Daniel, I. (2004). Mechanical and Thermal properties of graphite platelet/epoxycomposites, Polymer, 45, 8221-8229.