Enhancement of strength and flexibility of high-density polyethylene using rubber leaves

Norin Zamiah Kassim Shaari¹, Nurfatheen Abd Rahman, Ahmad Redha Taha, Sakinah Mohd Alauddin, Suffiyana Akhbar

Department of Chemical and Process, Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, MALAYSIA

E-mail: norinzamiah@uitm.edu.my¹

Abstract. High density polyethylene (HDPE) polymer suffers with lack of strength and flexibility that result in fracture of vessels and leakage of piping system. One way to overcome the brittleness problem of the polymer is by reinforcement of fillers such as fibers into the polymer matrix to form a polymer composite. In this study, the effect of incorporating rubber leaves as the filler into high density polyethylene (HDPE) polymer matrix on the tensile properties and morphology of the polymer composite was investigated. The composites were prepared with or without addition of glycerol as plasticizer and citric acid as cross linker. Despite using a common size of the filler, the sieve sizes of the rubber leaves were varied at 200µm, 300µm and 500µm respectively. Results show that the presence of 200 µm rubber leaves with glycerol and citric acid increased the strength of the polymer composites, where the tensile strength achieves 22.1 MPa without jeopardizing the elongation of the composite. The image from SEM reveals that rubber leaves fibers and plasticizers are dispersed homogeneously in the polymer matrix HDPE. This potential used of rubber leaves in the manufacturing of HDPE polymer composites will help to utilize the abundant amount of rubber leaves.

1. Introduction

There are two type of polymers derived from polyethylene which are low-density polyethylene (LDPE) and high-density polyethylene (HDPE). Both of these have different properties and being used in different applications LDPE is produced by free radical polymerization at high pressure about 1000 atm and high temperature of 200°C. HDPE is obtained using Ziegler-Natta catalysis at pressure less than 100 atm and temperature below 100°C. As compared to LDPE, which is more flexible, softer and can melt at a lower temperature, HDPE is harder, has high chemical resistance and can withstand high temperatures [1]. Therefore, HDPE is the most commonly used material for the pipe system, toys, shampoo bottles as an insulator in electrical appliances and chemical containers due to its high quality, highly versatile and affordability [2]. The HDPE density is higher than LDPE with longer chain branching. This chain branching provides HDPE for its stronger tensile strength and intermolecular forces compared to LDPE [3]. However, HDPE still suffers with lack in toughness, strength and flexibility, which has resulted in the fracture and leakage of the storage tank and piping used in the chemical industries. This phenomenon is due to crack can grow rapidly in a brittle manner for large-scale HDPE products like polyethylene pipe, where this type of fracture is known to be in the plane-strain condition, which has much lower toughness than that in the plane-stress condition [4].

The toughness can be described as a property of a material that has an ability to absorb and distribute relatively huge amount of energy of repeated impacts before it cracks or fractures by deformation. A polymer that has low toughness is called brittle materials. For instance, ceramic has
high strength but it is brittle and has low toughness [5]. Brittle is hard but reliable to break easily because the brittle materials absorb little energy prior to fracture even at high strength with a snapping sound. One way to avoid the brittleness problem of the polymer is by reinforcement of fillers such as fibers and nanotubes into the polymer matrix to form a polymer composite [6]. The most widely used filler is natural fibers due its environmentally friendly material and has a light weight [7]. The combination of fiber filler and polymer such as HDPE enhances the physical and chemical properties of the composite without increasing the weight and cost of the polymer composites [8].

Other than fillers, a softening substance or a solvent called plasticizer is also incorporated in the polymer composite to improve its flexibility or ductility. The improvement is achieved through the increment in the mobility of polymer chains by decreasing the intensification of intermolecular interaction. The most common plasticizer used for films and polymers is glycerol because of its ability to increase the strength properties of the materials. There is a finding from a research, which proves that the presence of glycerol can increase the tensile strength of polymer but too much amount of glycerol may lead to a decrease in the strength of the polymer [9]. Thus, the best solution is to combine glycerol with other chemicals such as citric acid and sorbitol [10]. The citric acid is a nontoxic metabolic product with approval by FDA (Food and Drug Administration) for its use in human and also known as nutritionally harmless which can help to prevent retrogradation (recrystallization) [11]. The combination of citric acid and glycerol produces a various type of biodegradable polymer particularly in the area of biomedical applications [12]. A research by Pramanick and Ray [13] proves that cross-linked co-polysters of citric acid and glycerol are degraded by \textit{Aspergillus niger} and \textit{E. coli}, and the possible use of these cross-linked co-polysters are as matrices for controlled release of drugs.

In addition to that, the mixture of glycerol and citric acid would encounter high moisture and brittleness of the polymer composite which would enhance or improve the blend polymer flexibility in terms of tensile strength. The modification HDPE polymer with glycerol and citric acid results in the increment of tensile strength and the maximum elongation of the polymer to break due to intermolecular forces was reduced and addition of polymer chain [14]. Citric acid is one of an organic agent that acts as an additive in plasticizer and inhibits the degradation of polymer, and also enhances both barrier and mechanical properties of the blend polymer [15].

Peninsular Malaysia generates large amounts of wood and agricultural residues, where the major agricultural crops grown in Malaysia are rubber (39.67%), oil palm (34.56%), cocoa (6.75%), rice (12.68%) and coconut (6.34%). Only 27.0% from the residues are used either as fuel for the kiln drying of timber, manufacture of bricks, and for the manufacture of products such as particleboard and fibre board, and the rest are disposed of by burning. As an effort towards environmental protection and saving of energy, the domestic waste, biodegradable wastes and natural fibers can be utilized to produce green composites [16]. Materials that have been utilized to make the composite material are wheat straw [17] banana, bamboo, coir, coconut husk, sisal, rice husk [18] and sugarcane baggage. Rubber leaves are abundant in Malaysia because they are not utilized for any other products. The scientific name for the rubber leaves is \textit{Hevea Brasiliensis Leaves} (HBL) [19]. Rashidi et al. [20] has conducted a study on utilizing HBL as the fiber filler for the polymer composites by mixing the rubber leaves with cogon grass which is known as the worst weed in the world. The filler was varied at 5 wt%, 15 wt% and 25 wt%. The rubber leaf was chosen to improve the strength of the composite and to make the cogon grass able to disperse, colonize, spread and subsequently compete with other vegetables [21].

This research is intended to evaluate the potential of rubber leaves as the fiber filler to enhance the strength of HDPE polymer. Three different sizes of the filler were prepared, and the fabrication processes of the polymer composite were adjusted accordingly to ensure the polymer composite was successfully produced.
2. Materials and methods

2.1 Materials

The rubber leaves were obtained from the rubber trees in Semenyih, Selangor, Malaysia. Glycerol with a purity of 95% and citric acid were purchased from Sigma Aldrich Malaysia. The industrial grade high density polyethylene (HDPE, molecular weight 200000 g/mol) was purchased from Chevron Phillips.

2.2 Methods

2.2.1 Preparation of fillers

The dried rubber leaves were ground to a finer structure by using the Panasonic dry blender as shown in Fig. 1. The ground fiber was then sieved into few different sizes in a range of 200 µm, 300 µm and 500µm, respectively by using Endecott Octagon 2000 Digital Sieve Shaker. The sieving process was conducted for 1 hour.

![Figure 1. Finer structure of rubber leaves.](image)

2.2.2 Mixing of composite solution

Five grams of citric acid was added into 10 g glycerol, which was then heated at 90°C and continuously stirred at 100 rpm for 30 minutes. Then 35 g HDPE pellet 15 g citric acid-glycerol mixture and 0.75 g rubber leave fibers were mixed in a beaker and stirred until perfectly mixed as shown in Fig. 2. Subsequently, internal mixing process was conducted which take place at 200°C since the melting point temperature for HDPE is in a range of 120-180°C. The mixing velocity was increased 5 rpm in every 30 seconds until the rotation reached 55 rpm. The melting process was conducted for about 12 minutes to make sure that the polymer was completely melted [22].

The formulation of the composite used a fixed ratio 7:3 of HDPE to plasticizers (glycerol and citric acid) [10]. The mass of the rubber leaves fibers was fixed at 5% w/w of plasticizer. There were 6 formulations that were prepared and the details are shown in Table 1. As all the compositions in the composite were fixed, the only thing varied was the size of fiber filler. This is because different size of the fiber can give different effects on the polymer composites [22].
Table 1. Formulation of composites.

| Code | Formulation                        |
|------|------------------------------------|
| M1   | Pure HDPE                          |
| M2   | HDPE + Filler (200µm)              |
| M3   | HDPE + Filler (300µm)              |
| M4   | HDPE + Filler (500µm)              |
| M5   | HDPE + Plasticizer                 |
| M6   | HDPE + Filler + Plasticizer        |

Figure 2. Mixing of all material in a beaker.

Figure 3. Structure of composite after undergoing internal mixing.
2.2.3 Compact crushing process
Before the crushing process, the sample was preheated and compressed for 5-10 minutes at 190°C by using the hot press to make it become thin and easy to crush. The sample was then cut into small pieces. The composite was then crushed thrice by using a crusher. The crushing process was repeatedly done to get small size of composite with large surface area and to avoid producing bubble during compression. Fig. 4 shows the composite after crushing process.

![Composite after crushing process.](image)

**Figure 4.** Composite after crushing process.

2.2.4 Compression moulding
The test was conducted by compressing the crushed sample by using hot press into a dumbbell-shaped for tensile test as shown in Fig. 5. The temperature was set at 190°C and the composite is compressed at constant pressure of $4.826 \times 10^6$ Pa. The specimens were preheated for 5 minutes and 10 minutes of compression time. After compression, the cooling process was conducted by setting the temperature to 30°C and the specimens was continuously compressed until the temperature reached the set temperature of 30°C which took about an hour. The composite was then taken out from the mould and was subsequently tested for mechanical properties.

2.2.5 Tensile test
The polymer composites were taken out from the mould. The tensile test was conducted by using universal testing machine, model: H50KT, brand: Tinius Olsen. The load cell used of 5 kN and crosshead speed was set to 500 mm/min. This test was conducted according to the technical standard method ASTM D638. For each formulation of the composite, 3 samples were tested and the average value was recorded. Fig. 5 shows the samples from formulations M1, M2, M3, M4 and M6.
2.2.6 Scanning electron microscopy (SEM)

The surface morphology of the polymer composite was examined using Scanning electronic microscope (SEM) (TM3000 TABLE top HITACHI, United State of America) with an acceleration voltage of 5kV, which was outsourced from Faculty of Applied Sciences, UiTM Shah Alam. The function of SEM is to generate high-resolution images the surface of the polymer composites and show spatial variations. Prior to the testing process, the composite was electrically-coated for 15 minutes as shown in Fig. 6. The investigation on the cross sectional morphology of each sample was made at an acceleration voltage of 10 kV [10]. The results of SEM images were recorded.

3. Results and Discussion

The results from the tensile test such as tensile strength, stress at break and the strain are shown in Table 2. Based on Table 2, the presence of rubber leaves as the fiber filler does increase the tensile strength of the composite portrayed by composites M2, M3 and M4. Without the filler and with the presence of citric acid and glycerol, composite M5 shows higher tensile strength as compared to M2, M3 and M4. Since M2, which consists of 200 µm size of fillers yield the highest tensile strength, formulation M6 was prepared by incorporating plasticizer together with 200 µm size of fillers. Based on Table 2, this formulation has produced a stronger composite where it has the highest tensile strength with higher stress at break without jeopardizing the elongation. Although the strain is lower as
compared to pure HDPE (M1), the difference is marginal. Smaller size of rubber leaves yields the highest strength because of its large surface area, which enables the fiber to fill the pores and making the polymer to become more compact and stronger. Furthermore, the matrices of HDPE polymer are modified by cross linking reactions due to the presence of citric acid. The citric acid cross linked the polymer composite and it was reported to occur at high temperatures from ranges 165 until 175 °C [23].

Table 2. Tensile properties of polymer composites.

| Composites | Tensile strength (MPa) | Stress at break (MPa) | Strain, % |
|------------|------------------------|-----------------------|-----------|
| M1         | 17.2                   | 15.5                  | 22.6      |
| M2         | 20.4                   | 18.3                  | 12.5      |
| M3         | 19.6                   | 17.7                  | 24.1      |
| M4         | 19.2                   | 17.2                  | 20.4      |
| M5         | 20.5                   | 18.4                  | 19.6      |
| M6         | 22.1                   | 19.8                  | 21.6      |

The results from scanning electron microscopy analysis are shown in Fig. 7. The images for surface morphology of composites M1, M2, M4 and M6 are displayed. Based on the images, the homogenous dispersion of rubber leaves fiber in the HDPE polymer matrix was observed even with 500µm of fiber size (M4). As shown in Fig. 7 (d), the plasticizers, citric acid and glycerol in composite M6 were also well mixing with HDPE and 200 µm fiber filler, which have yield higher tensile strength as discussed earlier. The images shown have proven that the fiber filler and plasticizer, which have smaller sizes than HDPE particle, have occupied the porous structure of HDPE [24].
Figure 7. Surface morphology of composites (a) M1, (b) M2, (c) M4, (d) M6, at 500x resolution
**4. Conclusions**

The findings from this research prove that rubber leaves can improve the strength of HDPE without reducing the elongation of the polymer. The fiber filler from rubber leaves regardless of their sizes is compatible with HDPE since the surface morphology of composites is homogenous and no agglomeration was observed. However, bigger sizes of the fiber filler reduce the strength of the polymer composite. The presence of plasticizer also helps to enhance the strength of the composite. The rubber leaves fiber with 200 µm size in the presence of plasticizers is the best formulation to improve the tensile properties of HDPE polymer. This potential use of rubber leaves in the manufacturing of HDPE polymer composites will help to utilize the abundant amount of rubber leaves.

**Acknowledgements**

The authors would like to thank Mr. Mohd Idris Md Desah and Mr. Amin Fafizullah Omar for their assistances on the equipment handling during the fabrication process of the polymer composite. Special thanks to the Faculty of Applied Sciences, UiTM for giving the opportunity in conducting SEM analysis. Special thanks also to Prof. Dr Azni Zain Ahmed for proof reading this article. The authors also would like to thank Universiti Teknologi MARA (UiTM) for sponsoring the research through grant Bestari Perdana with file number 600-IRMI/DANA 5/3/BESTARI (P) (009/2018).

**References**

[1] Singh V P, Vimal K K and Kapur G S 2016 High-density polyethylene/halloysite nanocomposites: morphology and rheological behaviour under extensional and shear flow Journal of Polymer Research 23 Article No. 43.

[2] Katz J 2014 Quality Plastic Film and Plastic Sheets. Retrieved from What is difference between HDPE and LDPE plastic sheets?: https://www.grafixplastics.com/difference-hdpe-ldpe-plastic-sheets/.

[3] Thakare K A, Vishwakarma H G and Bhave A G 2015 Experimental investigation of possible use of HDPE as thermal storage material in thermal storage type solar cookers Journal of Research in Engineering and Technology 4 92-99.

[4] Kwon H J and Jar P Y B 2006 Toughness of high-density polyethylene in plane-strain fracture Polymer Engineering and Science 46 1428-1432.

[5] Brostow W, Hagg L H E and Khoja S 2015 Brittleness and toughness of polymers and other materials Materials Letters 159 478–480.

[6] Brostow W and Hagg L H E 2010 Brittleness of materials: Implications for composites and a relation to impact strength Journal of Materials Science 45 242–250.

[7] Islam S, Kovalcik A, Hasan M and Thakur V K 2015 Natural Fiber Reinforced Polymer Composites International Journal of Polymer Science 2–4.

[8] Vignesh P, Venkatachalum G, Gautham S A, Singh A, Pagaria R and Prasad A 2018 Studies on Tensile Strength of Sugarcane Fiber Reinforced Hybrid Polymer Matrix Composite Materials Today: Proceedings 5 13347–13357.

[9] Yunos M Z B and Rahman W A W A 2011 Effect of Glycerol on Performance Rice Straw/Starch Based Polymer Journal of Applied Sciences 11 2456–2459.

[10] Sanyang M L, Sapuan S M, Jawaid M, Ishak M R and Sahari J 2015 Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (arenga pinnata) starch for food packaging Journal of Food Science and Technology 53 326-336.

[11] Shi R, Zhang Z, Liu Q and Han Y 2007 Characterization of citric acid / glycerol co-plasticized thermoplastic starch prepared by melt blending Carbohydrate Polymers 69 748–755.

[12] Halpern J M, Urbanski R, Weinstock A K, Iwig D F, Mathers R T and Recum H A 2013 A biodegradable thermoset polymer made by esterification of citric acid and glycerol Journal of
[13] Pramanick D and Ray T T 1988 Synthesis and biodegradation of copolyesters from citric acid and glycerol Polymer Bulletin 19 365–370.

[14] Shahrim N A A, Sarifuddin N, Zakri H H M and Azhar A Z A 2018 The effect of glycerol addition to the mechanical properties of thermoplastics films based on jackfruit seed starch Journal of Analytical Sciences 22 892-898.

[15] Khan B, Niazi M B K, Hussain A and Jahan Z 2017 Influence of carboxylic acids on mechanical properties of thermoplastic starch by spray drying Journal of Fibers and Polymers 18 44-73.

[16] Sain M M, Balatinecz J and Law S 2000 Creep Fatigue in Engineered Wood Fibres and Plastic Composites Journal of Applied Polymer Science 77 260-268.

[17] Wang D, Sun X S 2002 Low Density Particle Board from Wheat Straw and Corn Pith Journal of Industrial Crops Production 15 43-50.

[18] Rahman W A, Lee T S, Rahmatt A R, Isa N M, Salleh M S N, Mokhtar M 2011 Comparison of Rice Husk Filled Polyethylene Composite and Natural Wood under Weathering Effects Journal of Composite Materials 45 1403-1411.

[19] Barrera C S and Cornish K 2016 High performance waste-derived filler/carbon black reinforced guayule natural rubber composites Industrial Crops and Products 86 132–142.

[20] Rashidi A R, Muhammad A and Roslan A 2017 Morphology-Property relationship of high density Polyethylene/Hevea Brasiliensis Leaves/Imperata cylindrica hybrid composite: Impact strength AIP Conference Proceedings 1885.

[21] Ruksakulpiwat C, Wanusat W, Singkum A and Ruksakulpiwat Y 2013 Cogon grass fiber-epoxidized natural rubber composites Advanced Materials Research 747 375–378.

[22] Nurzam E Z 2017 Effects of Fibre Size on Sansevieria trifasciata/ Natural Rubber/ High Density Polyethylene Biocomposites Malaysian Journal of Analytical Sciences 1057-1064.

[23] Quiroz M J T, Diaz J J F and Pinotti A 2018 Characterization of methylcellulose based hydrogels by using citric acid as a cross linking agent Journal of Applied Engineering Research 13 13302-13307.

[24] Ayswarya E P, Vidya Francis K F, Renju V S and Thachil E T 2012 Rice husk ash – A valuable reinforcement for high density polyethylene Materials and Design 41 1-7.