

Mechanical and Thermal Properties of Polyurethane-Palm Fronds Ash Composites

Ahmed J. Mohammed¹, Einas A. Abood², Mahir A. Jalal³, and Ibrahim K. Ibrahim⁴

¹Materials Sciences Department, Polymer Research Center, University of Basrah, Basrah, Iraq, ahmed.mohammed@uobasrah.edu.iq

²Department of Chemistry and Polymer Technology, Polymer Research Center, University of Basrah, Basrah, Iraq, einas.obood@uobasrah.edu.iq

³Department of Chemistry and Polymer Technology, Polymer Research Center, University of Basrah, Basrah, Iraq, mahir.jalal@uobasrah.edu.iq

⁴Department of Chemistry and Polymer Technology, Polymer Research Center, University of Basrah, Basrah, Iraq, ibrahimkadhim29@gmail.com

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Abstract: The aim of the article is to study the influence of environmentally friendly palm frond ash on the mechanical and thermal properties of polyurethane used as filler. Various weight filler ratios with particle sizes around (125 μm) were examined and characterized using elongation, tensile strength, Young's modulus, compressive strength, average burning time, and infrared spectroscopy. The results showed that the addition of 20 wt.% palm frond ash powder significantly improved the hardness mixture by about 2.83 MPa. In addition to that, the highest value of the compressive strength of the polymer with the additive was recorded at 10 wt.%. Also, the most excellent value of Young's modulus was 2 MPa at a ratio of 50 wt. %, as was the average burning time of about 33 sec. The mechanical properties of polyurethane were affected by adding palm frond ash, which increases the tensile and compressive strengths, making it suitable for use in many applications. Moreover, the environmentally friendly material reflects the benefits of waste recycling. The addition of filler affects the morphology and strengthens the brittleness. Additionally, fly ash from palm frond combustion was found to be suitable as additive for reducing flammability in many applications where polyurethane used.

Keywords: polyurethane; Palm frond ash; mechanical properties; thermal properties; and fire retardant.

1. Introduction

A Polyurethane is a thermal insulator material generally produced by the polymerization reaction of polyol and monomers containing isocyanate groups. For the time being, polyurethane is widely used in different applications, such as furnishing, packaging, and building construction. Due to its low heat transfer coefficient and good mechanical properties, polyurethane is considered a suitable material for heat-resistant wall panels [1-3]. However,

polyurethane is susceptible to burning, which raises the fire risks when it ignites, burns rapidly, and then produces intense heat and gases that are irritating, flammable, and toxic. To reduce the risk, fire retardants based on polyurethane are used. Foam-fire retardants can be added either by manipulating the chemical structures of the backbone or by adding fillers.

Fillers, which play important roles in reducing flammability and may increase hardness (enhancing reinforcement properties), can be classified into natural and synthetic fillers. Natural fibers such as pineapple, leaf, kenaf, sisal, coir, flax, jute, hemp, and abaca have been used by researchers as reinforcement additives with polymers due to their advantages such as low density and cost, less abrasiveness, renewability, and biodegradability [4-7]. In literature [8, 9], ash from palm fronds can significantly enhance the mechanical properties of high-density polyethylene (HDPE) and low-density polyethylene (LDPE). In a comparison study, the ash of palm leaf was used as a component in the cement mixture to improve the compressive strength of concrete [10].

While Saleh et al. added 5 wt.% of palm tree ash to the concrete, which is working to improve the compressive strength and minimize the amount of used cement [11]. Bachtiar et al. [12] investigated the alkaline treatment with concentrations of 2 wt.% and 6 wt.% to improve the tensile properties of sugar palm fiber-reinforced thermoplastic polyurethane (TPU). The study showed that the tensile strength of the composites containing a 30% weight fraction of alkali-treated fiber was lower than that of untreated composites. Meanwhile, the composites with 2 wt. % treated fiber had a higher tensile modulus of 440 MPa compared to the 6% alkali-treated fiber. In another study, Atiqah et al. [13] revealed that the enhanced mechanical and thermal properties of the composites. The composite formulation with 40 wt% sugar palm fiber loading showed optimum values such as 17.22 MPa for tensile, 13.96 MPa for flexural, and 15.47 kJ/m² for impact strength. Kenaf fiber-reinforced thermoplastic polyurethane was produced by the processes of internal mixing and hot molding [14]. Various fiber loadings of 20, 30, 40, and 50 wt.% led to different properties of the kenaf-reinforced thermoplastic polyurethane. The results showed that the 30 wt.% kenaf/TPU composite presented the highest values for a tensile strength of 89 N/mm² and a flexural strength of 148 N/mm². Fly ash fillers have improved the mechanical and thermal properties of polyurethane composites, which is related to the barrier effect of the filler and the prevention of the release of gases from foam cells. For samples containing fly ash, the residue is from 3 to 10 wt.%, depending on the type and amount of ash. The presence of residues results from fly ash components, most of which, such as aluminum silicates, are non-flammable. Furthermore, the addition of fly ash improved the compressive strength of composites by 10% (approximately 220 kPa) [15]. In this article, the influence of using palm frond ash waste (in Iraq, the palms are the most growing plant and cover large areas) as filler on the mechanical and thermal properties of the polyurethane was investigated. Recycling palm waste like fronds, turning it into fly ash, and using it as eco-friendly additives for improving the mechanical and thermal properties of commercial polyurethane is the subject of the current research. The addition of filler (palm frond ash) affects the polymer's morphological properties and strengthens brittleness; this could contribute to the removal of palm waste and bring important economic benefits. And also, fly ash from palm frond combustion was found to be suitable as an additive for reducing flammability in many applications where polyurethane is used.

2. Materials and Methods

2.1. Preparation method

Polyurethane, as an abased material, was prepared by the reaction of 1:1 wt.% isocyanate and (polyester-polyol) supplied by Sigma-Aldrich, using trimethylamine (TEA) as

a catalyst and a few drops of water to release carbon dioxide that works to form cellular spaces within the mass of the mixture (Figure. 1).

As reported in literature [16], in polycondensation of polyester polyol and diphenylmethane diisocyanate, the reaction proceeds between isocyanate and alcoholic groups to form urethane linkages along polymer chains. During this process, nucleophilic attack of hydroxylic groups end capped polyester to carbonyl of isocyanate occurs and, in presence of TEA, an intermediate complex will form. A few drops of water lead to make foam. The process of forming is starts by reaction of water and some of isocyanate groups. The result is a critical group of carbonic acid which decomposed quickly to release CO₂ gas.

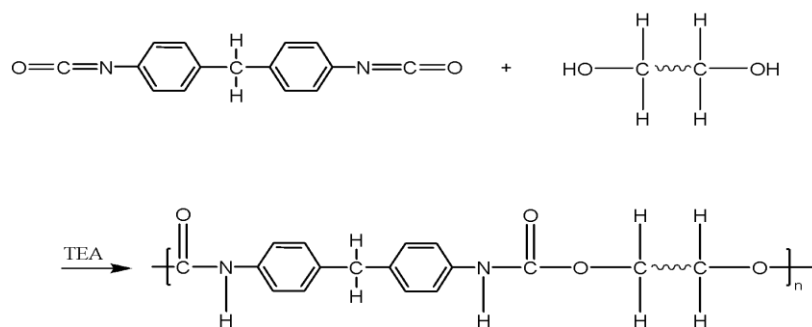


Figure. 1. Chemical composition of polyurethane

The palm frond ash was prepared by burning palm fronds at 455 °C for 15 minutes in a furnace. Then the powder was dealt with by a wire sieve (Allen-Bradley Sonic Sifter Model L3P, provided by ATM Corp., American) to obtain fine-grained ultrafine powder with particle sizes equal to around (125 μm), Figure. 2 shows the image of the ash palm fronds.



Figure. 2. Palm fronds ash.

The samples of polyurethane-palm frond ash were prepared at room temperature by adding various weight ratios (5, 10, 15, 20, 30, and 50 wt. %) of palm fronds ash to the polymer mixture during the polymerization processes. The mixing process was repeated until the mixture was homogeneous. Then the product was poured into a cylindrical and rectangular slab mold. Figure. 3 shows the dimensions of each Figure, where the measurements of cylindrical shape samples are 30 mm in length, and 30 mm in diameter, while the rectangular slab is 110 mm in length, 6mm in width, and 2.4 mm in thickness.

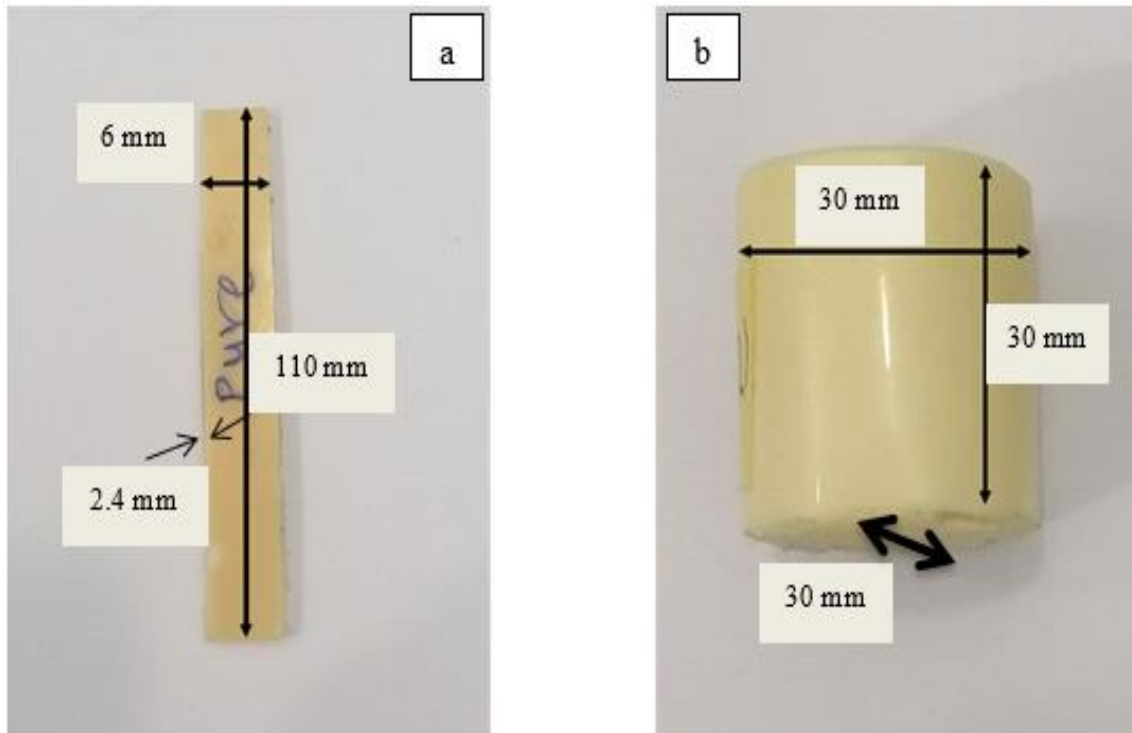


Figure. 3. Tensile and compressive strength test samples: (a) rectangular slab, (b) cylindrical.

2.2. Evaluation of mechanical properties

The models were examined using a German-made (Tensile) instrument (Z wick Reil, type (BTI-FR2.5 TN.D 14), that measured tensile strength, bending resistance and compression resistance. The tensile strength was calculated using equation (1).

$$Q = F/A \quad (\text{N/mm}^2) \dots \dots \dots (1)$$

F is cutting force (N).

A is cross-sectional area (mm^2).

The Young modulus was calculated using the stress-strain curves by the following relationship:

$$(\text{Young's modulus}) Y = (\text{Max Stress})/(\text{Max Strain}) \quad (\text{MPa}).$$

2.3. Evaluation of thermal properties

Using a combustion rate measurement device, average time of burning (ATB), the burning rate for each of the samples manufactured was determined using the standard technique 81 ASTM D635 [17]. The required time for burning 75mm of model was repeated three times for each sample. Figure. 4 added which shows the setup of average time burning.

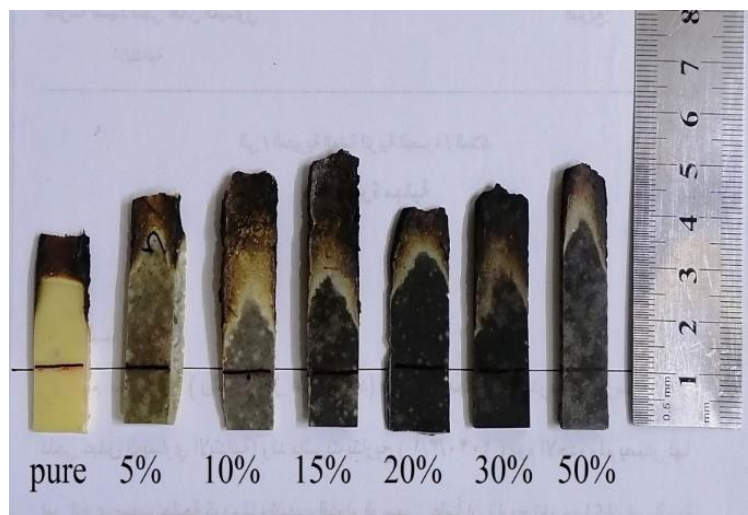


Figure. 4. Remaining unburned samples of 75 mm.

2.4. Characterization

Spectrometric analysis of polyurethane (PU) polymer and its composites with ash were obtained by using JASCO FTIR-4200 instrument, made in Japan. The range of the wave number used in this analysis is 400-4000 cm^{-1} and tested samples were made by using KBr disks contain 1:10 well-dispersed of polymer composite and KBr. Scanning electron microscope (SEM), Quattro S model, made in USA, was used to study morphological properties of samples. The magnification power was 10000-20000X, 10kV applied voltage and the working pressure of argon to oxygen mixed flow was 6×10^{-2} mbar.

3. Results and Discussion:

3.1. Fourier transform infrared Spectroscopy (FTIR):

Figure. 5 depicts their FTIR spectra of polyurethane containing different weight percentages of palm frond. Figure. 5 indicates the appearance of broadband absorption at 3351cm^{-1} assigned to stretching of unreacted hydroxyl groups (OH), and urethane amino groups (N-H) [18]. Two bands at 2972cm^{-1} and 2879cm^{-1} related to (C-H) bond stretching of aliphatic methyl and methylene groups, respectively [19], while, bond stretching of (C-H) aromatic group showed weak absorption bands between 3100cm^{-1} and 3010cm^{-1} [20]. It also indicated the appearance of a strong bond at 1719cm^{-1} related to the stretching of the urethane carbonyl group (C=O). The absorption band at 1510cm^{-1} and the two bands at 1229cm^{-1} and 1088cm^{-1} are related to the bending of (N-H) bond and stretching of (C-O) bond of the urethane group, respectively [20]. All other recorded blends showed a similar pattern spectrum. But a difference was observed with the increasing ash percentage. Spectrum brooding at a wide range of frequencies, between 1000cm^{-1} – 1200cm^{-1} , is associated with increasing ash percentages, obviously seen in Figure.5, due to an increase in the amount of (C-O) bonds of the different oxidized groups in the ash. These results were in agreement with other literature [18].

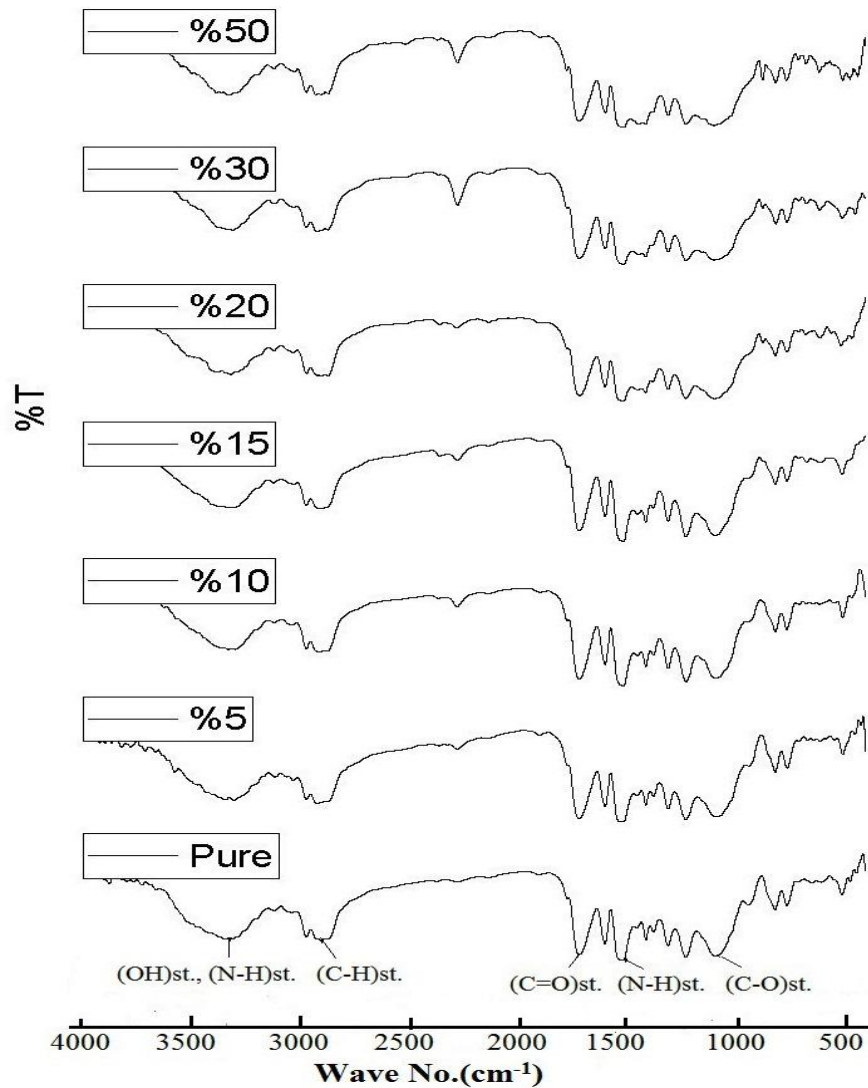


Figure. 5. Depicts their FTIR spectroscopy of polyurethane containing different weight percentages of palm frond

3.2. Scanning Electron Microscope (SEM)

Figure. 6 shows SEM images of polyurethane with various additive weight percentages: (a) 5%, (b) 10%, (c) 20% and (d) 50%. During the scanning process, there will be minor damages on the surface of the polymers. The applied electrons beam burns polymeric composites of low filler percentages, 5 wt. % and 10 wt. %. However, higher filler percentages, 20 wt. % and 50 wt. %, showed a good proof against same electrons beam and this is due to the homogeneity of polymer-filler microstructures.

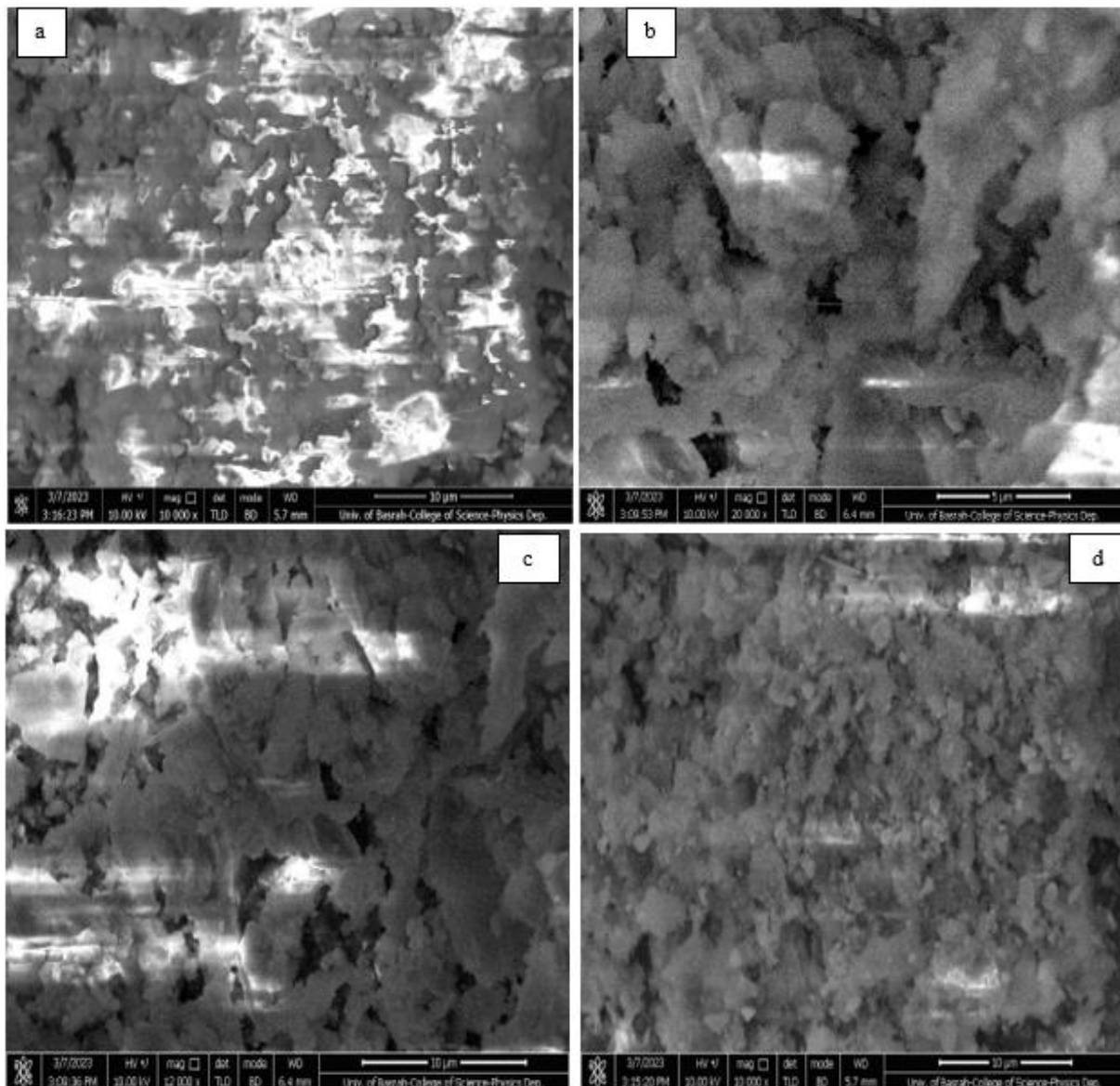


Figure 6. SEM images of polyurethane with various additive weight percentages: (a) 5%, (b) 10%, (c) 20% and (d) 50%

3.3. Average Time of Burning (ATB)

Flame retardants have the potential to reduce the burning time of flammable materials and have attracted much interest recently, especially in the field of applied polymers. The mechanism of fire retardants has two main pathways: the physical and the chemical [21]. The current study includes a study of the effect of palm frond ash fillers on the rate of burning time of polyurethane. Figure.7 shows the relation between the average time of burning and the weight ratios of the filler content. The rate of burning time of the polymer increased with increasing filler ratios, as was obviously observed at higher concentrations (about 33.2 sec. for 50 wt. %). From a physical perspective, the formed ash layer on the surface of the polymer works as an insulating layer on the surface, which prevents the spread of flame inside the polymeric matrix. In contrast with non-additives, polymer was burned for 15 sec.

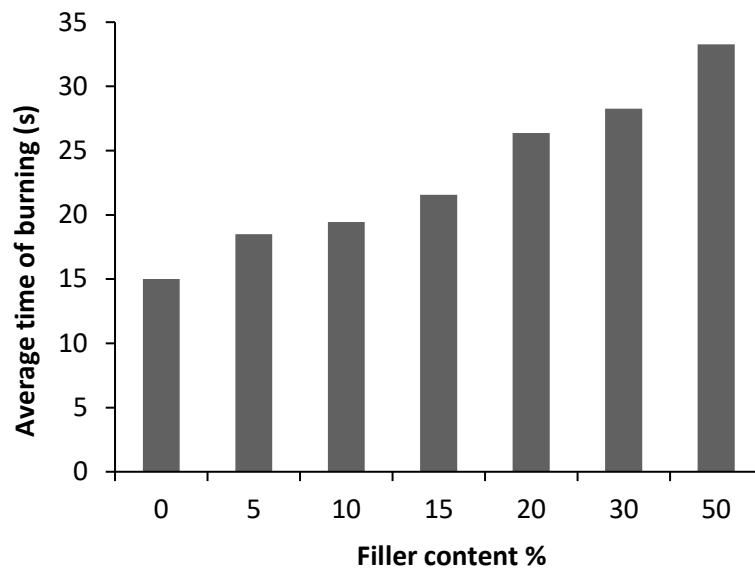


Figure.7. Relationship between the average time of burning with the concentration of palm frond ash additive to the polyurethane polymer.

Table 1. Shows the values of the average time of burning and the burning time percentage, where the percentage of burning time was calculated using equation 2.

$$\text{Burning time percentage} = \frac{A-B}{B} \times 100\% \dots\dots\dots(2).$$

Where,

A is the value of the average time of burning for polymer with additive and B is the value of the average time of burning for pure polymer (without any additives). The rapid change was observed in the range of (10- 20) wt.%, in which the burning percentage increased rapidly around 46-time by adding more 10 wt.% of filler content.

Table 1. The relationship between the percentage of burning time and the concentration of the additive palm frond ash for a polyurethane polymer.

Additives % Test	0	5	10	15	20	30	50
ATB (Sec.)	15	18.5	19.44	21.55	26.37	28.26	33.27
Burning Time Percentage%	-	23.3	29.6	43.6	75.8	88.4	121.8

3.4. Mechanical properties

Figure. 8 shows the relation between the tensile force (stress force) and the percentage of the polymeric additives. There was a slight decrease in the tensile strength at the lower percentage of the filler content, as low as 15 wt. %, while at 20 wt. % the maximum strength is similar to that of pure polymer because the additive powder is in homogeneous distribution with the polymeric chains. However, at higher percentages, the maximum strength is decreased especially at the percentage of 30 wt. %, where the Max stress was recorded at 2.3 MPa. [22].

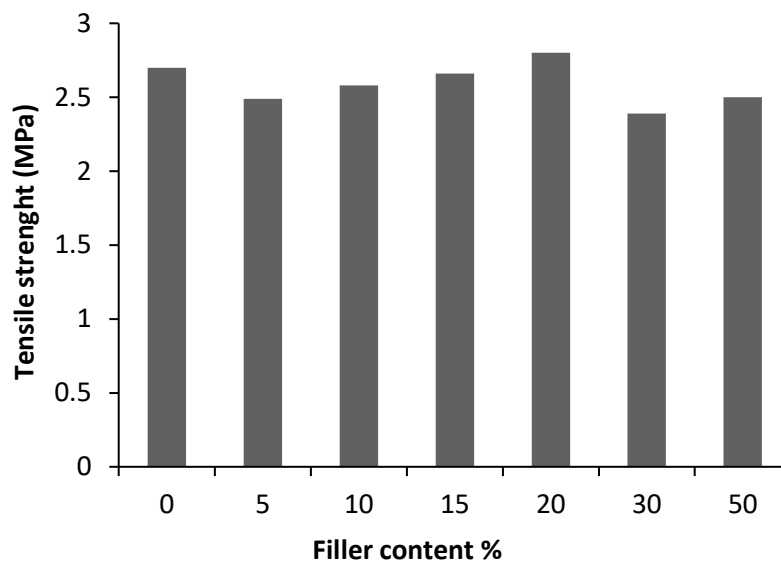


Figure. 8. *The relation between tensile strength and the filler content.*

The elongation model of polymers with the concentration illustrated in Figure. 9 the effect of adding filler to the polymer on the elongation percentage decreased noticeably with increasing ash percentages, the elongation is decreased especially at the percentage of 50 wt. %, where the Max stress was recorded at 1.2%. The elongation decreased as the polymer filler content increased because the particles filled the spaces between the polymeric chains, which hindered and limited the movement of that chain [22].

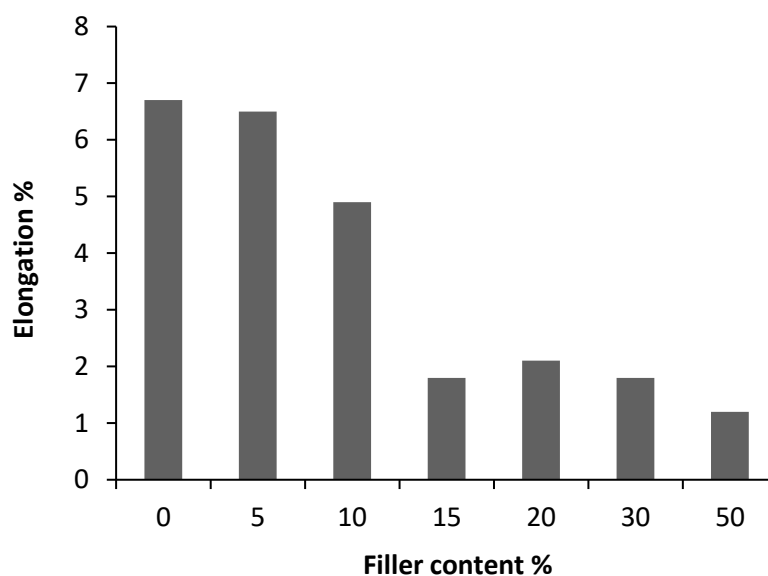


Figure. 9. *The relation between elongation and the filler content.*

While Fig.10 shows the effect of palm frond ash powder on the elasticity modulus (known as Young's modulus), which is defined as stress to strain for solids only, Generally, there was a positive impact on elasticity modulus with increasing filler content. Since the powder works on the hardness of the polymer, the elasticity would be reduced while the homogeneity would be upgraded. The expectation includes 5 wt.% as a consequence of the heterogeneity of the mixture, even though the samples were mixed under the same conditions.

Thus, it indicates that the polymer has high elasticity because the polymer chains are freely moved [23].

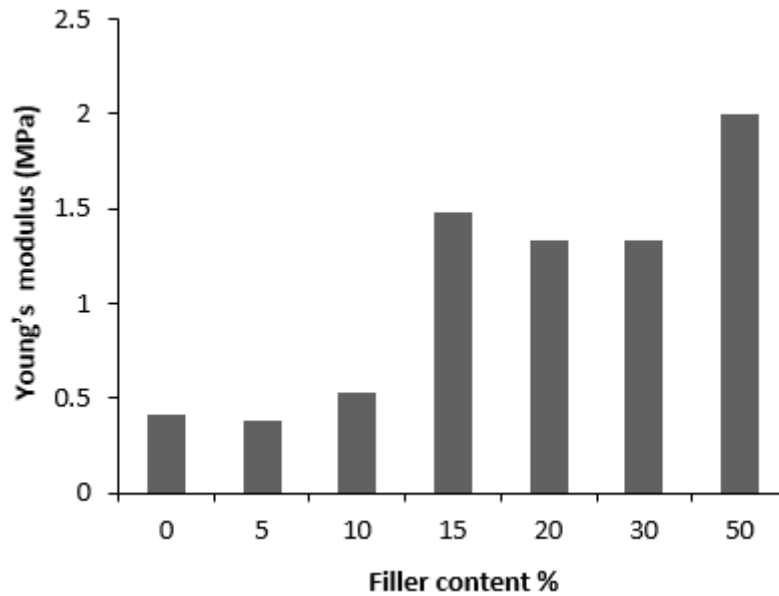


Figure. 10. *The relation between Young's modulus and the filler content.*

Figure. 11 shows the effect of palm frond ash powder on the compressive coefficient, which is defined as the ability of the material to resist the compressive forces perpendicularly for solid materials. The compressive modulus of 0 wt.% is considerably low, nearly (1.08 MPa), while the greatest value of the compressive modulus is (3.49 MPa) at 10 wt.%. It's a fact that the additive imposes on the hardness of the polymer by the homogeneity of the interphase with the polymeric chains. However, the behavior of the polymer begins to decline at high percentages of the additive, especially at the percentage of 30 wt. %, where the compressive strength was recorded at 3.35 MPa. It may be due to excessive bubble formations that make walls easier to collapse.

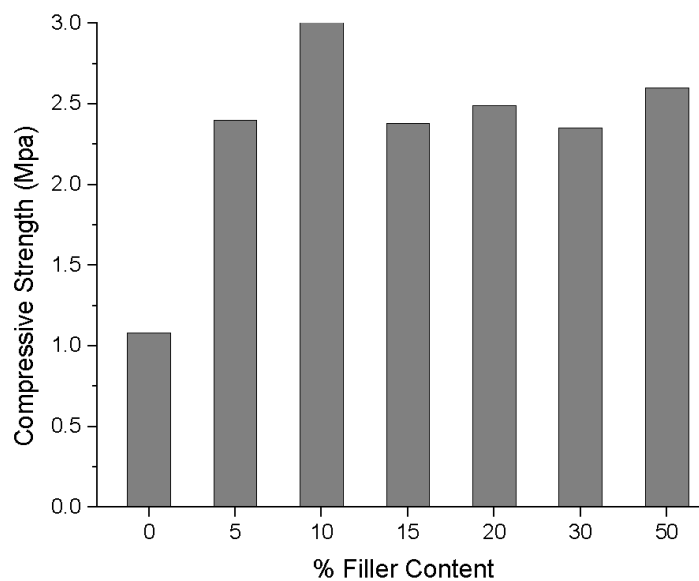


Figure. 11. *The relation between compressibility modulus and filler content*

The relationship between the bending resistance and the additive percentage is shown in Figure. 12, where the pure polymer shows a bending resistance of (9.04 MPa), i.e., the elasticity of the sample is high, but the hardness is low, compared to the other samples. The presence of the rigid filler between polymer chains restricts chain movements, which results in lower flexibility and higher hardness [24]. This observation is clearly seen at a ratio of 15 wt. %, in which high compatibility between the filler and polymer chains occurs. However, as the percentage of additives increased, the particles of the additive dispersed more homogeneously.

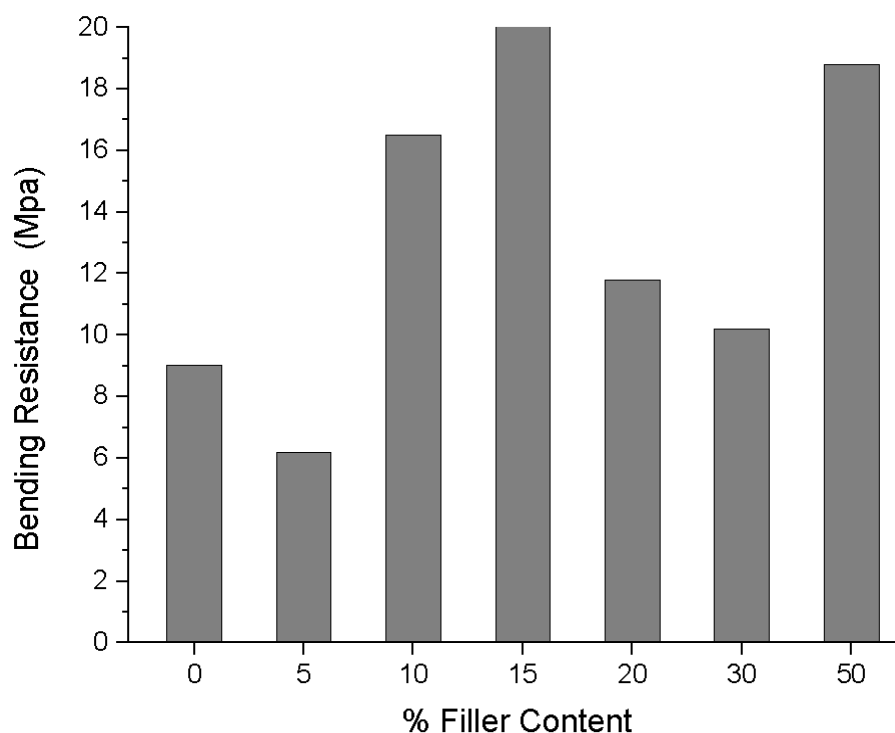


Figure. 12. *The relation between the compressive strength and the filler content*

4. Conclusions

As a result of the homogeneous distribution of filler powder with the polymer, experimental results indicated that conclude that adding ash powder to polyurethane has a significant effect on the mechanical properties, and that (20 wt.%) of the powder additive was the best for the hardness of the mixture, which is estimated at (2.83MPa), while the ratio (0 wt.%) is the best for the elasticity of the polymer, also the greatest value of Young's modulus is (2 MPa) was recorded at the ratio (50 wt.%), and the practical study showed that the highest value recorded for the compressive strength of the polymer with filler was at the ratio (10 wt.%), which is (3.49 MPa), also the behavior of the average time of burning of the polymer with filler, increases with the increase in the percentages of the additive, which ranges from (20-50) wt.%, as it was recording the highest value of the average time of burning (33Sec.) at the percentage (50 wt.%). The experimental results indicated that the optimum filler concentrations were obtained in the measurements of the percentages (20 wt.%, 50 wt.%), in terms of the highest value of hardness as well as the young's modulus and average time of burning, respectively.

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