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OPTIMIZATION OF MECHANICAL PROPERTIES OF CHITOSAN/PHENOL FORMALDEHYDE COMPOSITE

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ABSTRACT

The Frechet distribution which has a scale and shape parameters, has been found to have wide application in modelling extreme events such as radioactive emission, flood, rainfall, seismic analysis, wind speed, etc. In this research paper, the Bayesian analysis of scale parameter of Frechet distribution was considered. It is necessary to know the best combination of prior distribution and loss function for the parameter estimation. Posterior distribution was derived by uniform and Jeffrey's prior under the square error, Precautionary, Quadratic and Weighted balance loss function. Bayes estimation and their corresponding risk was obtained by the above stated priors and loss function. Monte Carlo simulations was conducted to compare the performance of the estimators. It is evident that weighted balance loss function when used with uniform prior provides the least posterior risk.

Keywords: Frechet Distribution, Non-Informative Prior, Bayesian Estimation, Loss Functions, Monte Carlo Simulations

INTRODUCTION

During the past years (1907), phenol formaldehyde resins were the first synthesized thermosetting resins in the world. Today, phenolic resins were widely used, especially insulation materials, wood productions. The relationship between the synthesis conditions, structures, and mechanical properties have not yet been completely clarified. Phenolic resins are two types, the resole type and the novolac type, depending on the method of synthesis and the catalysts used. Novolacs are prepared with a

formaldehyde (CH₂O) to phenol (C₆H₅OH)(F/P) molar ratio < 1.0 in the presence of an acid catalyst producing methylene bridges between the phenol molecules, reported in scheme 1, whereas resole usually have F/P molar ratio > 1.0 and employed an alkali catalyst. The polymer matrix used is novolacs originally Novolak, the name given by Leo Baekeland. Composites of different fibres were used to change the properties of the Novolac in the field of synthesis, properties and characterizations.

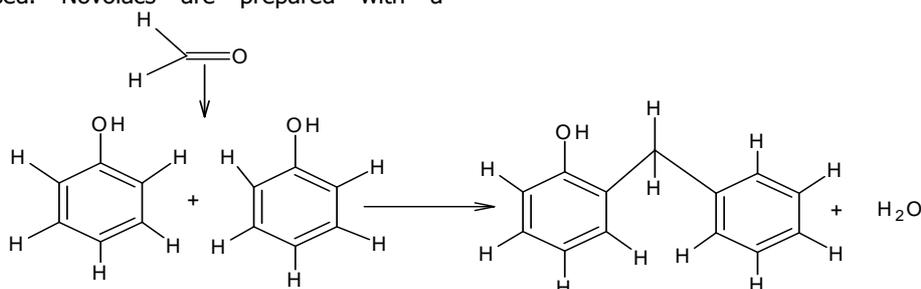


Figure 1 Condensation reaction for the formation of phenolformaldehyde.

Chitin and chitosan are described as a naturally occurring of linear polysaccharides consisting of varying amounts of β (\rightarrow 4) linked units of N-acetyl-2-

amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-glucose units, similar to cellulose as shown in Figure 2 (Muzzarelli, 1997).

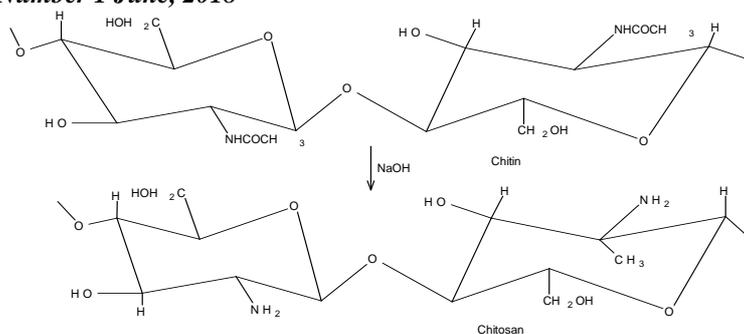


Figure 2 Chemical structure of chitin and chitosan

Chitin has the same backbone as cellulose, but it has an acetamide group on the C-2 position instead of a hydroxyl group and molecular weight (Mw), purity and crystal morphology are dependent on their source (Hudson, and Smith 1998).

A composite is a material developed by combining two or more composites, one of which is a structural component (carbon fibre, vegetables fibres etc) and the matrix, composite (resin), to obtain specific characteristics and properties (Mano, 1991). Recent years have witnessed rapid growth in the use of polymeric composites reinforced with fibre, producing a combination of high performance, great versatility, and other advantages at a favourable cost. One of the fibre used for these polymeric products, chitosan has become an important class of strengthening materials. In the recent work, the commercial chitin was treated with alkali NaOH solution to increase the degree of deacetylation (DD) and then reinforced with the P: F matrix at different mole ratios to obtain the optimum. Thus, the aim of this study is to manufacture composites of phenol formaldehyde/chitosan at different DD% and determined the optimum from them. The optimized sample from the reinforced composites of chitosan phenol formaldehyde testing will be analysed in terms of tensile, flexural, impact and hardness of the chitosan reinforced P: F composites.

MATERIALS AND METHODS

Materials

Sieve 100 micro designation and 60 mesh chitosan were used. Chitin, from shrimp shells, practical grade, and coarse flake was supplied by sigma Aldrich. Mettler balance model HR-200 was used thought the measurement. The compression moulding machine Carver Model 3851-D was used tensile properties were performed using dump-bell shaped specimens on Hounsfield (Monsanto) Tensometer (W) S/No 9875. Flexural properties was measured using Universal Testing Machine 100KN. Impact testing using charpy impact testing machine Cat. Nar412 capacity of 15/25J. Hardness testing (Indentec universal testing, Model 817.5LVN (V). All chemicals employed were of analytical reagent grade and were used without further purification Distilled water was used throughout the investigation.

Methods

Deacetylation (DD) of the Commercial Chitin

The commercial chitin (20g) was charged into a 600 ml beaker containing 200ml of 50% (W/W) NaOH and NaBH₄ as an antioxidant to prevent yellowing of chitosan under the severe alkaline reaction conditions.

The reaction mixture was heated at 110°C for 2hrs while stirring, filtered over a glass funnel with perforated plate, and washed continuously with 50% NaOH solution and filtered in order to retain the solid matter, which is the chitosan. The samples were then left uncovered and air dried. The chitosan obtained were in a creamy white form Muzzarelli (1985).

Distilled water and hydrochloric acid (HCl) were used for the neutralization of the chitosan. Each time about 0.5g was taken for titration to determine the DD%.

Fabrication of the Composites

Each P: F resin was thoroughly mixed with different weight percentages of chitosan of 10%, 20%, 30%, 40% and 50%, using 5% W/W hexamethylenetetramine (HMTA), (equivalent of the resin) as the hardening agent under atmospheric pressure and temperature. The mixture degassed at 35°C in a vacuum oven for 10 minutes. The mixture was poured in mould, the surfaces of moulds were coated on the inside with oleic acid to avoid adhesion of the mixture and allow easy removal of the composite. Composite sheets of size 130mm × 8.5mm × 5mm were prepared by compression moulding technique on compression moulding machine, and were cured at 120°C and a pressure of 400 kg/cm² for 15 minutes was applied.

Determination of Optimum Composite from Different Filler Loading

From the prepared composites at different filler loading of 10% to 50%. Filler loading of 40% with 1P:2F and 1P:4F gave excellent results in terms of mechanical properties. To prove the results, optimization of 1P:2F and 1P:4F were carried out with the fiber at different DD% values. In this case, the DD% values were increased by increasing the concentration of the alkali. In this case, sodium hydroxide (NaOH) concentration were increased to 30%, 40% and 50% w/v at a temperature of 120°C. The calculated 70%, 81% and 91% DD of the chitosan was prepared and reinforced with the P: F molar ratio of 1P:2F and 1P:4F composite were prepared. The composites were subjected to mechanical analysis.

Mechanical Properties Testing

Tensile Testing

The tensile properties were performed using dump-bell shaped specimens on Hounsfield (Monsanto) Tensometer (W) S/No 9875 at a crosshead spread of 5mm/min and gauge length of 40cm as per ASTM standard D 3039.

Flexural Testing

The three point bend test was conducted on all the composite samples according to ASTM D 790 and ISO 178 using (universal testing machine 100KN at a constant rate of 2mm/min and gauge length of 70cm. The dimension of the specimen was 10mm X 4mm X 80mm.

Impact Testing

The test was conducted in accordance with ASTM D 256 using charpy impact testing machine Cat. Nr412 capacity of 15Jk/25J. Composite samples are made up to strict dimensions 120mm X 15mm X 5mm and Charpy impact tests were conducted on unnotched samples.

Hardness Testing

Hardness of the composite sample was tested using a rock well hardness testing [Indentec universal testing, Model 817.5 LKV (V): using the F- scale 60kg as major load and 10kg as minor load with a1/16 inch indenter steel bath and was measured in HRF.

RESULTS AND DISCUSSION

Optimization of 40% 1P:4F and 1P:2F composites

It has been observed that phenol formaldehyde/chitosan composites of 40% filler loading ratio of 1P:4F and 1P:2F exhibits optimum mechanical properties. Hence, they were taken for further analysis.

Tensile Strength and Tensile Modulus

Table 1 and Figure 3 shows the tensile behavior of chitosan P: F composites. The untreated and neat matrix were also presented in the same Table. The brittle nature of the untreated and the virgin polymer had the low values of 8.90MPa and 11.92MPa tensile strength and tensile modulus of 128.89MPa and 150.03MPa respectively. Table 1 shows the variation of tensile strength and tensile modulus of composites 1P:4F and 1P:2F with different chitosan filler loading and DD values.

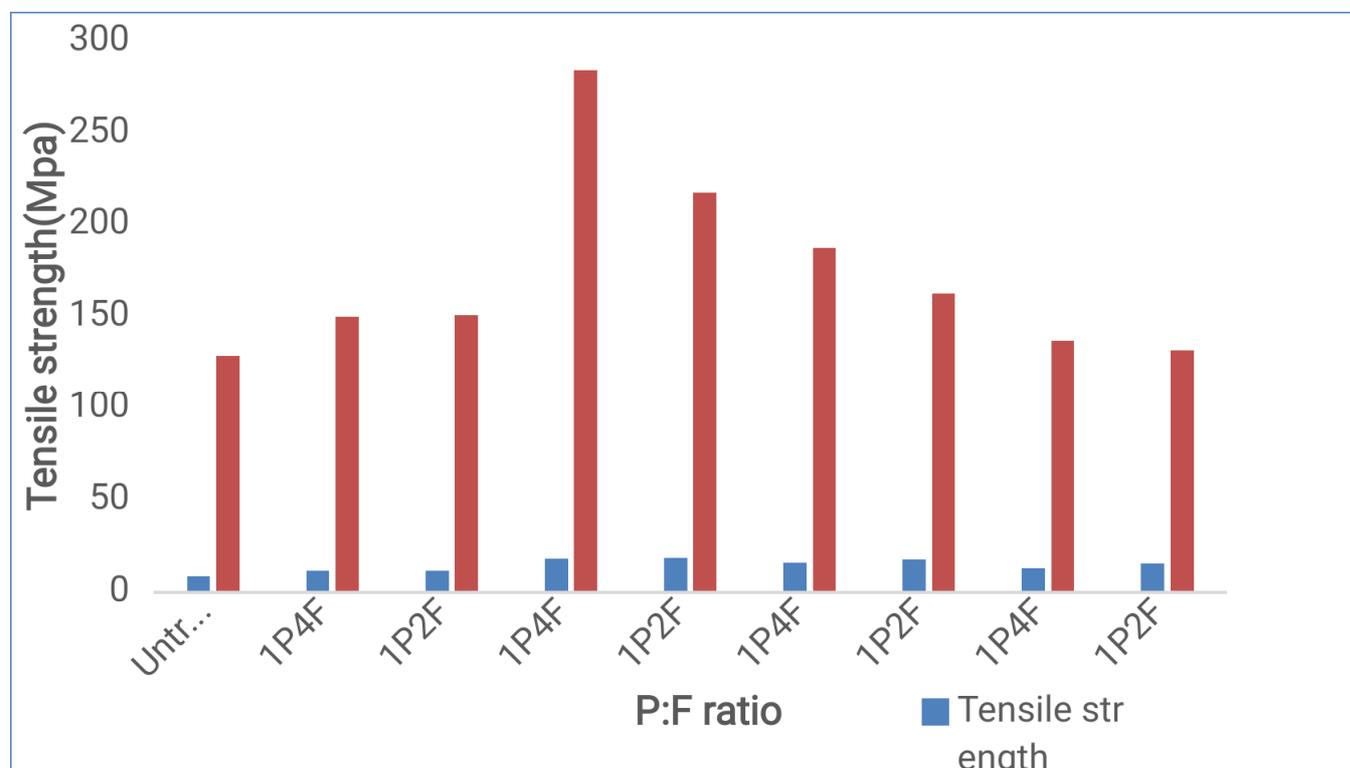


Figure 3 Tensile strength/modulus of 1P:4F and 1P:2F at different DD

The tensile strength linearly decreases with increase degree of deacetylation DD% and also the tensile modulus decreases with the increase of the DD%. The highest tensile strength was observed at 70% DD with a value of 18.40 MPa in 1P:4F and 18.83 MPa in 1P:2F, while the tensile modulus was 284.19MPa at 1P:4F and 217.53MPa at 1P:2F composites respectively. The least value was observed at 91% DD with a value of 13.20 MPa tensile strength and tensile modulus of 137.31 for 1P:4F composite, and 15.75 tensile strength and 131.87 MPa tensile modulus for P: F1P2F composite.

When the values of tensile properties of 1P:4F and 1P:2F were compared with the virgin polymer and the

untreated fibre, the performance increases with DD% values. Chitosan is primarily characterized by its M.wt, which is responsible for a number of its physicochemical properties such as hydrophilicity Pistin (2002). The higher the alkali treatment the higher was the DD and lower M.wt. Also, crystallinity decreases with increased of DD and low M.wt of chitosan and it is hydrophilic contains a large number of hydroxyl groups which are easy to combine with another group and formed new bond Ogawa *et al.*(1992). It was observed that at very high DD% lower the crystallinity and the higher the rate of degradation obtained.

Flexural strength and Flexural modulus

Flexural modulus is a measure of strength and stiffness of the composite. It can be seen from the Figure 4 and Table 1, flexural strength and flexural modulus of 40% at P: F ratio 1P:4F and 1P:2F composites decreases with the increased in DD. where a peak flexural strength and flexural modulus

of 70% DD with values of 1P:4F and 1P:2F were found to be 2,284 Nmm² and 4,738 Nmm² respectively. And the least flexural strength and modulus was observed at 91% DD with a value of (1P:4F) 105.79 Nmm² and 835.05 Nmm² and (1P:2F) 277.66 Nmm² and 897.00 Nmm² respectively.

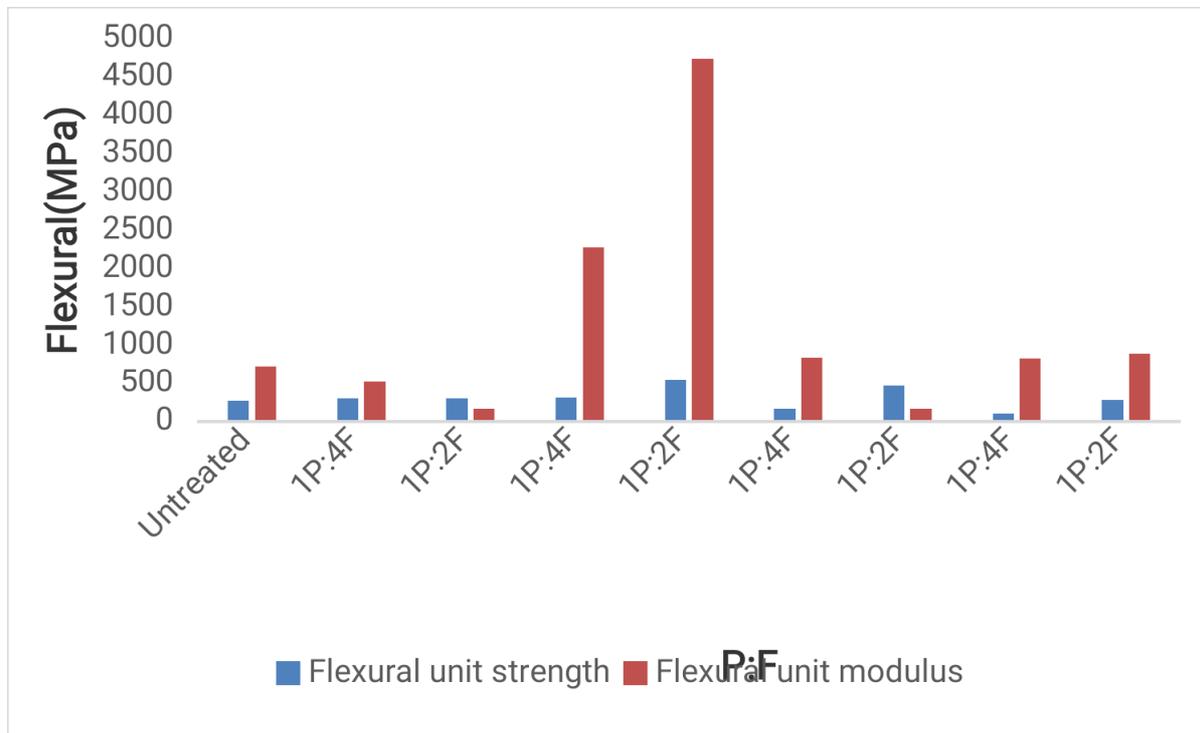


Figure 4 Flexural strength and Flexural modulus of 1P:2F and 1P:4F at different DD%

The flexural strength and flexural modulus of 70% DD is higher than 81% and 91%DD. The decrease in the values upon modifications is attributed to the weaker interfacial bond formed due to the alkali treatment. The highly deacetylated composite have more amino and hydroxyl groups for bonding. Beside, deacetylation at high level disrupt the structure of the composite from the crystalline material to less crystalline sample.

From the same Table 1, the values of flexural test of untreated and the unreinforced composite (neat matrix) were given and showed a lower value compared to that of the reinforced composites. The untreated fibre have a value of flexural strength and modulus of 271N/mm²/730.43Nmm² and the virgin polymer have 305.37N/mm²/517.51N/mm². It was observed that as the DD% increased there was a decline in the flexural strength and flexural modulus. Therefore, based on the relatively high flexural

strength of the 40% at 1P:4F reinforced composite. This is in agreement with many natural fibres as reported by Bledzki and Gassan (1999). The increase in DD at higher level reduces the flexural properties. It shows a strong potential of being used as a suitable material for composite purposes. Decrease in the values upon modifications is attributed to the weaker interfacial bond formed.

Impact Strength

Table 1 and Figure 5 shows the variation of values of DD % of chitosan/P: F composites with different filler loading, neat polymer and the untreated. Impact strength shows its highest value at 40wt% filler loading of 1P:4F and 1P:2F mole ratio. The neat P: F sample shows very low impact strength of 284.44J/N² and the untreated have 146.66J/N². An enhancement in impact strength was observed by different percentage degree of deacetylation DD%

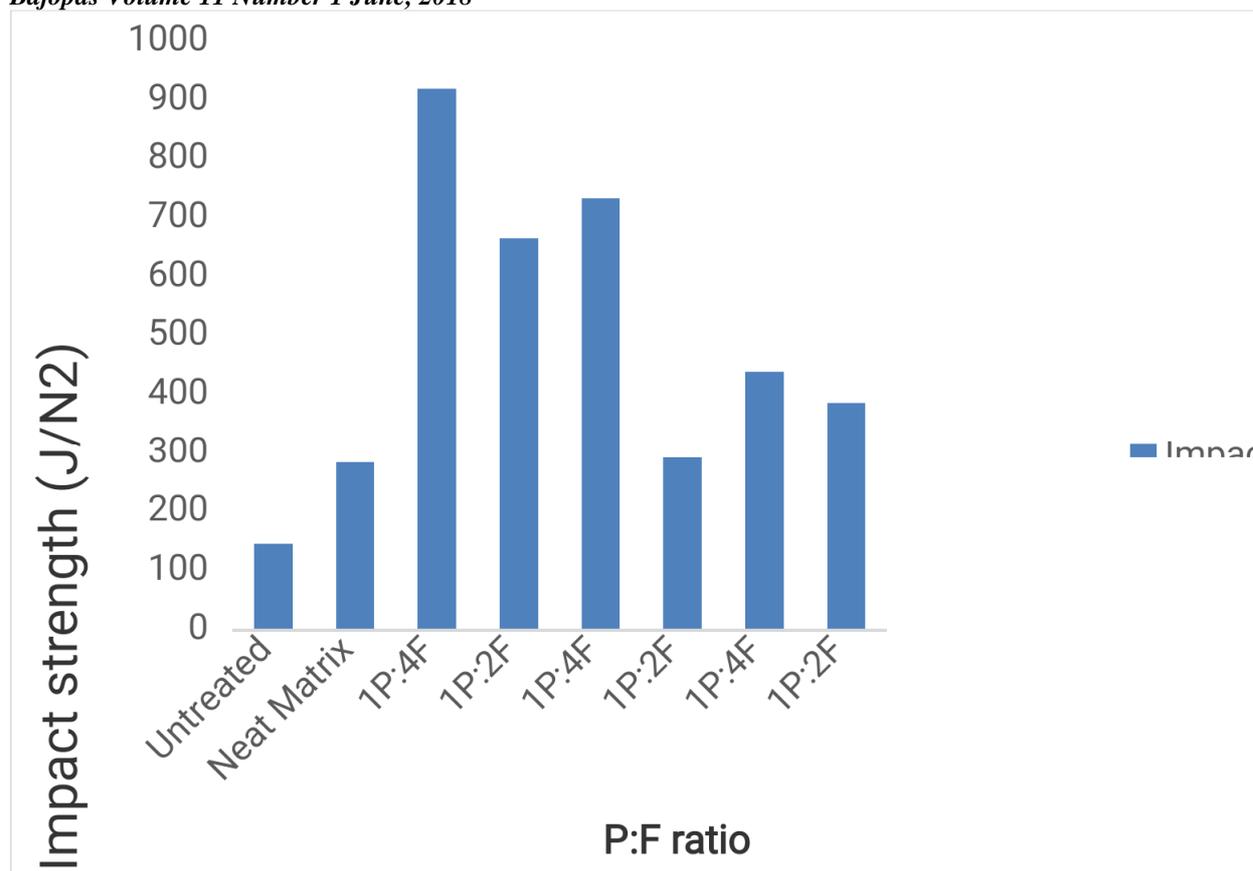


Figure 5 Impact Strength of 1P:4F and 1P:2F at Different DD

From Table 1 the relationship between the average energy and impact strength of the composites was clearly shown. 1P:4F at 91% DD composite has the least impact strength (440.00J/m²), which was followed by 1P:4F at 81% DD composite with impact of (733.33J/m²), and highest value of 920.00J/m² from 70% DD of 1P:4F. Similarly, 1P:2F composite shows similar trend in impact strength with little variation with the values as 666.66, 293.33 and 386.66J/m² for 70%, 81% and 91% DD. The increased filler content is improving its capability to absorb more energy. Similarly the work of Elvine *et al* (2011) shows an increase in impact strength with an increase in chitosan content. The lower DD%, (70 %) with the highest values is an indication and proved to have the highest impact strength. This can be attributed to the presence of strong fibre/matrix interface. Here, But at higher DD 81% and 91% fibre to fibre contact decreases and fibre breakage will be the predominant failure mechanism. The decrease in impact strength with the increase DD% is attributed to the poor interfacial adhesion between the hydrophobic (PF) matrix and hydrophilic chitosan filler with void formation in the composite thereby reducing the toughness of the composites as reported by Raje *et al*, (2012). The inter filler interaction decreases the

effective stress transfer between the fibre and matrix. This contributes to a decreased in impact properties at higher DD% (Josiah 2014; Mohammad 2012). Therefore it can be concluded from the values in Table and Figure 3 that the relationship between DD percent of chitosan loading and impact strength exhibit an approximate linear increase. Generally, increase in the degree of the deacetylation (DD %) of chitosan content from 70 – 91wt% DD caused the decrease of the impact energy, because of the reduction of cohesion's which exist between the fibre and the polymer. This is due to the high removal of the acetyl group from the fibre which brings strong crosslinking between the fibre and the polymer and more hydroxyl group Elvy *et al* (1995). The chemical treatment has reduced the crystallinity through the crosslinking reaction. The hydrogen bond between polymer chains from the two functional groups of –NH₂ and -OH was broken due to the mercerization at high level. Then, the amorphous region of the polymer was increased Li *et al*, (2007).

Hardness Testing

Hardness was a measure of resistance to indentation and the values obtained were used to evaluate the mechanical strength of each composite. The hardness of untreated, neat matrix and DD of 70%, 81% and 91% samples were shown in Figure 6.

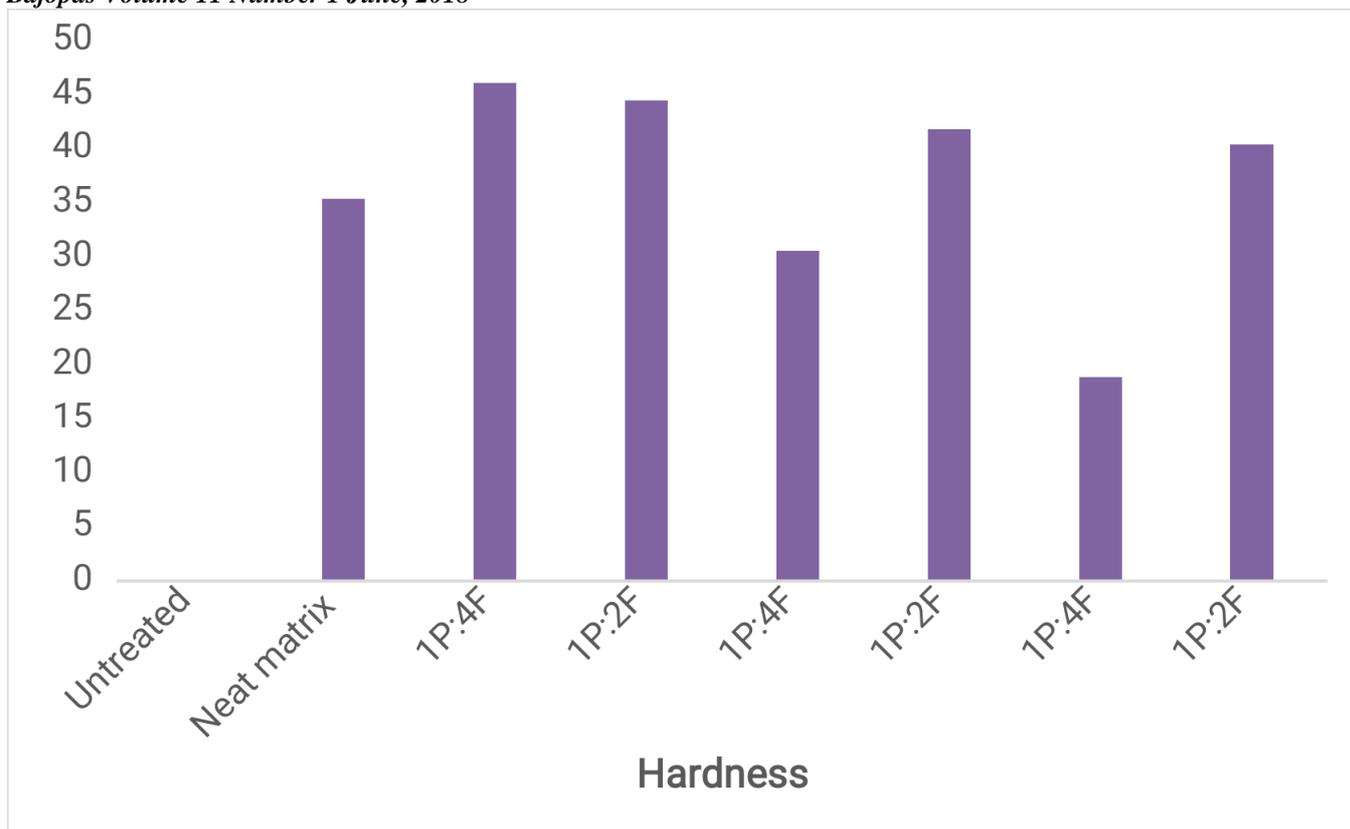


Figure 6 Hardness of 1P:2F and 1P:4F at different DD%

Hardness testing values were given in Table 1 and Figure 6, it shows an average value and phenol formaldehyde itself is very hard with a value 35.34 HRF scale and the untreated show brittleness. From the same Table 1 shows the average values of hardness of the composites of 40% filler loading of 1P:4F and 1P:2F ratios. The hardness of 1P:4F and 1P:2F were found to be 46.07HRF /44.47HRF as the highest value at 70% DD, and 18.90HRF/40.43HRF as the least values at 91% DD. The hardness of the untreated is brittle. It was observed that hardness of the treated reinforced composite at different DD values decreases with the increase of DD percent. It was observed that the treated at different DD 70% to 91% values exhibited better hardness compared to the raw polymer (neat matrix) from 70% to 91%DD Rahman *et al* (2008). Furthermore, there was considerable improvement in the hardness for the treated fibre P: F composites. This phenomenon could be attributed to the better adhesion of the polymer to the chitosan fibre brought about by the chemical treatment Elvy *et al*(1995).

The highest was observed at 70% DD 40% filler loading and raw polymer (neat matrix) with the values of 35.34HRF and 46.07HRF. This could be attributed

of the good dispersion formed between the matrix and the filler besides the reducing of voids and stronger interfacial bonding between the fibre and matrix. The decreased in flexibility and increase of stiffness of the respective composites enhance the hardness properties as reported by other researcher Rezaur *et al*(2010) Thus it is evident from the results that chitosan filler as reinforcement has improved the mechanical properties of the P-F composites.

CONCLUSION

An optimum composites of 40% of 1P:4F and 1P:2F mole ratio were determined and gave excellent results at 70% DD. Their mechanical properties such as tensile strength, tensile modulus, flexural strength, flexural modulus, Impact strength and Hardness of reinforced chitosan phenol formaldehyde composites were excellent. Behavior of composites were reported and these could be used as determining parameters for the applications of these composites. The overall results of the study shows that reinforced chitosan phenol formaldehyde composites, which were deacetylated and cured with the hardener (HMTA) at 70%,81% and 91% DD gave excellent mechanical properties enhancement than those without deacetylation and curing agent.

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