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Synthesis, Chemical Resistance and Thermal Behavior of Polyfurfural Alcohol

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Abstract

Polyfurfural alcohol (PFA) is a thermosetting polymers of furan class which has gained great importance mainly due to it being obtained from renewable resources, so in this study PFA was synthesis through polymerization of furfural alcohol in acidic medium. PFA was evaluated, and the chemical resistance of cured PFA toward some chemical compounds was study and it was observed that the cured resin was stable towards most of these chemical compounds during the test time. On the other hands heat treatments of cured resin was study at different temperatures, and the results shown that the resin has high char contents, and the FTIR study of the heat cured resin indicates some chemical change in the polymer structure

Keywords: PFA, FTIR, heat cure ,chemical properties

1-Introduction

Furfural has been identified as a very important and promising chemical precursor directly derived from biomass(1) .Furan monomers including furfural alcohol (FA) are aromatic heterocyclic derived from the hydrolysis of pentosan rich biomass like (corn husks, bagasse and rice hulls) (2),(3)in the presence of acid as shown in Figure 1.



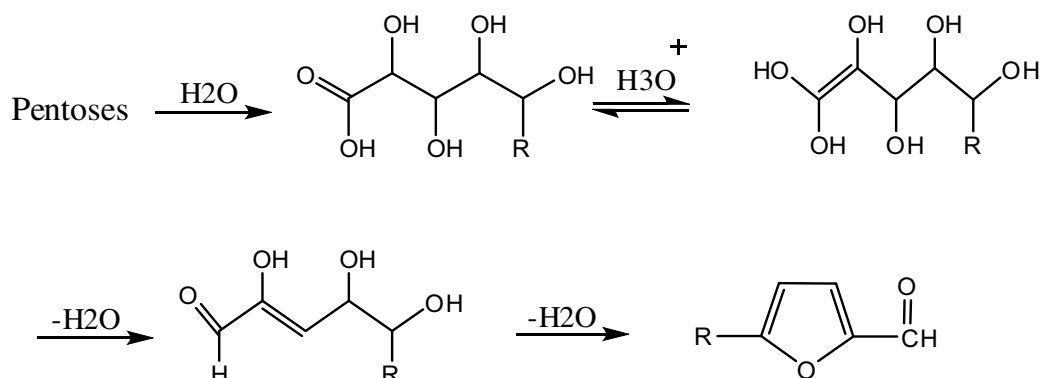


Figure 1. Synthesis route of furfural

Furfural alcohol (FA) was obtained from hydrogenation of furfural(4), which can be readily polymerized using acidic medium(5, 6) like hydrochloric acid, sulfuric acid, and p- toluene sulphonic acid.

Poly furfural alcohol (PFA) has excellent thermal stability, resistance to acidic condition and anticorrosion polymer(7), therefore has largely used in the formation of wood adhesives, in glass -fiber reinforce composites as binding agent in foundry sand (8, 9).

Also (PFA) used in the synthesis of green composites(10), and have gained interest using in the synthesis of gas separation membranes(11) due to their properties. Biofilms with low water uptake could be a promising route to potential environmentally friendly applications using PFA (12) . PFA is largely used in the fabrication of nanostructure carbons and Nano composites (13). Furan resins also offer excellent fire resistance and comparable mechanical strength when combined with glass fibers(14, 15).

Different organic polymers used to produce Nano porous carbon (NPC), Among them, PFA is a common typical thermosetting resin that forms carbon with a fairly high yield on pyrolysis and carbonization due to it is strong resistance to transformation to graphite when annealed at temperature above 2000 C⁰ (16, 17), due to the presence of extensive cross-linking in the precursor. Because of these properties furan resins offer several advantages over other synthetic resin based banded system such as unsaturated polyester, epoxy resin and etc , In this study the chemical resistance of cured PFA using different chemicals were stuaned heat treatment were evaluated and also the heat treatment of the cured polymers at different temperature were studies, from the result ,the polymer show very interested properties against chemical and heat resistance.

2- Experimental part

2.1-Materials.

- Furfural alcohol (FA), sulfuric acid 90 % and sodium bicarbonate were obtained from Merck company.
- Conc. perchloric acid 70 %, conc. Hydrochloric acid 35-37 % , conc. Nitric acid 68% and sodium chloride were supplied from Fluka company .
- Acetone, hexane and ethanol were supplied BDH company. these materials were used without other purification.

2.2-Instruments:

- Viscosity Measurements.

The viscosity of uncured PFA was measured using Brookfield rotary viscometer type Alpha series code V100002 with the spindle at 23 C⁰ .

- Fourier Transform Infrared (FTIR).

The FTIR spectra of uncured and cured PFA were performed in shimadzu , FTIR - 8400 S ,in a frequency range of 400-4000 cm using sodium chloride and potassium bromide cell .

- Resin Solid content

The percent of resin solid content (S). Was calculated by the following equation.

$\%S = S_1/S_0 \times 100$. Where S₀ and S₁ are the weight of the resin before and after dried (3 hrs. .at 105 C⁰) respectively .

- Absorption Study.

Absorption was determined according to the standard ASTM DS 70-98 test methods. The cured and composite PFA samples were initially dried at 50 for 1 hr, weighted, and placed in desiccator. Then, the initial mass of samples was recorded and then immersed in deionizer water and weighted for 24 hr.

2.3- Synthesis.

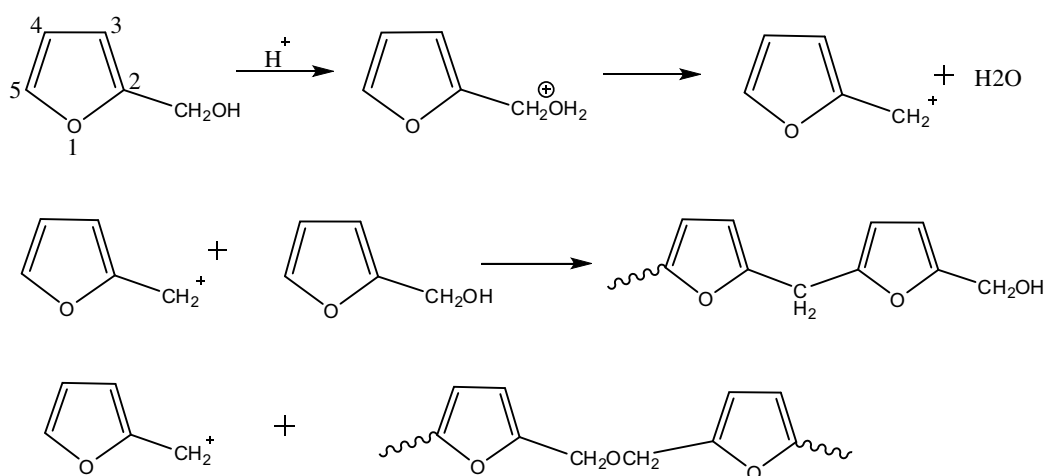
Polymerization of FA was carried out in flask provided with stirrer, 5 ml of 1 M sulphuric acid was added slowly to 50 g FA, after complete the addition, the mixture was kept out at room temperature. After about 2 hrs, the viscosity. was increase which in dictate the polymerization of this mixture. Then 50 ml of hexane was added and washed with distilled water several times to remove the acid, and finally washed with saturated solution of sodium bicarbonate. Hexane layer was removed and dried over Magnesium sulphate, filter and, evaporate the solvent

using rotary evaporator to obtain brown viscous material which was characterized by FTIP, and several other characteristic were determined, acid number, hydroxyl value, Molecular weight and the viscosity of the final product On the other hand cured PFA was done by heating weight sample of PFA in oven at 120 C⁰ until no change in weight, then post cure at 140-150 C⁰ for 3 hrs. Solid brittle polymer was obtained and characterized by FTIR , TGA and other study.

3-Resultion and Discussion.

3.1-Reation scheme and FTIR study.

The first step on acid-catalyzed polymerization of FA is the alkylation at C5 position of furan heterocyclic structure (18),i.e. condensation between hydroxyl group forming ether linkage as showing in scheme .1, While the behavior and repeating unit of the polymer was represented in Figure 2and 3.



Scheme 1. Condensation polymerization of FA

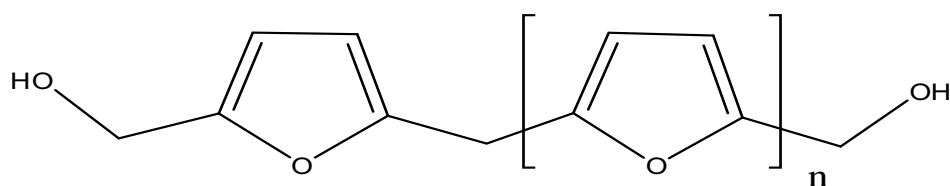


Figure 2. Repeating unite of PFA



Figure 3. Image of PFA prepared in this study

The product was characterized by FTIR, represented spectrum was shown in Figure 4. bands at 735, 1014, 1149, and 1508 cm^{-1} are attributed to the furan rings (19). While bands at 790 and 1560 cm^{-1} due to the bending vibration (out of plane) of CH_2 linkage and to stretching vibration & $-\text{C}=\text{C}-$ groups in the 2,5- di substituted furanic rings respectively (20).

Also, band at 3450 cm^{-1} is assigned to the stretching vibration of the hydroxyl end group formed in the to the carbonyl formed during to the ring opening of some furan ring (28).

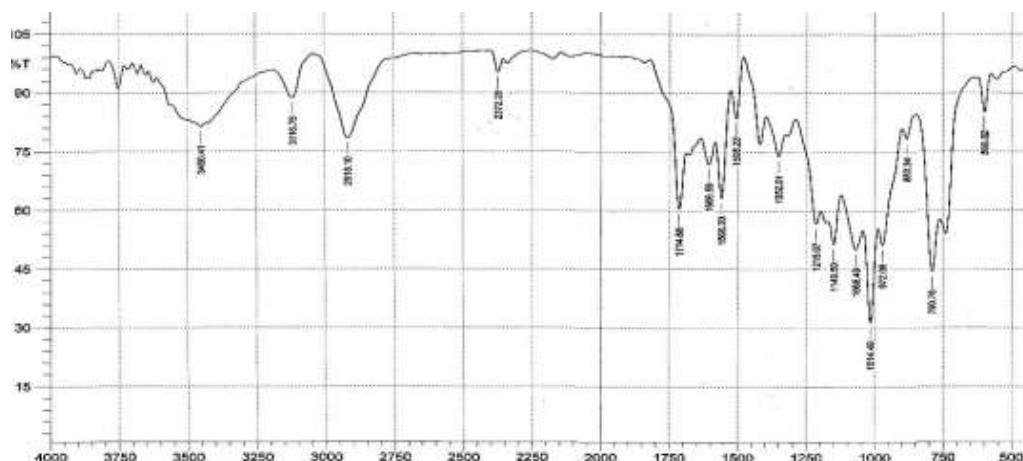


Figure 4. FTIR spectrum of PFA

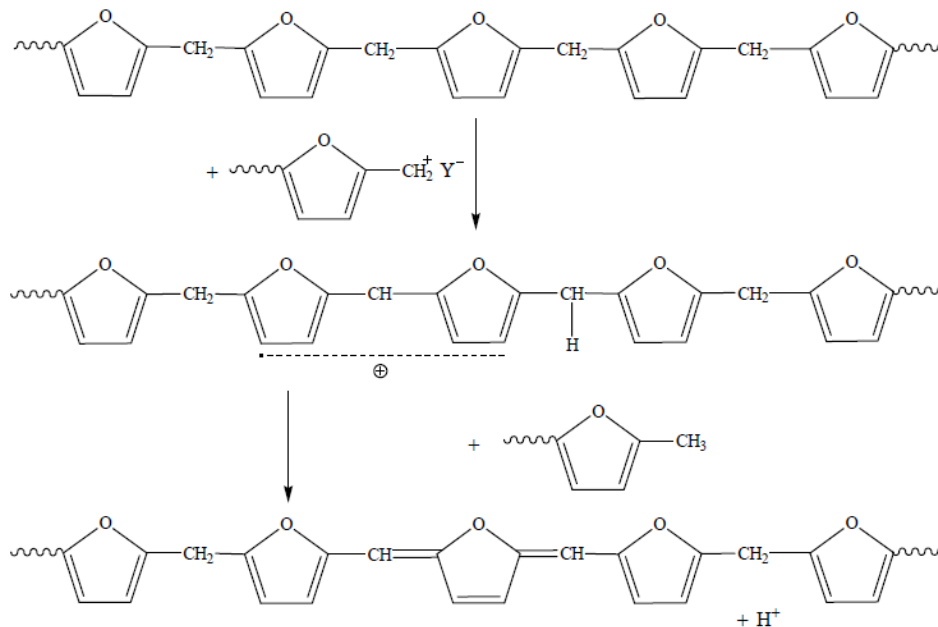
From the acid number, hydroxyl number obtained data by end group analysis (21). The molecular weight M_n of PFA was determined according to the equation below:

$$M_n = (2 \times 56.1 \times 100) / (A+B)$$

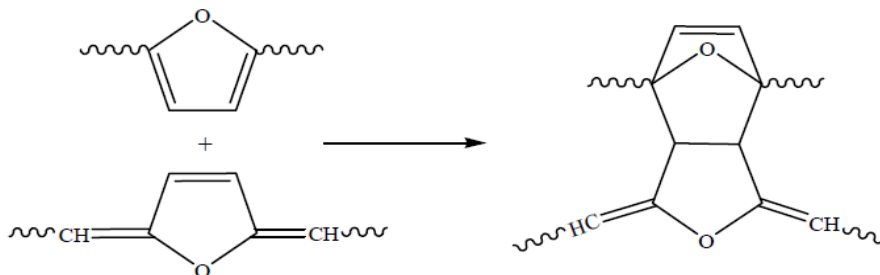
Where 56.1 g/mol is the molecular weight of KOH, A is the acid number and here was calculated according to the literature procedure (22), and equal to 1.9 mg

/ KOH g. sample, while B is the hydroxyl value equal to 98 mg/KOH g. sample, so the molecular weight of PFA is equal to 1123 g/mole. Also, the viscosity of the polymer was 420 poise which was determined using Brook field rotary viscosity, while the solid resin content was 53 %.

The cross linking of PFA was carried out by heating the polymer leading to obtained three-dimensional structure, this involve macro radical mechanism, while poly unsaturated sequence was produced, by successive hydride – ion/proton abstraction from the methylene group as shown in scheme .2. Also, a novel Diels-Alder condensation may occur between the furan ring acts as a diene, and conjugated sequence acts a dienophile as shown in scheme 3.



Scheme.2 Sequence of reactions leading to conjugation along the backbone of PFA.



Scheme.3 Diels-Alder condensation reaction to form cross-link PFA

3.2. Chemical Resistance Study:

The chemical resistance of the cured PFA was studied, polymer samples with dimension (32X3 mm) as shown in Figure 5. was immersed in different chemical solution for exposure periods one month at room temperature, the result of this study was listed in Table 1. and Figure 6. While the solution absorption from these sample were listed in Table 2.



Figure 5. Image of cured PFA used in chemical resistance study before immersion in chemical solution.

Table.1- Remarks on cured PFA after chemical resistance study

| Type of chemical solution | Remarks |
|---------------------------|---|
| Conc. Nitric acid | after 5 days the sample has crashed and collapse |
| Conc. Sulfuric acid | after 7 days the sample has crashed and collapse |
| Conc. Perchloric acid | Small change in the color of solution during period of study and no change in sample size |
| Conc. Acetic acid | Small change in the color of solution during period of study and no change in sample size |
| Conc. Hydrochloric acid | no change in the color of solution and sample size during period of study |
| 2 % Sulfuric acid | no change in the color of solution and sample size during period of study |
| 2 % Perchloric acid | no change in the color of solution and sample size during period of study |
| 2 % Nitric acid | no change in the color of solution and sample size during period of study |
| 2 % Hydrochloric acid | no change in the color of solution and sample size during period of study |
| 10 % Acetic acid | no change in the color of solution and sample size during period of study |
| 10 % Sodium hydroxide | Small change in the color of solution during period of study and no change in sample size |
| 10 % Phosphoric acid | no change in the color of solution and sample size during period of study |
| Diestel water | no change in the color of solution and sample size during period of study |
| Saturated sodium chloride | no change in the color of solution and sample size during period of study |

Table.2- Absorption results of cured PFA

| Type of chemical solution | Absorption % |
|---------------------------|--------------|
| Conc. Nitric acid | 2.122 |
| Conc. Sulfuric acid | 1.879 |
| Conc. Perchloric acid | 2.938 |
| Conc. Acetic acid | 1.321 |
| Conc. Hydrochloric acid | 1.008 |
| 2 % Sulfuric acid | 0.909 |
| 2 % Perchloric acid | 1.491 |
| 2 % Nitric acid | 2.388 |
| 2 % Hydrochloric acid | 1.049 |
| 10 % Acetic acid | 1.912 |
| 10 % Sodium hydroxide | 2.161 |
| 10 % Phosphoric acid | 1.672 |
| Distel water | 1.409 |
| Saturated sodium chloride | 0.741 |

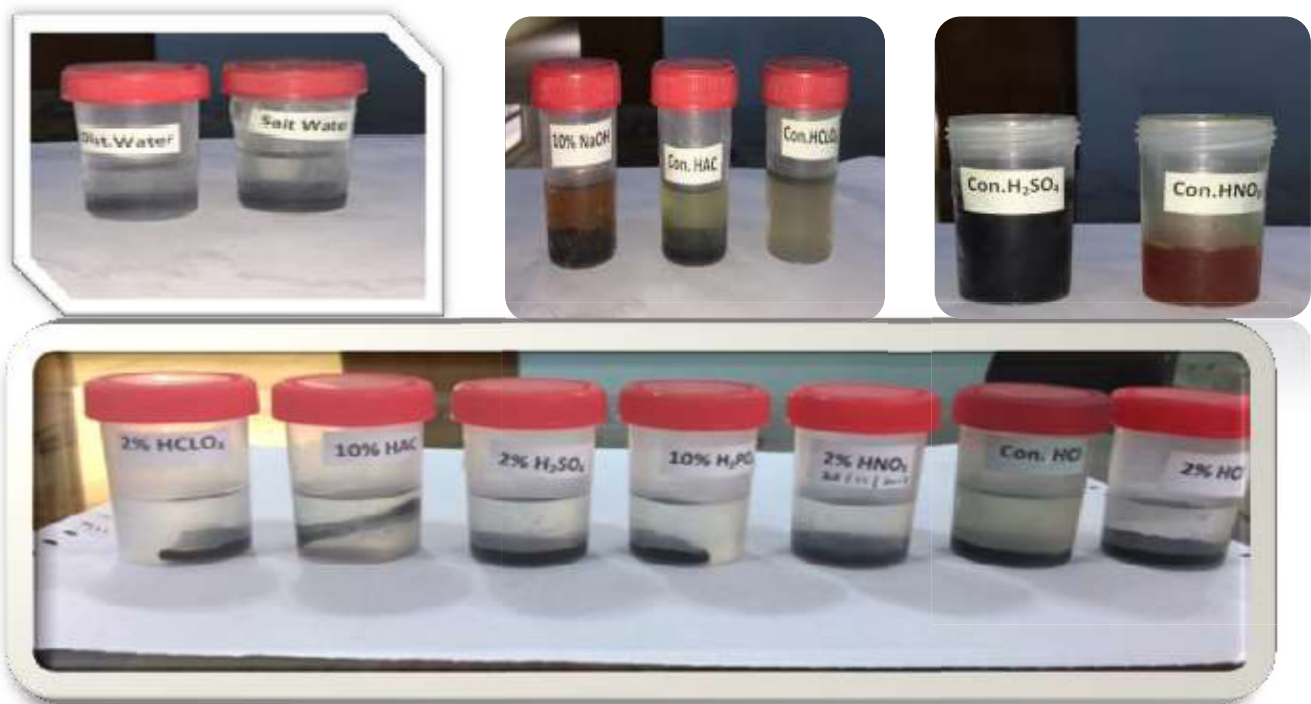


Figure.6- Image of chemical resistance study, (this image taken after one month).

From the result show that the polymer samples immersed in concentration nitric and sulfuric acid was crashed and collapsed after 6 days while the other. Samples immersed in 10% . of sodium hydroxide, concentrated acetic acid and perchloric acid) only change in colors of the solution and the other samples were stable to word chemicals during the period time of study.

3.3- Heat treatment of Cured PFA.

Heat treatment of the cured polymer was carried at different temperatures (250,300,350,400 and 500 C⁰) respectively in muffle furnace at hold time 2 hrs. The weight change of the polymer after heat treatment was determined and the result was listed inTable.3.

Table.3 weight loss of cured PFA at different temperature

| Temp.c ⁰ | % weight loss / Hold time 2hrs. |
|---------------------|---------------------------------|
| 250 | 1.20 |
| 300 | 5.52 |
| 350 | 10.14 |
| 400 | 28.26 |
| 500 | 35.73 |

From the data on table 2. the weight loss was increase with increasing temperatures , also no change in color of PFA samples was observed and the low weight loss of cured PFA at high temperature is a good indication for use PFA as thermal insulators On the other hands the FTIR Spectra of the cured samples after heat treatment was recorded and listed in Figure (7-11) , as we increase the heat treatment of cured PFA to 250 c⁰ , we found that many of the characteristic band of PFA before heat treatment were still present .The FTIR spectrum of cured PFA heated at 300 c⁰ exhibited new band at 1427 cm⁻¹ indicate of the formation of methylene link between furan ring ,also the spectrum show disappearance band at 3116 cm⁻¹ ,while the spectra of heat treatment PFA at 350,400 c⁰ show the same bands as in heat treatment PFA at 300 C⁰ but the shape of band around 1712 and 1600 c⁰ was different . Finally, the spectrum of heat treatment PFA at 500 c⁰ show disappear of a band around 2900 cm⁻¹, this means the formation of poly aromatic structures, also new band appear at 1743 cm⁻¹ suggesting the presence of additional carbonyl groups, Figure 12. Show several structural models PFA and its carbon, the poly aromatic domain is shown as consisting of six-membered rings.

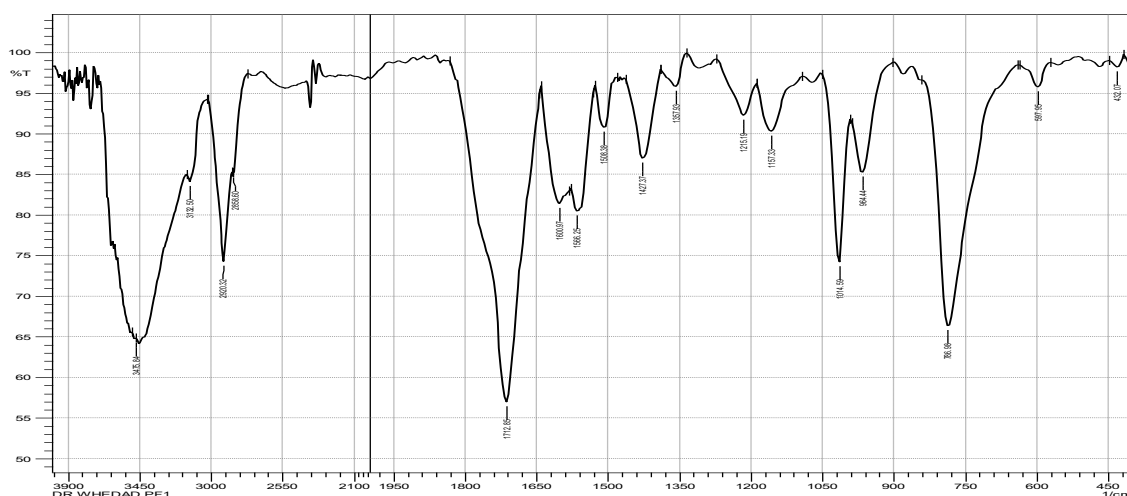


Figure 7. FTIR spectrum of PFA after heat treatment at 250 C⁰

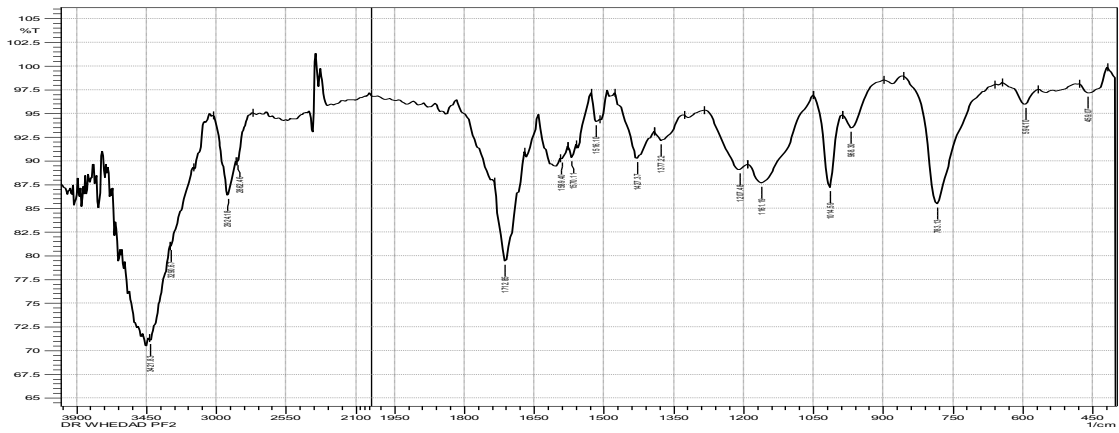


Figure 8. FTIR spectrum of PFA after heat treatment at 300 C⁰

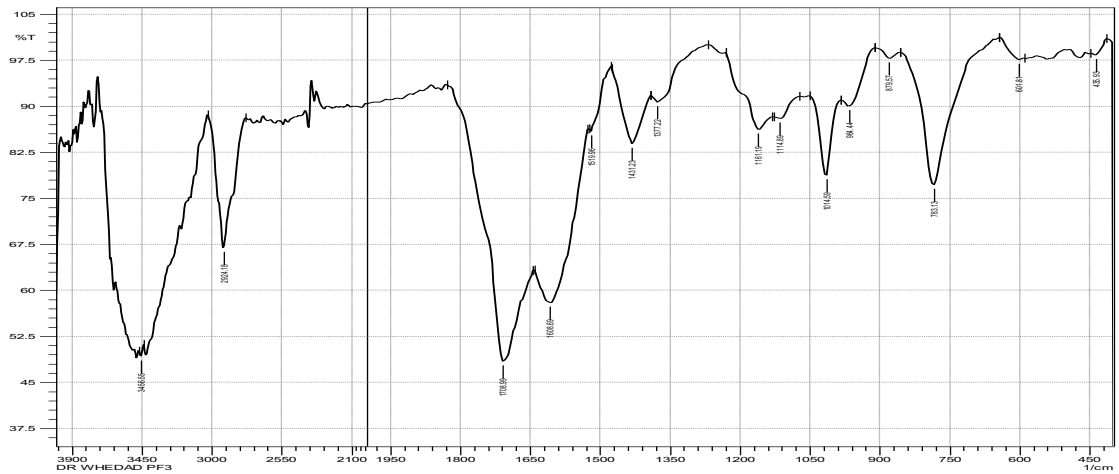


Figure 9. FTIR spectrum of PFA after heat treatment at 350 C⁰

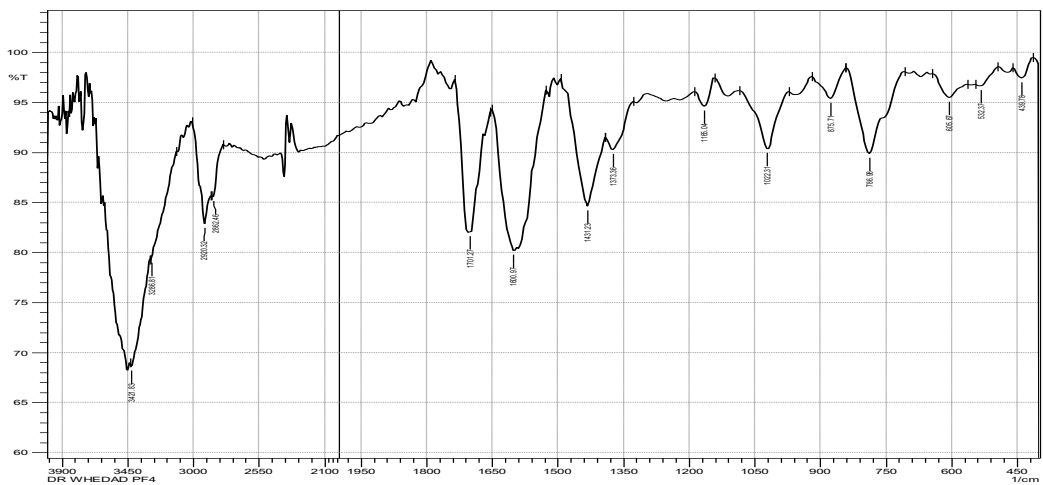


Figure 10. FTIR spectrum of PFA after heat treatment at 400 C⁰

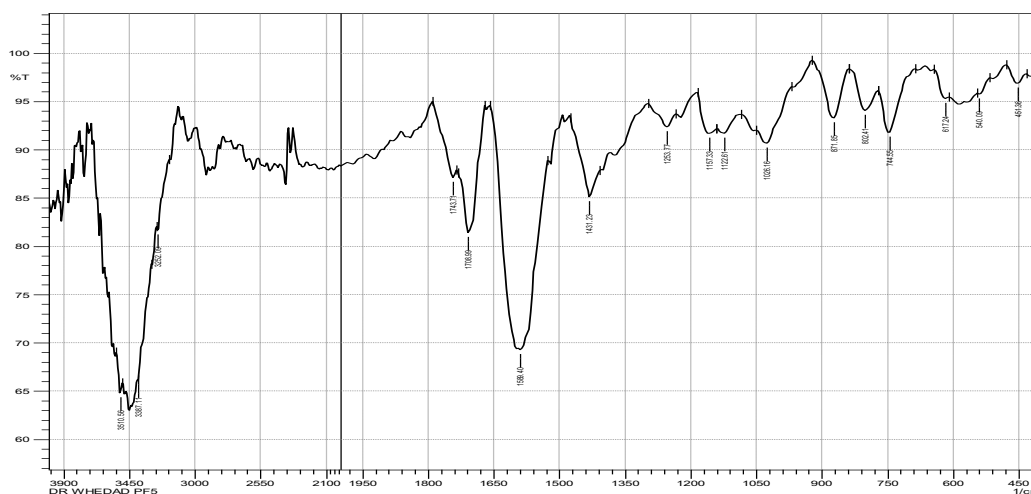


Figure 11. FTIR spectrum of PFA after heat treatment at 500 C⁰

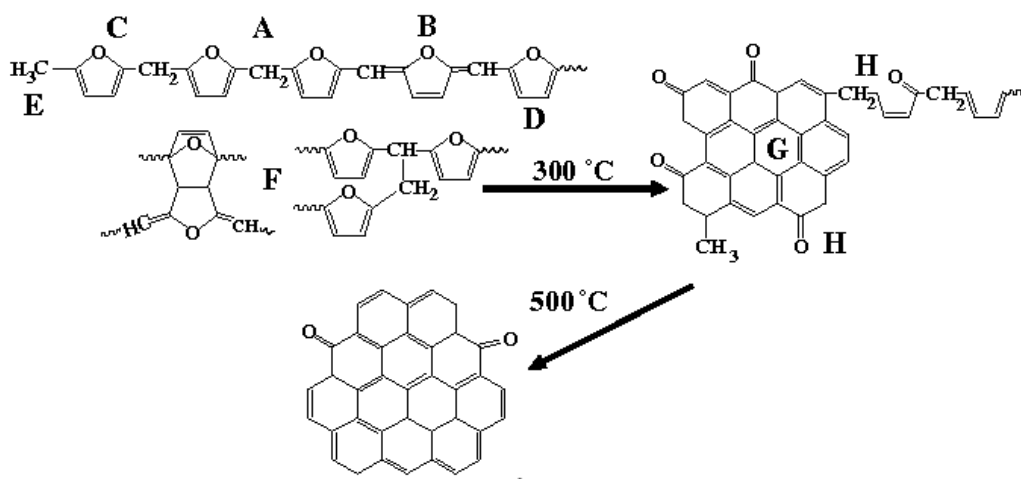


Figure 12. proposed chemical structure of cured PFA after heat treatments.

A refer to methylene linkage, C refer to 2,5-linkage on the furan ring , B refer to conjugated double bonds, F refer to crosslink reaction during heat treatments ,G refer to formation of aromatic rings during heating (polyaromatic) and H refer to formation of carbonyl groups during heating at high temperatures.

Conclusion

PFA was prepared using acidic medium and crosslink PFA was obtained after curing of the resin. Cured PFA was resistance to most of the chemical compounds used in this study, on the other hand the result of heat treatment of the cured resin show that the char content is high and the weight loss of the resin at 500 C was less than 40 % this leads to used of PFA as thermal insulator.

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