

**ABSTRACT**

We report the synthesis, characterization, thermal and microbial properties of a series of [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Acrylonitrile] [C1-PAMI-B], [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Acrylic acid] [C2-PAMI-B], [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Vinyl acetate] [C3-PAMI-B] copolymers and [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide - Acrylonitrile - Vinyl acetate] [T1-PAMI-B] and terpolymer [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide - Acrylic acid - Vinyl acetate] [T2-PAMI-B] terpolymers of maleimide containing compounds. Polymer's structures of different side groups with same chain back-bone of maleimide are performed for the study of effects on glass transition point along with chain-flexibility. All polymer's structure are confirmed by C/H/N-elemental analysis, FT-IR and <sup>1</sup>HNMR spectral analysis. Molecular weight and polydispersity are determined by gel permeation chromatography (GPC). Thermal stability of polymers are investigated from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Microbial activities of the polymers are also examined on various bacteria / fungi.

**KEYWORDS:** Thermal stability, Microbial Activity, Terpolymer, Copolymer, TGA, DSC.

**INTRODUCTION**

The work performance prediction was depends on the chemical constitutions of chained molecules in polymer materials. The great efforts have been made for the selections, improvements and design to achieve a desired quality-class of polymers. In recent last years, attention has been paid to the homopolymerization and copolymerization of maleimide containing compounds to catch the useful range of glass transition temperature (T<sub>g</sub>) and the thermal degradation temperature. N-substituted maleimide copolymers with acrylates showed amazing thermal properties accompanied by characteristic polymerization behavior and it has been proven experimentally and theoretically [1-5] but exceed of N-substituted maleimide moiety, increases chain-rigidity, causes the drop of mechanical properties such as tensile strength and impact strength and achieved with enhancement of T<sub>g</sub>-value [6-11].

However, acrylic polymers have poor heat resistance efficiency and the glass transition temperature (T<sub>g</sub>) are generally between 80 °C to 110 °C that is very low and not applicable in processing segments in concern industries. The copolymerization of N-substituted maleimide and acrylates / vinyls has been known as one of the best path to improve the heat resistance capacity of acrylates / vinyls. The presence of N-substituted maleimide structure in polymeric chain inevitably increases both the T<sub>g</sub> and The decomposition temperature of the targeted acrylates / vinyls [12]. However to enhance the T<sub>g</sub> value and thermal stability of acrylates / vinyls derivatives and to overcome the rigidity behavior of maleimide compounds in polymeric chain included with some antimicrobial properties, we are mainly focused on synthesis of thermal-stable, microbial resists, flexible bearing with processing range T<sub>g</sub> temperatured terpolymers and copolymers of N-substituted maleimides, acrylates and vinyls and to established the relative comparison among their copolymers and terpolymers.

## MATERIALS AND METHODS

Maleic anhydride (AR), Diphosphorus penta oxide (AR), Tetra hydro furan (THF), DMF, 4-Bromo aniline (AR), Sodium nitrate, Hydrochloric acid, 4-N-Phenyl ethanamide were purchased from Aldrich. Other reagents and solvent were used as received.

### Experiments

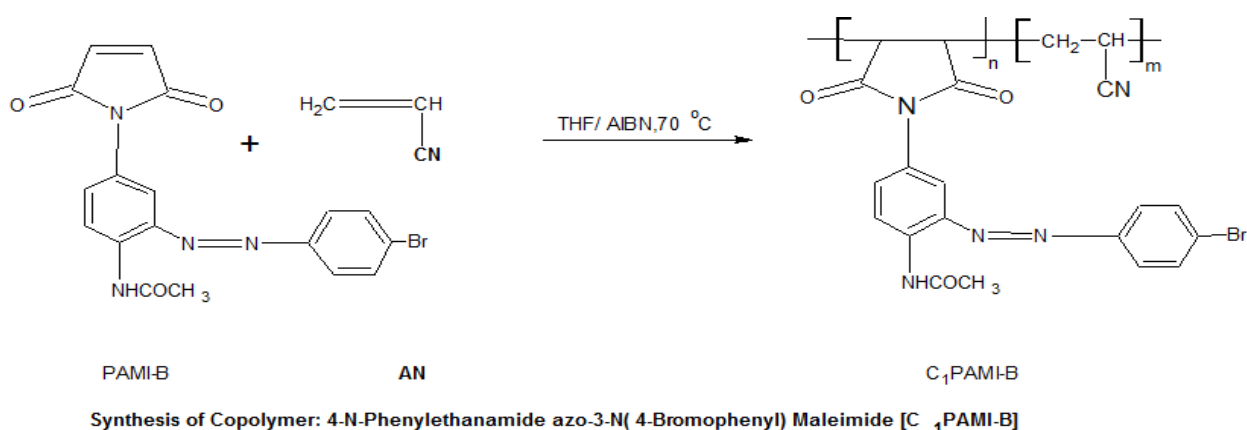
#### A.Synthesis of monomer (PAMI-B):

4-N-Phenyl ethanamide (PAMI) was synthesized according to previously published procedure<sup>[13]</sup>. The preparation of monomer compound (PAMI-B) is shown in [scheme 1].

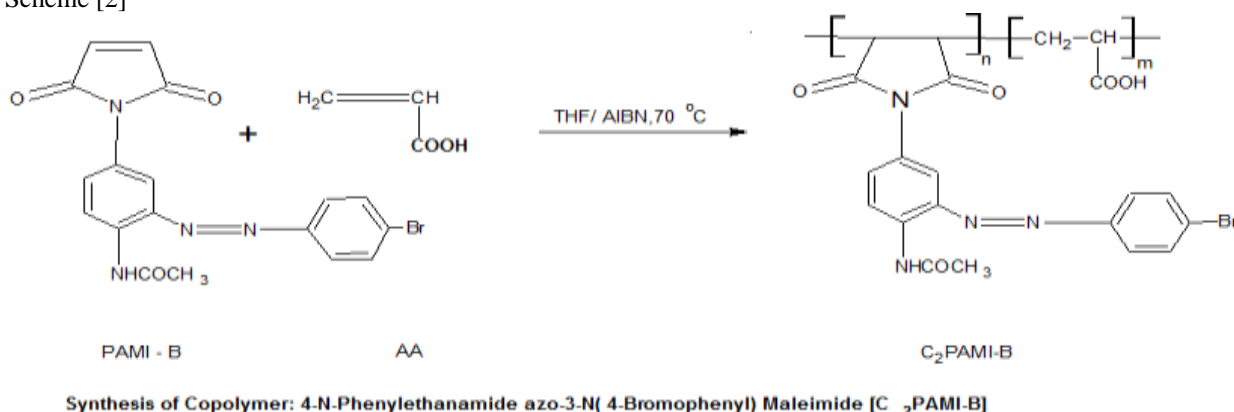
#### B. Synthesis of Polymers C1-PAMI-B / C2-PAMI-B / C3-PAMI-B / T1-PAMI-B / T2-PAMI-B:

Copolymers C1-PAMI-B, C2-PAMI-B, C3-PAMI-B was synthesized from acrylonitrile (AN), acrylic acid (AA) and vinyl acetate with monomer, scheme [1-3]. Furthermore, Terpolymer T1-PAMI-B (PAMI-B-AN-VA), T2-PAMI-B (PAMI-B-AA-VA) were synthesized Scheme [4-5] and the process was similar as previously reported [8].

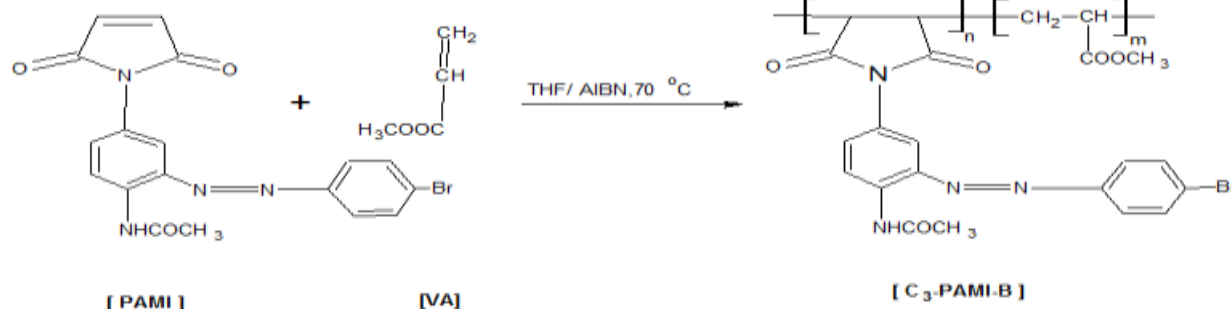
Scheme [1]



Scheme [2]

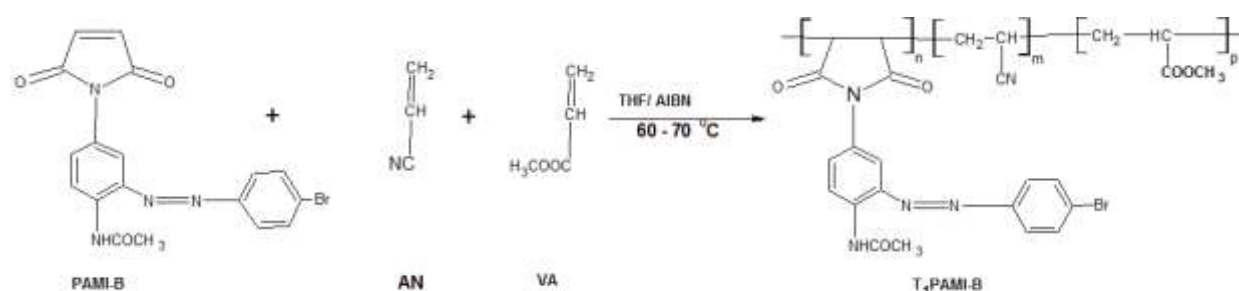


Scheme [3]



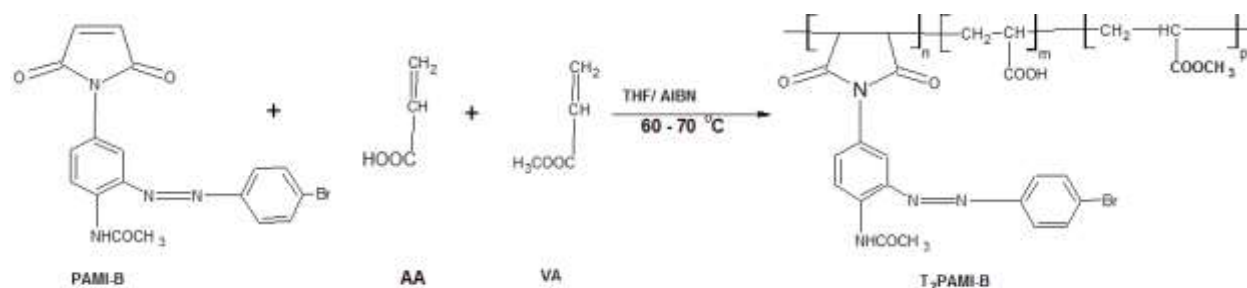
Synthesis of Copolymer: 4-N-Phenylethanamide azo-3-N( 4-Nitrophenyl) Maleimide [C<sub>3</sub>-PAMI-B]

Scheme [4]



Synthesis of Terpolymer: 4-N-Phenylethanamide azo-3-N( 4-Bromophenyl) Maleimide [T<sub>4</sub>PAMI-B]

Scheme [5]



Synthesis of Terpolymer: 4-N-Phenylethanamide azo-3-N( 4-Bromophenyl) Maleimide [T<sub>2</sub>PAMI-B]

## RESULTS AND DISCUSSION

### Instrumentation

FT-IR spectra were measured at room temperature in perkin-Elmer spectrometer mode RX-I FT-IR equipped with a high purity dried KBr pellets as beam splitter. The <sup>1</sup>H-NMR spectra was obtained using a Bruker Avance II 400 MHz NMR spectrophotometer with TMS as an internal reference. CHN micro-element analysis were performed using Thermofinnigan Combustion Analyzer. The entire samples were weighted and dissolved in DMSO.

### A.Characterization

**1. 4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide[PAMI-B] Compound I** -Yield 87%, melting point 148-50 oC; color dark brown, FT-IR (KBr): 1704 cm<sup>-1</sup> (C=O),3300 cm<sup>-1</sup> (N-H), 3095 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1602 cm<sup>-1</sup>(C=O, amide), 1666 cm<sup>-1</sup>(CH=CH, C-C Stre.), 1372 cm<sup>-1</sup>(C-N-C), 1532 cm<sup>-1</sup>(N=N), 516 cm<sup>-1</sup>(Ar-Br), 837 cm<sup>-1</sup> and 711cm<sup>-1</sup>(Para, Ortho); 1H-NMR(CD3OD): 7.22-7.69 (Aromatic), 6.96-7.20 (HC=CH of Maleimide), 7.68 (Ortho-H of N=N-Ar), 7.67 (Meta -H of N=N-Ar), 10.06 (CO-NH).

**2. [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Acrylonitrile] [C<sub>1</sub>-PAMI-B] (Ia)**-Yield 85%, melting point 145-46 oC; color dark brown, FT-IR (KBr): 1709 cm<sup>-1</sup> (C=O),3428 cm<sup>-1</sup> (N-H), 3065 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1606 cm<sup>-1</sup>(C=O, amide), 1395 cm<sup>-1</sup>(C-N-C), 1515 cm<sup>-1</sup>(N=N), 524 cm<sup>-1</sup>(Ar-Br), 832 cm<sup>-1</sup>

1 and 652 cm<sup>-1</sup>(Para, Ortho); 1H-NMR(CD<sub>3</sub>OD): 7.31-7.82 (Aromatic), 6.96-7.31 (HC=CH of Maleimide), 7.84 (Ortho-H of N=N-Ar), 8.18 (Meta -H of N=N-Ar), 3.94 {(CH-CH)-n}, 10.06 (CO-NH).

**3.[4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Acrylic acid] [C2-PAMI-B]**-Yield 80 %, melting point 193-95 oC; color dark brown, FT-IR (KBr): 1707 cm<sup>-1</sup> (C=O), 3353 cm<sup>-1</sup> (N-H), 3069 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1605 cm<sup>-1</sup>(C=O, amide), 1398 cm<sup>-1</sup>(C-N-C), 1515 cm<sup>-1</sup>(N=N), 526 cm<sup>-1</sup>(Ar-Br), 834 cm<sup>-1</sup> and 744 cm<sup>-1</sup>(Para, Ortho); 1H-NMR(CD<sub>3</sub>OD): 7.15-7.66 (Aromatic), 6.65-7.14 (HC=CH of Maleimide), 8.12 (Ortho-H of N=N-Ar), 8.19 (Meta -H of N=N-Ar), 3.69 {(CH-CH)-n}, 10.43 (CO-NH).

**4.[4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Vinyl acetate] [C3-PAMI-B]**-Yield 85 %, melting point 154 oC; color darkbrown, FT-IR (KBr): 1712 cm<sup>-1</sup> (C=O), 3364 cm<sup>-1</sup> (N-H), 3064 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1606 cm<sup>-1</sup>(C=O, amide), 1394 cm<sup>-1</sup>(C-N-C), 1515 cm<sup>-1</sup>(N=N), 527 cm<sup>-1</sup>(Ar-Br), 833 cm<sup>-1</sup> and 743 cm<sup>-1</sup>(Para, Ortho); 1H-NMR(CD<sub>3</sub>OD): 7.14-7.68 (Aromatic), 7.02-7.40 (HC=CH of Maleimide), 7.55 (Ortho-H of N=N-Ar), 8.18 (Meta -H of N=N-Ar), 3.62 {(CH-CH)-n}, 10.05 (CO-NH).

**5.Terpolymer [4-N-Phenylethanamideazo-3-N-(4-Bromophenyl)Maleimide – Acrylonitrile - Vinyl acetate] [T1-PAMI-B]**- Yield 85 %, melting point 154 oC; color dark brown, FT-IR (KBr): 1713 cm<sup>-1</sup> (C=O), 3344 cm<sup>-1</sup> (N-H, broad peak), 3064 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1607 cm<sup>-1</sup>(C=O, amide), 1393 cm<sup>-1</sup>(C-N-C), 1514 cm<sup>-1</sup>(N=N), 524 cm<sup>-1</sup>(Ar-Br), 833 cm<sup>-1</sup> and 650 cm<sup>-1</sup>(Para, Ortho); 1H-NMR(CD<sub>3</sub>OD): 7.16-7.76 (Aromatic), 7.01-7.30 (HC=CH of Maleimide), 8.18 (Ortho-H of N=N-Ar), 8.35 (Meta -H of N=N-Ar), 3.62 {(CH-CH)-n}, 10.07 (CO-NH).

**6. Terpolymer [4-N-Phenylethanamideazo-3-N-(4-Bromophenyl)Maleimide – Acrylic acid - Vinyl acetate] [T2-PAMI-B]**-1709 cm<sup>-1</sup> (C=O), 3448 cm<sup>-1</sup> (N-H, broad peak), 2990 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1606 cm<sup>-1</sup>(C=O, amide), 1396 cm<sup>-1</sup>(C-N-C), 1515 cm<sup>-1</sup>(N=N), 528 cm<sup>-1</sup>(Ar-Br), 832 cm<sup>-1</sup> and 648 cm<sup>-1</sup>(Para, Ortho); 1H-NMR(CD<sub>3</sub>OD): 7.15-7.67 (Aromatic), 7.02-7.48 (HC=CH of Maleimide), 7.31(Ortho-H of N=N-Ar), 8.14 (Meta -H of N=N-Ar), 3.66 {(CH-CH)-n}, 10.01 (CO-NH).

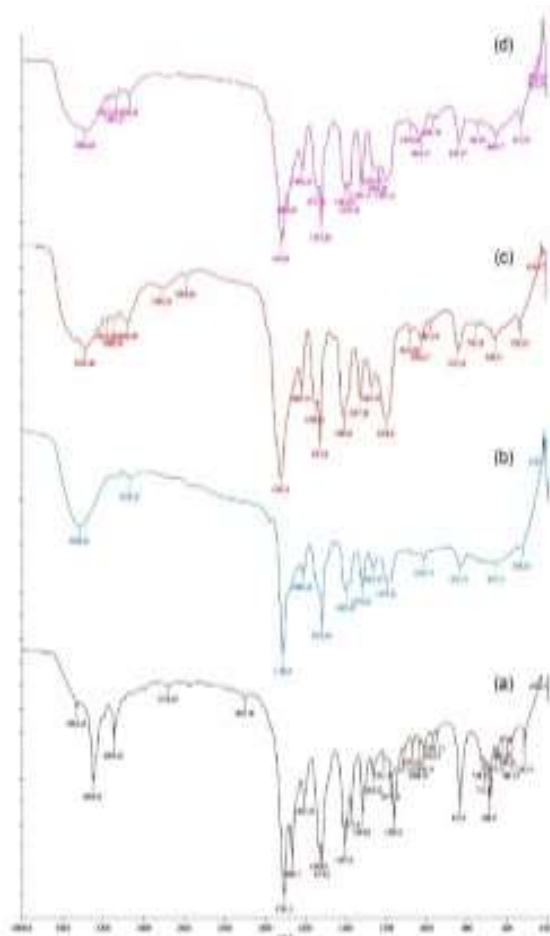


Fig. 1 FT-IR Spectra of (a) PAMI-B Monomer (b) C1-PAMI-B(c) C2-PAMI-B(d) C3-PAMI-B

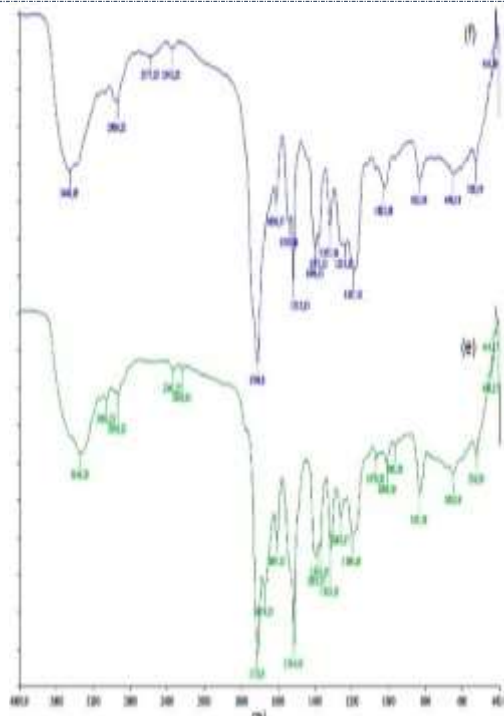


Fig. 2 FT-IR Spectra of (e) T1-PAMI-B (f) T2-PAMI-B

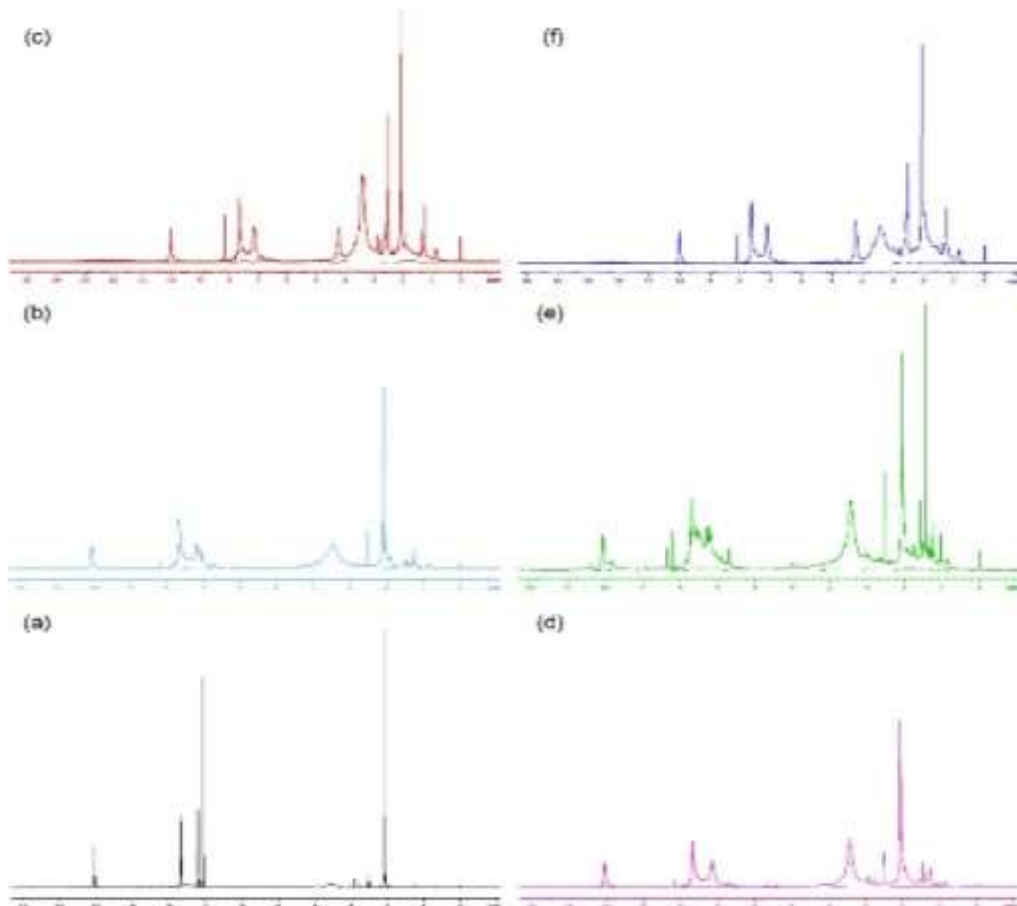


Fig. 3 <sup>1</sup>H-NMR spectra of (a) PAMI-B monomer (b) C1-PAMI-B (c) C2-PAMI-B (d) C3-PAMI-B (e) T1-PAMI-B (f) T2-PAMI-B

**THERMAL ANALYSIS**

TGA of all polymers have been carried out using Perkin Elmer-Purix-TGA Thermal Analyzer. Thermograms are shown in [figure no. 3]. The measurements of weight change in taken sample materials as a function of time and temperature and the thermal stability of compounds. The analysis is typically carried out in milligrams by sample size with a heating rate of 10 °C/min. from 50°C to 800°C in inert N<sub>2</sub>- surroundings. The polymer thermograms of C1-PAMI-B, C2-PAMI-B, C3-PAMI-B, T1-PAMI-B and T2-PAMI-B shown the one major weight loss beginning from 200-250 °C and ending at 600-640 °C. Once the decomposition triggered out, it continue until the whole weight is consumed. In these thermograms there are some small fluctuations stages reaveled the degradations in small amounts with continuously. The cause of continuous degradation is followed eliminations of attached pendant groups due to chain scission. The continuous weight loss % curve are explained in three segments. The first rapid stage (up to 200 °C) of decomposition may be due to loss of water and polar solvents which is used in synthesis. The second stage (200-500 °C) may be due to bond breaking and releasing of pendant groups and the third stage (500-640 °C) high transition temperature may be located for residue of char/carbon. The results in table no. [1] Indicated that the relative thermal stability by % weight loss.

The glass transition temperature T<sub>g</sub> determined from differential scattering colorimetric (DSC). The T<sub>g</sub> value of copolymers and terpolymers C1-PAMI-B, C2-PAMI-B, C3-PAMI-B, T1-PAMI-B and T2-PAMI-B are respectively present in table [2]. The comparison of T<sub>g</sub>-values reflects that presence of acrylonitrile (AN) and acrylic acid (AA) group in terpolymers T1 and T2 increases the T<sub>g</sub> then their copolymers. The T<sub>g</sub>-value of copolymers and terpolymers of maleimide with AN and AA are greater respectively and the sequence seen as T2-PAMI-B > T1-PAMI-B > C2-PAMI-B > C3-PAMI-B > C1-PAMI-B. Due to the acidic functionality of acrylic acid in terpolymer T2-PAMI-B shown exclusively weak Hydrogen-bonding, that is the core reason to point out high T<sub>g</sub>-value of T2-PAMI-B terpolymer [183.8 °C] than T1-PAMI-B and among the copolymers, [C2-PAMI-B] copolymer also sited with high T<sub>g</sub>-value [155.7 °C] influenced by H-bonding [Fig.2][Table 2] and between C1-PAMI-B and C3-PAMI-B, the T<sub>g</sub>-value of vinyl acetate containing of [C3-PAMI-B] copolymer reaveled greater T<sub>g</sub>-value as compared with [C1-PAMI-B] copolymer which is indicated the presence of acetate-group functionality respectively. Therefore, all these polymers have a useful range of glass transition temperatures (T<sub>g</sub>) for both low-temperated processing units (for low T<sub>g</sub> polymers) and high-temperated processing units (for high T<sub>g</sub> polymers) in desired polymer industries and it may provide large opportunity for many applications in related sectors.

**Table 1: % weight-loss in Thermal Decomposition of Copolymers and Terpolymers at Various temperature range from TGA**

Polymer Code	Weight loss (%)					
	100 °C	200 °C	300°C	400 °C	500 °C	600 °C
<b>C1-PAMI-B</b>	3.35	6.96	14.65	31.43	47.15	88.83
<b>C2-PAMI-B</b>	3.76	6.75	23.53	37.68	58.5	99.09
<b>C3-PAMI-B</b>	4.50	7.39	17.9	33.16	50.03	95.2
<b>T1-PAMI-B</b>	3.49	9.03	20.85	37.77	54.88	99.41
<b>T2-PAMI-B</b>	1.88	10.97	16.97	46.83	86.71	99.99

**Table 2: Glass Transition Temperature of Copolymers and Terpolymers**

Polymer Code	C1-PAMI-B	C2-PAMI-B	C3-PAMI-B	T1-PAMI-B	T2-PAMI-B
<b>T<sub>g</sub> in °C</b>	70.7	155.7	80.1	135.8	183.8

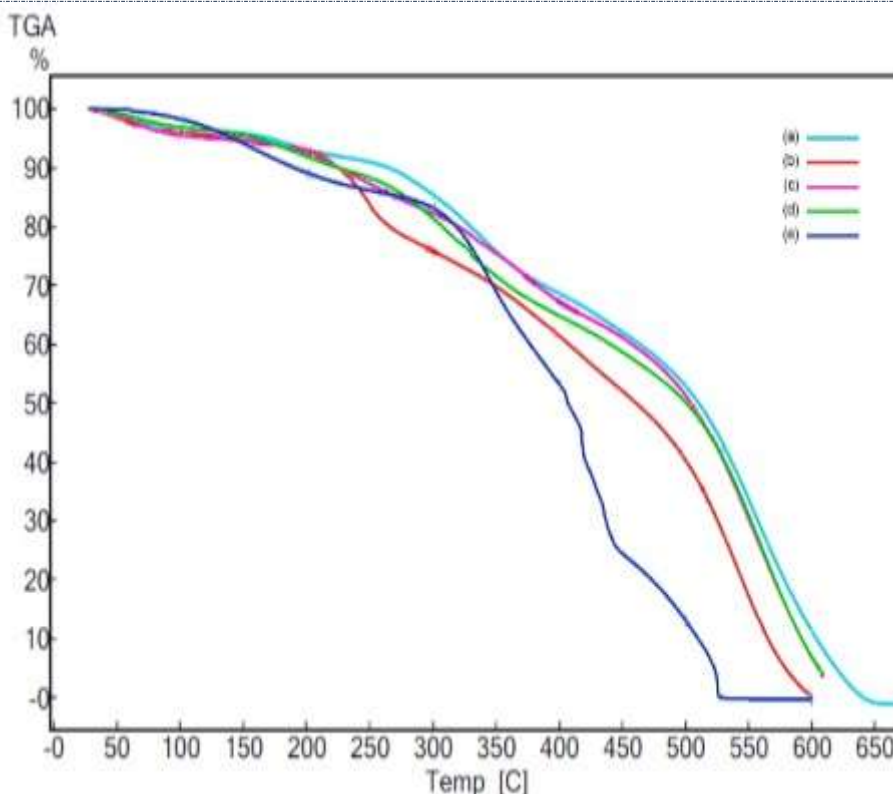


Fig. 3 TGA Thermograms of (a) C1-PAMI-B (b) C2-PAMI-B (c) C3-PAMI-B (d) T1-PAMI-B (e) T2-PAMI-B

### MICROBIAL STUDY

In sequences to explore the utility of synthesized polymer have been examined on bacterial and fungal environment. The antimicrobial activities carried out against bacteria *Escherichia aerogenes*, *Staphylococcus aureus* and antifungal activities were observed against *Aspergillus nizer*, *Alternaria solani* with 500 micrograms in concentration for 24 hours durations. According to results, all synthesized polymers show good activity against considered bacteria and fungi and among all the polymers, T2-PAMI-B (AA) has shown excellent antibacterial and antifungal activities.

The order of toxicity of these polymers for microbes is T2-PAMI-B > T1-PAMI-B > C2-PAMI-B > C3-PAMI-B > C1-PAMI-B. The results are shown due to acidic/acetate functional groups are attached within polymeric structures that's why, this is basic and desire properties for the applications of material packaging, storage etc.

Table 7: Antibacterial activity of C1-PAMI-B, C2PAMI, C3-PAMI-B, T1-PAMI-B, T2-PAMI-B against bacteria *Escherichia aerogenes*, *Staphylococcus aureus*

Code	500(µg/ml) Concentration of compound taken	
	Zone of Inhibition For <i>E. aerogenes</i> (mm)	Zone of inhibition for <i>S. aureus</i> (mm)
C1-PAMI-B	7	7.8
C2-PAMI-B	9	10
C3-PAMI-B	8	9.2
T1-PAMI-B	11.6	11
T2-PAMI-B	12.7	13.2

**Table 8: Antifungal activity of C1-PAMI-B, C2-PAMI-B, C3-PAMI-B, T1-PAMI-B, T2-PAMI-B against fungus *Aspergillus nizer*, *Alternaria solan***

Code	100(µg/ml) Concentration of compound taken	
	Zone of Inhibition For <i>A. nizer</i> (mm)	Zone of Inhibition For <i>A. solani</i> (mm)
<b>C1-PAMI-B</b>	8	9.2
<b>C2-PAMI-B</b>	10	11.7
<b>C3-PAMI-B</b>	9	11.2
<b>T1-PAMI-B</b>	12	13.5
<b>T2-PAMI-B</b>	12.8	15.1

## CONCLUSION

Variety of copolymers and terpolymers synthesized with the incorporation of AN, AA, VA comonomer units via addition type free radical copolymerization and terpolymerization. Synthesized copolymers C1-PAMI-B, C2-PAMI-B, C3-PAMI-B and terpolymers T1-PAMI-B and T2-PAMI-B are characterized and structures are confirmed from FT-IR, <sup>1</sup>HNMR spectral and elements analysis. Physiochemical properties tagged out on bases of solubility test, density and viscosity measurements. The thermal behavior observed by TGA and DSC. All polymer exhibited good thermal stability but all are almost decomposed at zero level at 600 oC - 640 oC and the Tg value of all copolymers and terpolymers are in the range of 70-184 oC. All polymer compounds are shown good antimicrobial activities that would be gives the quality frame –work in concern areas.

## ACKNOWLEDGEMENTS

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## References

- [1] L. Yang and D. Sun, “Synthesis and characterization of terpolymer of N-cyclohexylmaleimide, methyl methacrylate and acrylonitrile”, J. Appl. Polym. Sci., Vol. 104, pp. 792-796, April 2006.
- [2] L. Yang , L. Zhang, G. Liu, J. Gao, S.Y. Yang and R. Jin, “Synthesis and thermoanalysis of emulsion terpolymers of N-phenylmaleimide, Styrene and Acrylonitrile”, J. Appl. Polym. Sci., Vol. 79, pp. 1067-1073, 2001.
- [3] Y. Li, L. Xu , X. Yao, T. Luo and G. Liu, “Thermal degradation kinetics of poly {N-[(4-bromo- 3,5-difluorine)-phenyl] maleimide-co-styrene} in nitrogen”, International symposium on Functional Materials Conference Series, J. Phys., Vol. 339, pp. 2, 2012.
- [4] L. Lou, A. Tagaya, Y. Ide, Y. Koike and Y. Okamoto, “Copolymers of methyl methacrylate with N-trifluorophenyl Maleimides: High glass transition temperature and low birefringence polymers”, J. Polym. Sci., Part A: Polym. Chem., Vol. 50, pp. 3530–3536, 2012.
- [5] T. Akihiro, L. Liping, D.I. Yoko, K. Yasuhiro and O. Yoshiyuki, “Improvement of the physical properties of poly(methyl methacrylate) by copolymerization with N-pentafluorophenyl maleimide; zero-orientational and photoelastic birefringence polymers with high glass transition temperatures”, J. Sci. Chin. Chem., Vol. 55, pp. 850-853, 2012.
- [6] J. Chaudhary and N.P.S. Chauhan, “Synthesis, thermal and antimicrobial properties of copolymers derived from 2, 4-dinitrophenylaminomaleimide and alkyl substituted acrylates”, Malays. Polym. J, Vol. 8, pp.18-25, 2013.
- [7] P. Hemalatha, M.K. Veeraiah, S. Prasannakumar and K.V. Anasuya, “Synthesis, characterization and antibacterial activity of copolymer (N-Vinylpyrrolidone-maleic anhydride) with N-Diethylethanolamine”, Int. J. Res. Eng. Technol., Vol. 03, pp. 33-36, 2014.
- [8] Y. Qin, “The synthesis and properties of emulsion copolymerization of styrene with N- substituted phenyl maleimide”, Adv. Mater. Res., Vol. 1025-1026, pp. 683-687, 2014.
- [9] A.F. Hai, A.H. Wahab and G.A. Ibrahim, “Synthesis, characterization and thermal properties of thiazole containing polymers”, Malays. Polym. J., Vol. 09 (1), pp. 1-9, 2014.
- [10] A.I. Mohammed and A. Mustapha, “Synthesis of new azo compounds based on N-(4-hydroxyphenyl)maleimide and N-(4-methylphenyl) maleimide”, J. Mol., Vol. 15, pp. 7498-7508, 2010.
- [11] B.L. Hiran and S.N. Paliwal, “Free radical initiated polymerization of N-[4-N\_-(4-chlorophenyl) amino-carbony] phenyl] maleimide and characterization of homopolymer and Copolymers with MMA”, J. Macromol. Sci., Part A: Pure Appl. Chem., Vol. 46, pp. 713-721, 2009.



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- [12] S.L. Oswal, N.N Chapaneri and N.L. Malek, "Radical of N-(4-butoxycarbonylphenyl) maleimide, its copolymerization with methylmethacrylate, styrene and acrylonitrile, and the properties of the resulting polymers", *Design. Monom. Polym.*, Vol. 10 (6), pp. 487-506, 2013.
- [13] C. Jyoti, J. Suman, P. Swati, "Synthesis and Characterization of Copoly (Azo-Maleimide – Acrylonitrile / Vinyl Acetate) and Terpoly (Azo-Maleimide – Acrylonitrile – Vinyl Acetate): Studies on Influences of Reaction Feed Compositions on Thermal and Microbial Behavior", *American International Journal Research, Formal, Applied and Natural Science*, Vol. 15, pp. 538, 2015.