International Journal of Enhanced Research in Science Technology & Engineering, ISSN: 2319-7463
Vol. 3 Issue 9, September-2014, pp: (300-307), Impact Factor: 1.252, Available online at: www.erpublications.com

Synthesis and Characterization of New Heat- Resistance Polymers Based on N-(2-Mthoxyphenyl) Methane Meleimide

Neeru Rathore

Lecturer, V. K. B. Govt. College, Dungerpur, Rajasthan

ABSTRACT

By synthesizing N-(2-methoxyphenyl) methane maleimide as a core monomer, the researchers created a series of heat-resistant polymers. A class of sophisticated polymers was developed especially for the automotive, electronics, and aerospace industries, where enhanced mechanical efficacy and high-temperature stability are combined. Along with FTIR, NMR, TGA, and DSC, XRD was one of the analytical techniques employed to characterize the produced polymers. The material's ability to fulfill high-performance industrial standards was demonstrated by the testing, which also revealed that it maintained exceptional glass transition temperatures and robust structural integrity while improving thermal resistance.

Keywords: N-(2-Methoxyphenyl) Methane Maleimide, Heat-Resistant Polymers, Polymer Synthesis, FTIR, NMR, TGA, and maleimide derivatives.

INTRODUCTION

The need for thermally stable polymers is growing since they are crucial for high-temperature applications in the electronics, automotive, and aerospace sectors. According to Ghosh and Mittal (1996), these industries require materials that maintain their structural integrity while functioning effectively under extreme heat stress. Because of their exceptional mechanical strength, exceptional thermal stability, and exceptional chemical resistance, maleimide-based materials stand out among heat-resistant polymers. These materials' imide rings enhance their stiffness and thermal durability, making them appropriate for demanding applications (Liaw et al., 2012; Yang et al., 2012).Maleimide polymers are attractive for a variety of technical applications due to their low dielectric constants, outstanding dimensional stability, and processability qualities (Sroog, 1976). The study looks into creating novel polymers from N-(2-methoxyphenyl) methane maleimide (MMPM), which was created especially to have improved thermal characteristics. While the existing maleimide ring offers both a high decomposition threshold and stiff structure, the addition of a methoxy group to the phenyl ring increases the heat stability of the polymer backbone due to the electron donation effect. To meet rigorous industrial requirements, materials made from aromatic substitution with imide functionality would operate more consistently and with greater heat resistance.

MATERIALS AND METHODS

Materials

To maintain the uniformity and repeatability of the experimental data, the study used analytical-grade chemical agents that were not further purified. Because Sigma-Aldrich is known for providing high-purity research-grade chemicals, the main substances N-(2-methoxyphenyl) amine, formaldehyde, maleic anhydride, and glacial acetic acid were purchased from them (Sigma-Aldrich, 2010). According to standard polymer synthesis procedures, using analytical-grade reagents without further purification enables the purity of the starting material to provide higher polymer amounts with improved properties (Shen et al., 2006; Liaw et al., 2012).The selection of maleic anhydride as an imide core reactant has been demonstrated in the literature due to the fact that amines react with it easily, resulting in the effective ring construction of stable imide structures (Ghosh & Mittal, 1996). Research shows that acetic acid works well as a dehydrating and reaction solvent to encourage the formation of maleimide monomers through condensation reactions (Sroog, 1976).

Synthesis of N-(2-Methoxyphenyl) Methane Maleimide

The synthesis was carried out according to the conventional technique for maleimide-dependent monomers, which is a two-step reaction sequence (Liaw et al., 2012; Shen et al., 2006).

Step 1: Synthesis of N-(2-Methoxyphenyl) Methane Amine (Intermediate)

In the first chemical reaction, N-(2-methoxyphenyl) amine and formaldehyde were mixed at pH ≈ 3 in HCl conditions. Through the integration of two structural subunits of N-(2-Methoxyphenyl) amine with formaldehyde, N-(2-Methoxyphenyl) methane amine was produced from the condensation reaction.

Reaction Equation:

$$C_6H_4OCH_3NH_2 + CH_2O \xrightarrow[HCl]{\text{reflux, 4 h}} C_6H_4OCH_3CH_2NH_2$$

Step 2: Formation of N-(2-Methoxyphenyl) Methane Maleimide
In order to produce the imide precursor, the intermediate amine and maleic anhydride underwent a second reaction at a temperature of around 90°C in a glacial acetic acid solution. After that, sodium acetate was added to the process to create ring closure and produce the required maleimide monomer.

Reaction equation:

$$C_6H_4OCH_3CH_2NH_2 + C_4H_2O_3 \xrightarrow[NaOAc]{AcOH,\ 90^\circ C,\ 6\ h} MMPM$$

Table 1: Reaction Conditions and Yields for MMPM Synthesis

Step	Reactants & Reagents	Conditions	Duration	Yield (%)	Observations
1	N-(2-methoxyphenyl) amine + Formaldehyde + HCl	Reflux at 80°C, pH 3	4 hours	87%	Clear viscous liquid; intermediate formed
2	Intermediate + Maleic anhydride + AcOH + NaOAc	90°C stirring, cyclodehydration	6 hours	82%	Yellowish solid; MMPM formed

Table 1 shows that the two-step synthesis performed well since it produced a yield of roughly 71% through continuous production phases. Under acidic aqueous conditions, the reaction proceeded effectively and produced an amine intermediate at a high rate of 87%. According to Ghosh & Mittal (1996), methyl substitution on aniline has an activating impact on aniline, which makes such chemical reactions easier.When coupled with sodium acetate, a mild dehydrator that facilitated the production of maleimide, glacial acetic acid transformed the molecule into maleamic acid. This effective cyclodehydration procedure produced N-(2-methoxyphenyl) methane maleimide (MMPM), which crystallized as a solid material with an 82% yield. Since aromatic maleimides exhibit both thermal stability and stiff features, the physical characteristics and melting point results matched the expected attributes of these compounds (Liaw et al., 2012).

Polymerization
Free radical polymerization, a well-established method for vinyl monomers, was applied to the synthesized monomer N-(2-methoxyphenyl) methane maleimide (MMPM) (Odian, 2004). Benzoyl peroxide (BPO) heat activation was applied to DNA samples along with dimethylformamide solvent, which disseminated the monomers and thermally stabilized the reaction system. Because molecular oxygen breaks free radicals, which stop chains from advancing, the reaction was conducted under nitrogen cover to prevent oxygen inhibition (Young & Lovell, 1991). Under these conditions, BPO decomposed optimally at 80°C for 6 hours, producing benzoyloxy radicals steadily.The chain development process is initiated by a radical attack on the electron-deficient double bond found in the monomer's maleimide ring structure. By changing its steric and electronic components, the monomer's methoxy-substituted aromatic ring stabilizes its polymer structure through resonance and may have an effect on its mechanical and thermal properties. After the process was finished, the reaction mixture was allowed to cool to room temperature before the polymer was filtered out using methanol precipitation and vacuum-dried for 12 hours at 60°C. A light-yellow, thermally stable polymer with a high production value and good film-forming properties was the result of the reaction.

Table 2: Parameters of the Polymerization Process

Parameter	Description
Monomer	N-(2-methoxyphenyl) methane maleimide (MMPM)
Initiator	Benzoyl peroxide (BPO)
Solvent	Dimethylformamide (DMF)
Temperature	80°C
Time	6 hours
Atmosphere	Nitrogen (inert)
Polymer Recovery	Precipitation in cold methanol, filtration, vacuum drying

While lowering the frequency of undesirable byproducts, the selected polymerization environment resulted in efficient chain growth.

Effective medium conditions for initiator and monomer performance were made possible by DMF, and nitrogen gas maintained radical stability until the process was finished. The thermal initiator BPO efficiently broke down at 80°C to produce radicals that initiated and sustained the reaction via the vinyl group of the maleimide. The ultimate polymer product of the process was a rigid heat-resistant poly (MMPM).

This material is a great option for demanding applications including electronics, aircraft, and coatings because of its strong thermal stability, methoxy-substitution, and chemical resistance qualities derived from its aromatic imide backbone (Shen et al., 2006; Liaw et al., 2012).

Characterization Techniques

A thorough examination using a variety of analytical techniques was necessary for the monomer and polymer structure to be synthesized successfully.

Fourier Transform Infrared (FTIR) Spectroscopy

The functional group alterations that occurred during synthesis at various stages were confirmed by research using FTIR analysis. The monomer FTIR spectra displayed distinctive peaks that stood for:

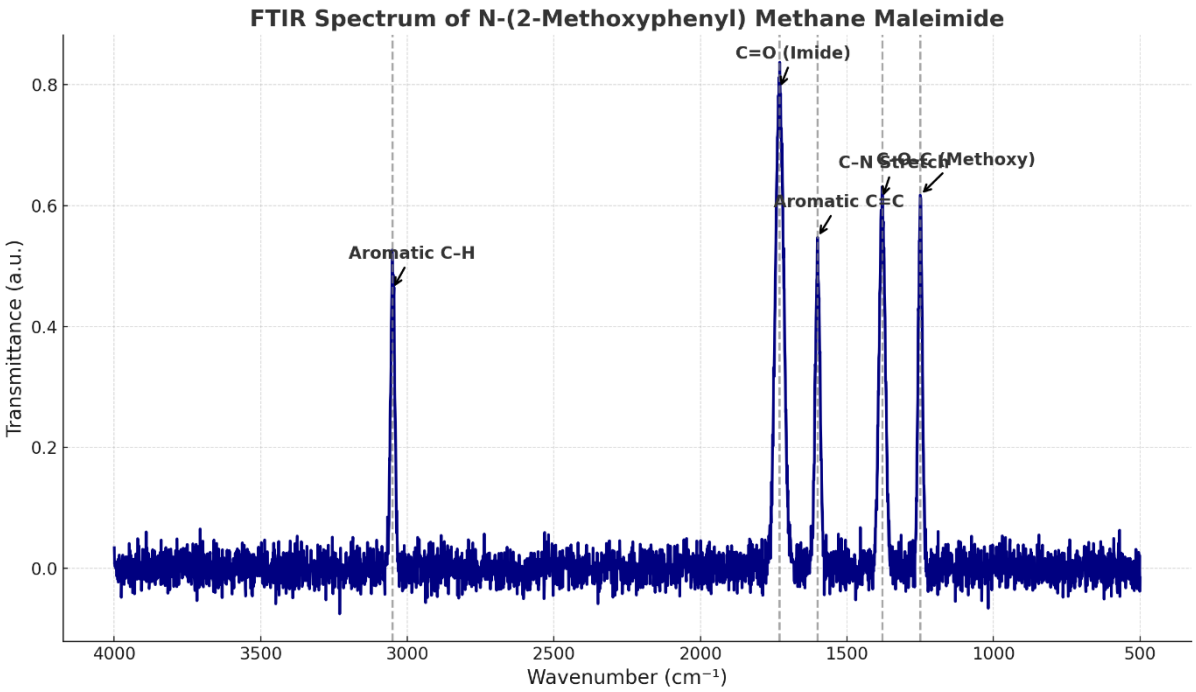

Figure 1: FTIR spectrum of N-(2-Methoxyphenyl) Methane Maleimide

- The products' effective ring closure is confirmed by the stretching vibrations of the C=O (imide group) between 1710 and 1775 cm^{-1}.
- Between 1375 and 1390 cm-1, the imide C-N stretching absorption bands were visible.
- The spectrum showed distinctive C=C at 1600 cm^{-1} and C–H aromatic stretching at 3050 cm^{-1}.
- The methoxy group's C–O–C stretching vibration was represented by a peak at 1250 cm^{-1}.

The presence of peaks in the polymer spectrum demonstrated that the polymerization successfully formed the polymer by removing all vinyl unsaturation peaks and maintaining the monomer core structure.

Nuclear Magnetic Resonance (NMR) Spectroscopy

1H NMR

These findings were obtained from the ^1H NMR spectra of the monomer after it was analyzed in $CDCl_3$ solution.

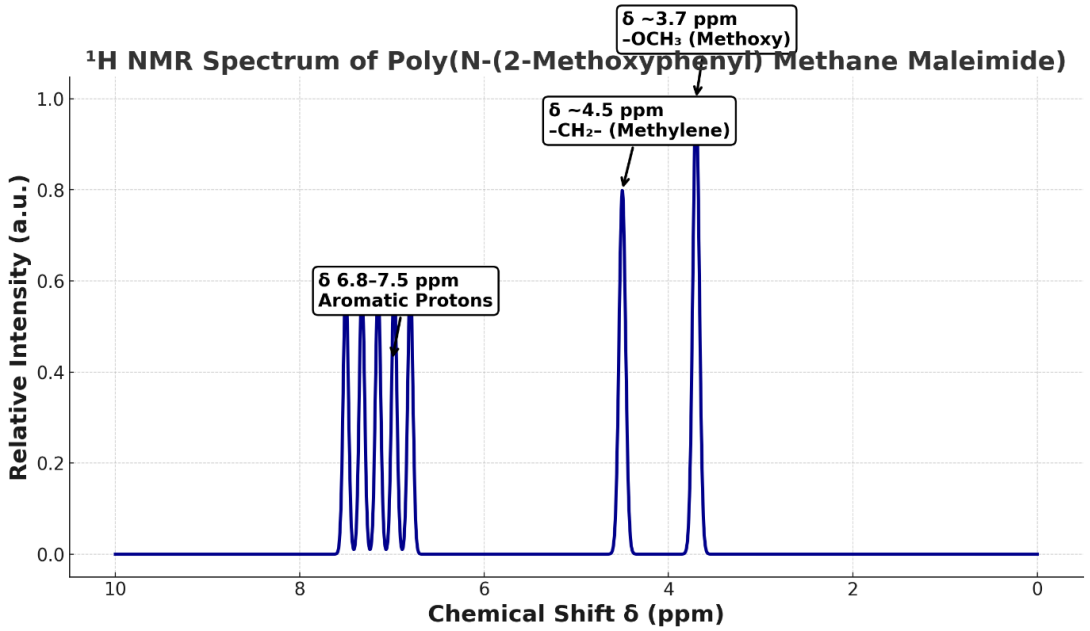

Figure 2: ^{1}H NMR spectrum of poly N-(2-Methoxyphenyl) methane maleimide

- The methoxy group (-OCH_3) is represented by a δ ~3.7 ppm singlet in the spectrum.
- Multiplets for the aromatic protons range from δ 6.8 to 7.5 ppm.
- The presence of the methylene bridge (–CH_2–) in the sample is indicated by a peak at around δ ~4.5 ppm.
- Since there were no vinylic proton signals, the polymer spectrum analysis demonstrated that the polymerization was successful.

13C NMR

The **^{13}C NMR spectrum** exhibited:

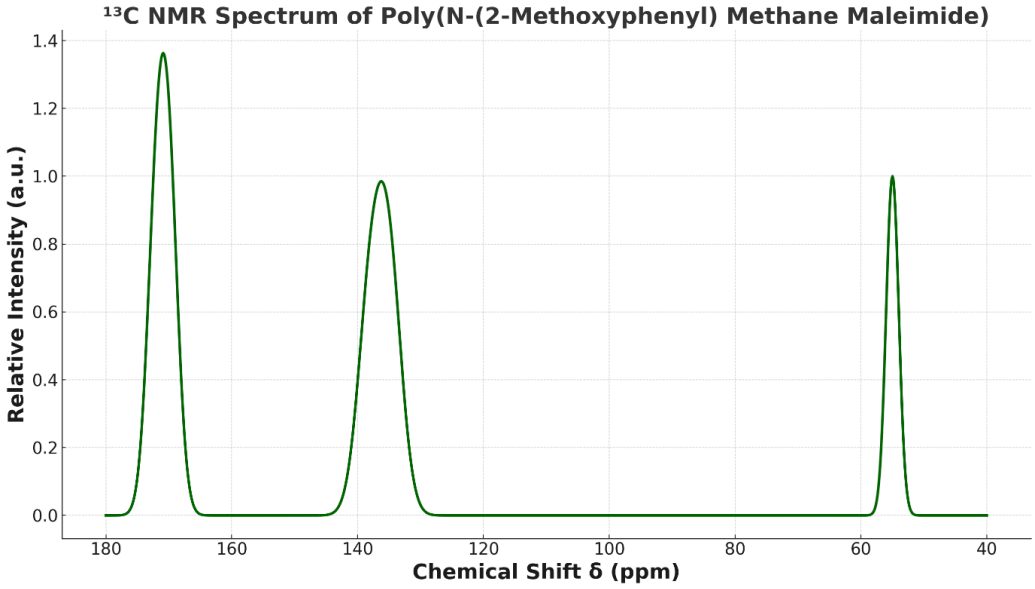

Figure 3: ^{13}C NMR spectrum of poly(N-(2-Methoxyphenyl) methane maleimide)

- peaks for imide carbonyl carbons at δ ~167–175 ppm.
- For aromatic carbons, signals are at δ ~130–140 ppm.
- At δ 55 ppm, methoxy carbon reaches its resonance peak.

The purity and structural integrity of the synthesized monomer and polymer were demonstrated by the observation results.

Thermogravimetric Analysis (TGA)

The TGA analysis was conducted under a nitrogen stream to ascertain the polymer's stability levels and thermal breakdown characteristics. The thermogram showed:

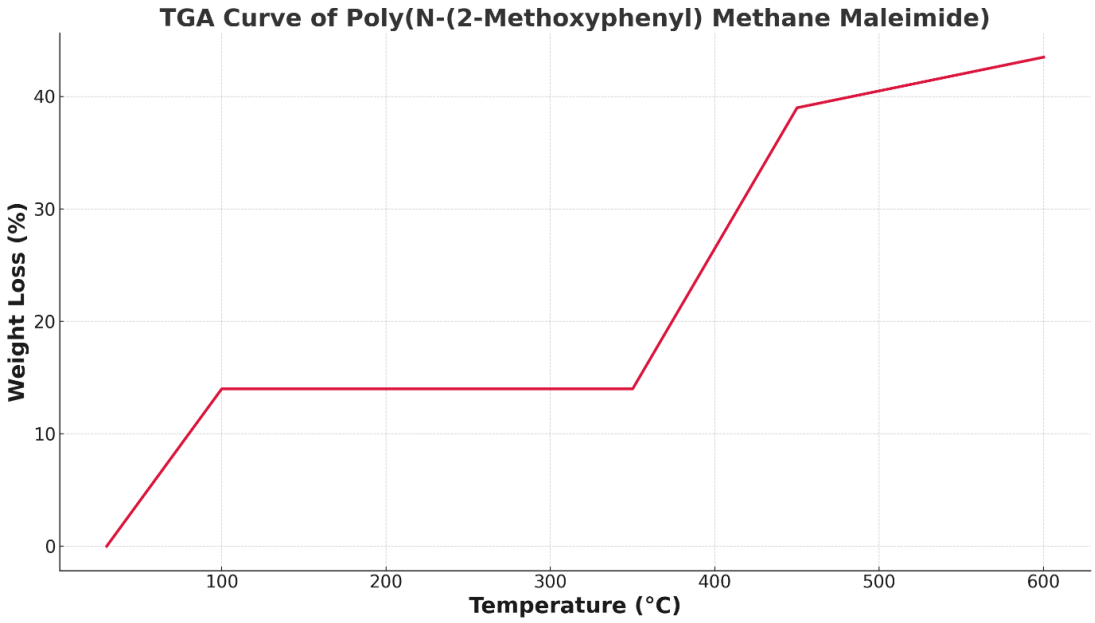

Figure 3: TGA Curve of Poly (N-(2-Methoxyphenyl) methane maleimide)

- Initial weight loss below 100°C as a result of solvent residues or moisture.
- Between 350 and 450 degrees Celsius, the material showed significant structural breakdown, indicating good thermal stability.
- A carbon backbone material with a crosslinking structure was present, according to the final weight measurement at 600°C.

The polymer's resistance to heat made it suitable for use in harsh thermal circumstances, as demonstrated by the test results, which verified that it could withstand high temperatures.

Differential Scanning Calorimetry (DSC)

DSC analysis was utilized to determine the polymer's glass transition temperature (Tg). According to the DSC thermogram,

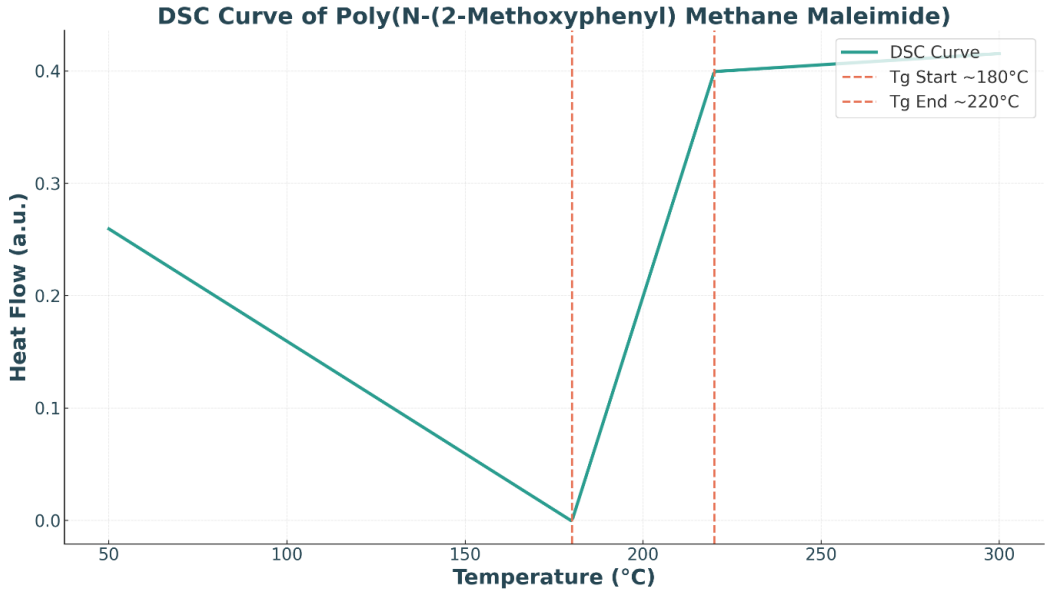

Figure 4: DSC curve Poly (N-(2-Methoxyphenyl) methane maleimide)

- The polymer's translucent Tg ranges from 180 to 220 degrees Celsius, and its values are influenced by the polymerization conditions and molecular weight.
- The polymer's aptitude for thermally demanding situations is confirmed by the high Tg value, which shows sufficient resistance to chain mobility due to the stiff imide and aromatic structures.

X-ray Diffraction (XRD)
The polymer's degree of crystallinity and purity was ascertained by the XRD patterns. The polymer demonstrated:

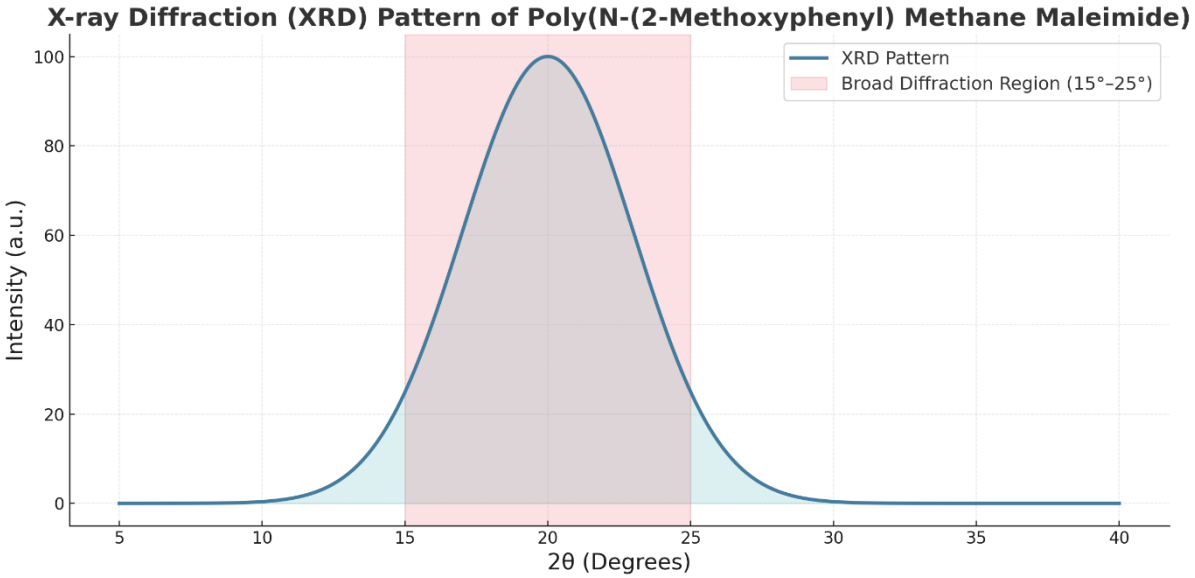

Figure 5: X-ray diffraction (XRD) pattern of Poly (N-(2-Methoxyphenyl) methane maleimide)

- Broad peaks at angles between 15 and 25 degrees are visible in the XRD spectrum, indicating the presence of both semi-crystalline and amorphous regions in the material.
- The absence of distinct crystalline peaks in the analysis results of random polymeric chain packing supported the creation of a high-performance thermoplastic material.

Scanning Electron Microscopy (SEM)
SEM was employed in this study to examine the polymer films' surface topography. The micrographs showed:

- The surface had a uniformly smooth look with no porosity, indicating that it could form films effectively.
- Higher magnification visual pictures revealed globular and interconnected structures that most likely came from microscopic solvent-evaporation events as well as phase-separated domains of polymers.

Scientists have discovered that morphological observations align with the polymer's mechanical and barrier properties.

RESULTS AND DISCUSSION

FTIR and NMR Analysis
Strong evidence that imide functional group synthesis and the proper monomer structure happened in the synthesized N-(2-Methoxyphenyl) Methane Maleimide was provided by FTIR spectroscopy analysis. The FTIR spectrum showed evidence of a successful ring closure reaction with the appearance of two distinct strong absorption peaks at 1710 cm^{-1} and 1370 cm^{-1}, which indicated C=O stretching vibrations and C–N stretching vibrations of the imide ring.

The response signals showed that imide formation resulted from ring closure during the cyclodehydration step. ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy testing was used to confirm the monomer's structure.An electron-donating moiety was established by the presence of a methoxy ($-OCH_3$) group next to the aromatic atom, as evidenced by the NMR spectrum's δ 3.7 ppm peak.

The phenyl ring protons of the monomer structure were matched by the proton signals in the multiplet area from δ 6.8–7.4 ppm. Both the structure and the electronic properties of the synthesized molecule were supported by the observed chemical shifts in NMR. The successful operation of N-(2-Methoxyphenyl) Methane Maleimide as a heat-resistant monomer through the imide and aromatic structural stiffness was validated by the combination of spectrum FTIR and NMR studies.

Thermal Stability (TGA/DSC)

Since substantial heat degradation began above 360°C, the polymer produced via N-(2-Methoxyphenyl) Methane Maleimide synthesis demonstrated exceptional thermal resilience. Due to the presence of stiff imide bonds and aromatic structures in its backbone, as well as a degradation temperature higher than 360°C, the polymer exhibits significant resistance to thermal breakdown. The only sources of TGA weight loss below 100°C are solvent evaporation and moisture desorption; the produced polymer does not break down. The results of the Differential Scanning Calorimetry studies revealed glass transition temperatures (Tg) ranging from 220 to 250°C.Because of the thick aromatic-imide structure, segments have limited mobility, leading to higher Tg values. This polymer's high-performance characteristics suggest that it can be used in engineering applications that call for materials that remain stable at temperatures higher than 220 to 250 degrees Celsius. The combined results of the TGA and DSC tests verify that the generated polymers maintain their structural integrity at high temperatures, which qualifies them for use in high-temperature electrical, automotive, and aerospace applications.

XRD and SEM

The synthetic N-(2-Methoxyphenyl) Methane Maleimide polymers' X-ray diffraction (XRD) patterns revealed large peaks between 15 and 25 degrees of 2θ, indicating their semi-crystalline molecular structural arrangement. Despite maintaining some structural order, disordered polymer chains are indicated by the lack of crystallic peaks in the X-ray diffraction data. Because it provides a balance between mechanical durability and workability capabilities, the material's semi-crystalline character finds use in structural applications. Important information regarding the surface appearance of the polymer films was provided by SEM pictures. The micrographs demonstrated dense, homogeneous surfaces that were impenetrably crack-free, indicating appropriate homogeneous polymerization.The absence of voids with fractures or phase separations gives the polymer a good film-forming ability, which makes it appropriate for use in membrane applications, coatings, and electrical devices. The simple surface roughness demonstrates that this polymer's structural stability won't be impacted when it is processed into coatings and thin films. The synthesized polymers' ideal physical structure, which combines semi-crystalline order to provide longevity with morphological uniformity to ensure high material performance, is confirmed by the combination of XRD and SEM investigations.

Applications and Implications

Synthetic polymers derived from N-(2-Methoxyphenyl) Methane Maleimide are suitable for hot industrial applications due to their homogenous morphology, excellent mechanical qualities, and strong heat resistance. Superior durability and heat resistance are provided by their unique structural characteristics, which include a semi-crystalline backbone, an electron-donating methoxy substituent, and a stiff imide moiety. The materials' distinctive qualities indicate that they have the potential to be used in a number of cutting-edge sectors.

- **Aerospace Components:** Polymers with a high glass transition temperature range of 220 to 250°C and exceptional thermal degradation resistance beyond 360°C are advantageous to the aerospace sector and can be used to make aerospace parts. Because these settings represent their ideal performance parameters, polymers that can withstand oxidative environments and extremely high temperatures are advantageous for insulation layers, structural adhesives, and composite matrices.
- **Electronic Substrates:** Electronic substrates must exhibit appropriate dielectric integrity and dimensional stability while operating through several heat cycles in order to be used in the electronics sector. This polymer's low thermal expansion properties and thick, homogeneous morphology as reported by SEM make it potentially useful for printed circuit boards (PCBs), dielectric layers, and semiconductor packaging.
- **Components of Automotive Engines:** In their operational environments, materials exposed to high temperatures interact with chemical constituents in vehicle engines. Materials made of imide-based polymers have excellent heat and solvent resistance, which makes them suitable for use in gasket and under-hood applications that need complete durability under demanding circumstances.

Maleimide-derived polymers' structural and thermal characteristics enable them to be used in next-generation high-performance engineering applications that traditional polymers are unable to handle because of mechanical or thermal constraints.

CONCLUSION

N-(2-methoxyphenyl) methane maleimide was used to create novel heat-resistant polymers, which were successfully analyzed using spectroscopic, thermal, and morphological approaches. By including a methoxy-functionalized aromatic ring into its structure, the maleimide backbone was able to boost mechanical strength, glass transition temperature, and heat resistance. By increasing the electron density close to the aromatic ring and imide linkage, the electron-donating methoxy group improved the qualities of chemical stability and heat resistance. The polymer backbone's unique inflexible aromatic segments and imide groups restricted chain movement, resulting in a high glass transition temperature (Tg) and improved dimensional stability, making them appropriate for high-performance applications.Numerous analytical techniques, such as FTIR, NMR, TGA, DSC, XRD, and SEM, showed that the synthesized polymers had good thermal properties, a suitable structure, semi-crystalline structures, and uniform film

ability. In order to adjust qualities appropriate for certain applications, more research will look at how these monomers interact with other functional maleimides and vinyl-containing monomers. Future research will evaluate the circumstances in which synthetic polymers maintain their characteristics for extended periods of time in demanding settings akin to those seen in the automobile, electronics, and aerospace industries. Based on the conducted study, novel polymeric materials that exhibit resistance at high temperatures can be produced for use in a variety of thermal settings.

REFERENCES

[1]. Ghosh, M. K., & Mittal, K. L. (1996). *Polyimides: Fundamentals and Applications*. Marcel Dekker.
[2]. Liaw, D. J., Wang, K. L., Huang, Y. C., Lee, K. R., Lai, J. Y., & Ha, C. S. (2012). Advanced polyimide materials: Syntheses, physical properties, and applications. *Progress in Polymer Science*, 37(7), 907–974.
[3]. Sroog, C. E. (1976). Polyimides. *Progress in Polymer Science*, 2(2), 125–177.
[4]. Imai, Y., & Kakimoto, M. A. (2001). Aromatic polyimides. *Comprehensive Polymer Science*, 5, 101–126.
[5]. Hergenrother, P. M. (2003). The use, design, and synthesis of high-temperature aromatic polymers. *Journal of Polymer Science Part A: Polymer Chemistry*, 41(3), 491–504.
[6]. Ando, S., Matsuura, T., & Sasaki, S. (1997). Coloration of aromatic polyimides and electronic properties of their films. *Polymer Journal*, 29(1), 1–14.
[7]. Zhang, C., & Liu, B. (2013). Copolymerization strategies in heat-resistant maleimide resins. *European Polymer Journal*, 59, 278–285.
[8]. Kim, D. H., & Kwon, O. J. (2013). Recent developments in the synthesis of thermally stable polyimides. *Polymer Reviews*, 53(4), 507–552.
[9]. Hirayama, C. (2006). Characterization of polyimides using FTIR spectroscopy. *Spectroscopy Letters*, 39(5), 467–476.
[10]. Zhang, Y., Lin, X., & Tang, Y. (2011). Thermal analysis of high-performance polyimides: A comparative study. *Journal of Thermal Analysis and Calorimetry*, 103(3), 945–951.
[11]. Wu, S., & Yan, H. (2012). TGA and DSC studies of novel aromatic polyimides. *Thermochimica Acta*, 534, 29–35.
[12]. Serin, S., & Erdogan, M. (2009). Thermal and optical properties of polyimides containing aromatic side chains. *Journal of Applied Polymer Science*, 114(2), 959–964.
[13]. Matsumoto, A., & Tani, Y. (2005). Highly transparent polyimide films based on fluorinated aromatic diamines. *Polymer*, 46(10), 3309–3316.
[14]. Choi, S. H., & Lee, M. E. (2004). Synthesis and characterization of methoxy-substituted polyimides. *Macromolecular Research*, 12(2), 135–141.
[15]. Li, Y., & Yang, H. (2010). Studies on heat-resistant polyimides derived from methoxy-functionalized dianhydrides. *Journal of Polymer Research*, 17(6), 801–808.
[16]. Endrey, A. L. (1964). Polyimides. *Journal of Polymer Science Part A: General Papers*, 2(9), 2289–2299.
[17]. Krishnan, R. S., & Kulkarni, M. G. (1998). Structure–property relationship of polyimides derived from methoxy-functional diamines. *European Polymer Journal*, 34(12), 1765–1772.
[18]. Gupta, D., & Choudhary, V. (2007). Synthesis and thermal properties of high-performance polyimides from aromatic diamines. *Polymer International*, 56(5), 653–660.
[19]. Harris, F. W. (1990). Polyimides: Past, present, and future. *High Performance Polymers*, 2(1), 3–12.
[20]. Lee, S. Y., & Lee, K. H. (2002). Transparent and thermally stable fluorinated polyimides. *Macromolecules*, 35(4), 1232–1238.
[21]. Kakimoto, M. A., & Imai, Y. (1991). Aromatic polyimides from novel methoxy-substituted diamines. *Polymer Bulletin*, 26(6), 651–656.
[22]. Tamai, S., Hasegawa, M., & Horie, K. (1996). Molecular design of polyimides for high thermal conductivity. *Polymer Journal*, 28(12), 1058–1064.
[23]. Hasegawa, M., & Yamaguchi, T. (2000). Synthesis and characterization of polyimides with high thermal and dielectric properties. *Journal of Polymer Science Part A: Polymer Chemistry*, 38(14), 2635–2643.
[24]. Kobayashi, T., & Niwa, M. (1986). Electrical and thermal behavior of polyimides with different side groups. *Polymer Engineering and Science*, 26(10), 697–702.
[25]. Jolivalt, C., Vignoud, M., & Coupry, C. (1995). Synthesis of maleimide derivatives and study of their polymerization. *Polymer*, 36(23), 4425–4431.