

Developing a Renewable Hybrid Resin System. Part I: Characterization of Co-Polymers of Isocyanate with Different Molecular Weights of Phenolic Resins

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Co-polymer systems of methylene diphenyl diisocyanate (MDI) and phenol-formaldehyde (PF) resins with different molecular weights were characterized by infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The FTIR and TGA coupled with differential thermogravimetric (DTG) results showed that higher molecular weight of PF resins not only promoted the reaction of isocyanate and PF co-polymer system, but also resulted in a better thermal property of prepared co-polymers. The XRD results revealed that higher molecular weight led to a higher proportion of ordered or crosslinking structures in the hybrid resin system. The relationship between the thermal resistance, mechanical properties and the molecular weights of phenolic resins needs further study.

Keywords: Isocyanate resin; Phenolic resins; Molecular weights; Morphology and structure

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INTRODUCTION

Phenol-formaldehyde (PF) resin (phenolic resin) has been widely used in the wood products industry as well as for other important commercial applications because of its excellent heat and flame resistance, electrical insulation, high tensile strength, and chemical resistance (Wu *et al.* 1997, 1998). However, the brittle nature of the resin limits its applications (Wu *et al.* 1997). For many decades, researchers have shown interest in improving the toughness of phenolic resins. In those studies (Matsumoto *et al.* 1991, 1992, 1993), different kinds of polymers were blended with phenolic resins to accomplish this goal. Among these polymers, isocyanate resin, known as methylene diphenyl diisocyanate (MDI), which is also an important binder used in the woodworking industry, has the highest potential to react with PF resin. The MDI resin has been used as a wood adhesive for more than 30 years because of its remarkable comprehensive properties (Pizzi and Walton 1992). Phenolic resin contains a high amount of hydroxyl groups which can interact with other polymers. The isocyanate group ($-N=C=O$), can easily react with a hydroxyl group (Conner *et al.* 2002; Alonso *et al.* 2004).

The declining fossil reserves and increasing demand in both developing and developed countries has caused the skyrocketing of the price of petroleum products. These concerns have become the major driving force in finding an alternative renewable resource

for chemicals (Pan 2011). Both PF resins and isocyanate resin can be obtained from other sources. Lignin and the bio-oil derived from lignocellulosic resources have been found to be potential sources of bio-phenol capable of replacing phenol in the production of phenol formaldehyde resins (Cheng *et al.* 2012). Isocyanate resin can be recycled from the non-saleable products or wastes from polyurethane foam, which is an important industrial product all around the world (Mao *et al.* 2014). A hybrid resin system based on the above raw materials, which was used in this research, can be renewable (non-petroleum), thus relieving political, economic, and environmental concerns over fossil-based resources.

In this study, the morphology and structure of a co-polymer system composed of isocyanate and phenolic resin with different molecular weights has been investigated. Although this kind of co-polymer system has shown very strong bonds, faster pressing time, and greater tolerance to higher moisture content than the traditional PF resins (Shafizadeh *et al.* 1999), very few reports have discussed the characterization of their reaction mechanism. As the intermolecular interactions play a key role in polymer compatibility (Lenghaus *et al.* 2000), different molecular weights of phenolic resins should display different properties when they react with the isocyanate group of isocyanate resin (Poljanšek *et al.* 2014). The objective of this research is to explore the MDI/PF resin co-polymer system, in which the impact of phenolic resin molecular weights on the properties of the system was also studied. This study will provide the basis for recycling isocyanate based polyurethane wastes and a method for improving adhesive properties in the wood product industry.

EXPERIMENTAL

Materials

Phenol, a 90% aqueous solution (USP), was obtained from Fisher Scientific Co., Ltd. Formaldehyde, a 50% stabilized solution, was supplied by Georgia-Pacific (GP) Chemicals (Taylorsville, MS, US). Isocyanate, a polymeric MDI with 33% -NCO functional group, was obtained from BASF Polyurethanes (Wyandotte, Michigan, US). Phenol was reacted with formaldehyde in a 2.1:1 molar ratio. During the reaction process, the viscosities (A, M, and W) of the resins were measured using viscosity tubes. Then they were allowed to cool for 24 h. Molecular weights were measured with gel permeation chromatography (GPC) (OMNISEC, Malvern Company, Worcestershire, UK.) with tetrahydrofuran (THF) as solvent. The measured molecular weights are listed in Table 1. Different molecular weights of PF resins thus prepared were mixed with isocyanate resin in a mass ratio of 1:1.

Table 1. Number Average Molecular Weight (M_n) and Weight Average Molecular Weight (M_w) of PF Resins of Different Molecular Weights

PF resin samples	Number Average Molecular Weight (M_n)	Weight Average Molecular Weight (M_w)	PDI
A	277.74	488.29	1.76
M	327.09	734.87	2.25
W	504.84	974.64	1.93

The purpose of this study was to obtain suitable molecular weights of PF resins able to react with MDI to produce a better wood adhesive based on PF resin itself. The PF resins with the middle molecular weight (labeled as “M”) were selected as the control sample.

Fourier Transforms Infrared (FTIR) Spectroscopy

The FTIR spectra of samples were measured with a Spectrum Two IR spectrometer (PerkinElmer, Waltham, MA, US) in the wavenumber range of 500 to 4000 cm^{-1} and 10 scans. The samples were oven dried at 50°C for 24 h and were ground to a powder.

Thermo Gravimetric Analysis (TGA)

The TG/DTG experiment was performed on a SDT Q600 (V20.9 Build 20) (TA instrument, New Castle, DE, US) instrument. The sample was put into an aluminum crucible and was heated with nitrogen at the rate of 10 °C/min, from room temperature to 1,000 °C.

X-Ray Diffraction (XRD)

The X-ray diffraction analysis was performed using an Ultima III Lab X-ray diffraction (Rigaku, Woodlands, TX, US) system. The wide-angle X-ray diffraction was used to study the d-spacing of the samples. The X-ray diffraction patterns were recorded using $\text{CuK}\alpha$ radiation ($\lambda=0.15418$ nm). The X-ray scanning was operated under 40 kV and 44 mA, and the data collection was recorded in the range of $2\theta=5$ to 90° with the speed of 1°/min. The pulverized samples were loaded on a zero background slide. Results were compared to the international center for diffraction data - powder diffraction file (ICDD PDF) database.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR analysis performed with the co-polymer system and PF resin with molecular weight of M is shown in Fig. 1. The characteristic band of the aromatic ring was observed at 1633 cm^{-1} to 1513 cm^{-1} region. The band detected in the 885 cm^{-1} was attributed to -CH out-of-plane (isolated H) stretching. The remarkable difference between the co-polymer system and the PF resin were the band features of the isocyanate group observed at 2259 cm^{-1} . This indicated that there were -NCO groups present in the co-polymer system, which means there were some isocyanate group left when using the 1:1 ratio of each material. Another study by Pizzi *et al.* (1993) also supported this conclusion.

Figure 2 displays the difference in the reaction of -OH and -NCO groups in MDI/PF co-polymers with different molecular weight resins. As mentioned above, with 1:1 mass ratio raw materials, there will be some residual isocyanate compounds left. This provided a perspective to compare co-polymers between PF resins with different molecular weights. It was obvious that there were variable -NCO groups left in the resin when using different molecular weights of PF resins. The peak intensity of the -NCO groups in lower-molecular weight PF resins was much stronger than that of higher-molecular weight PF resins. This indicates that the higher-molecular weight PF resins can promote the reaction of MDI and PF resins and the reaction between higher-molecular weight PF resins and MDI is much more completely towards the end. The relationship between this reaction and the bonding strength needs to be further studied.

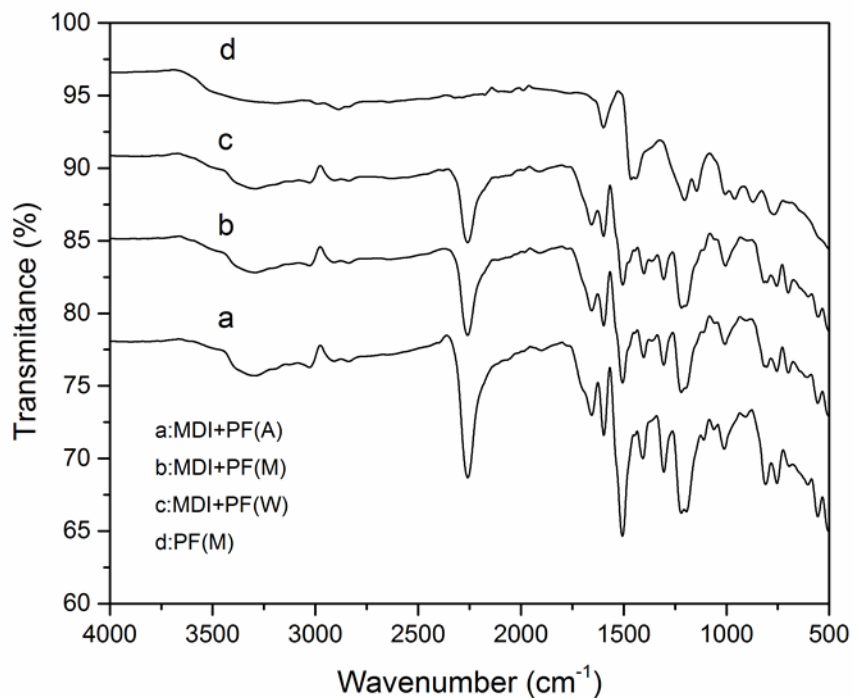


Fig. 1. FTIR spectra for MDI/PF co-polymer with different molecular weights

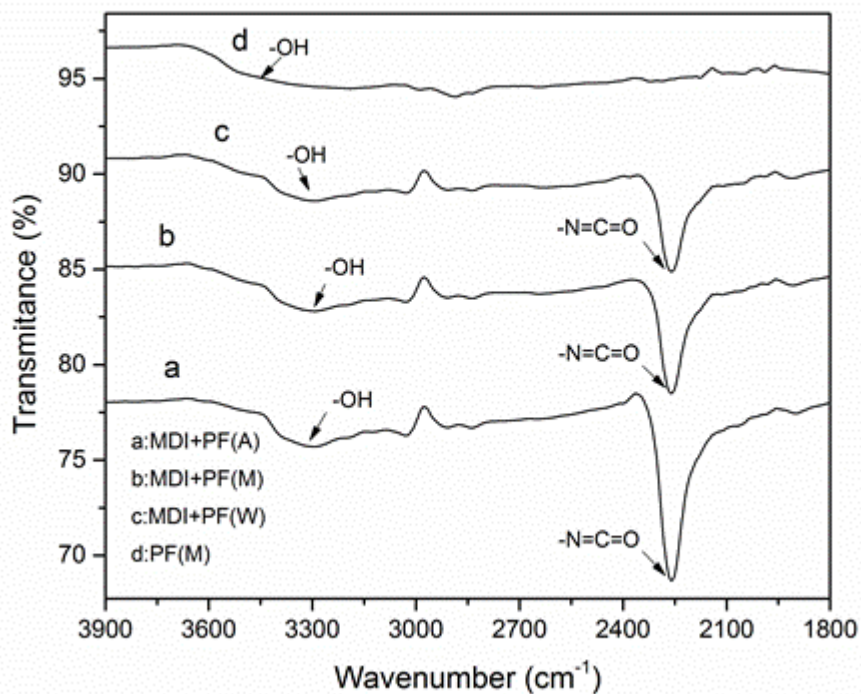


Fig. 2. FTIR spectra indicating -OH and -NCO groups in MDI/PF co-polymer

TG Analysis

Thermogravimetric analysis under an inert environment can provide insight into the composition through differences in the thermal stability of chemical bonds (Wandler and Frazier 1996; D'Souza *et al.* 2014). The thermal stabilities of co-polymer systems with different molecular weights of phenolic resins can be followed from Figs 3 to 8. It is obvious from the TG curve (Fig. 3) and DTG curve (Fig. 4) that the co-polymer decompositions occurred at various temperature ranges.

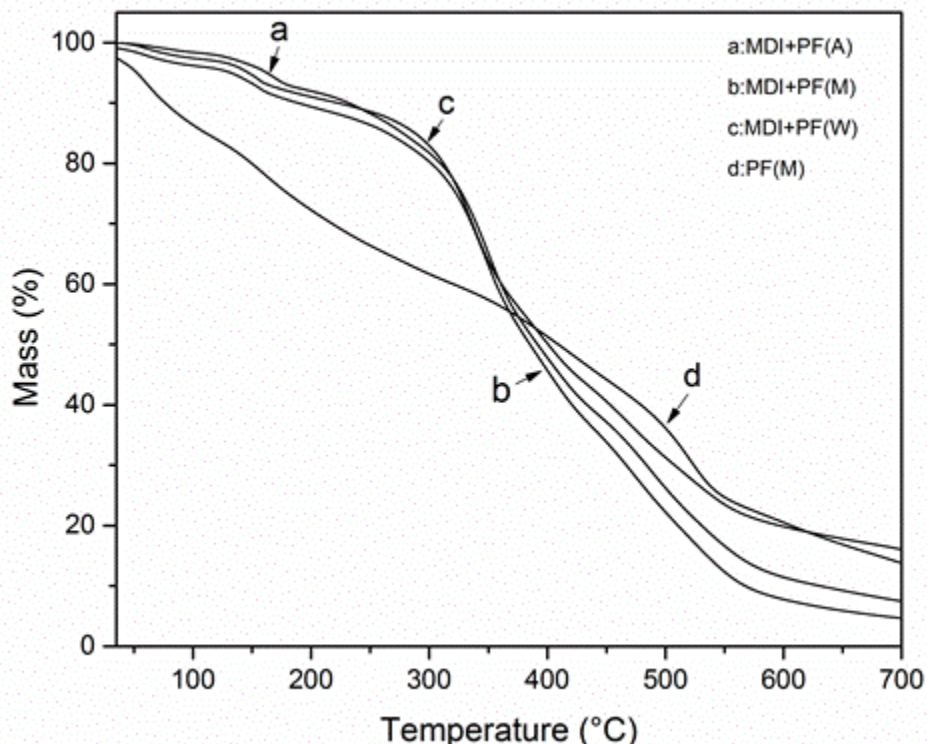


Fig. 3. TG curves of MDI/PF co-polymer with different molecular weights

There are two stages for the decomposition of MDI/PF co-polymer, while there is only one stage in the decomposition of PF resins. The initial decomposition rate of co-polymer is relatively slow. In the second decomposition stage, as the molecular weights of the PF resin increases, the mass loss rate becomes slower while the total weight loss rate decreases. The higher the molecular weight of PF resin, the better thermal property it showed.

The first stage represents the decomposition of MDI involving the breakage of urethane bonds, while the second stage denotes the ester decomposition. Under 320 °C, the higher the molecular weights of PF resins, the slower the decomposition rates of the co-polymer system (Fig. 4).

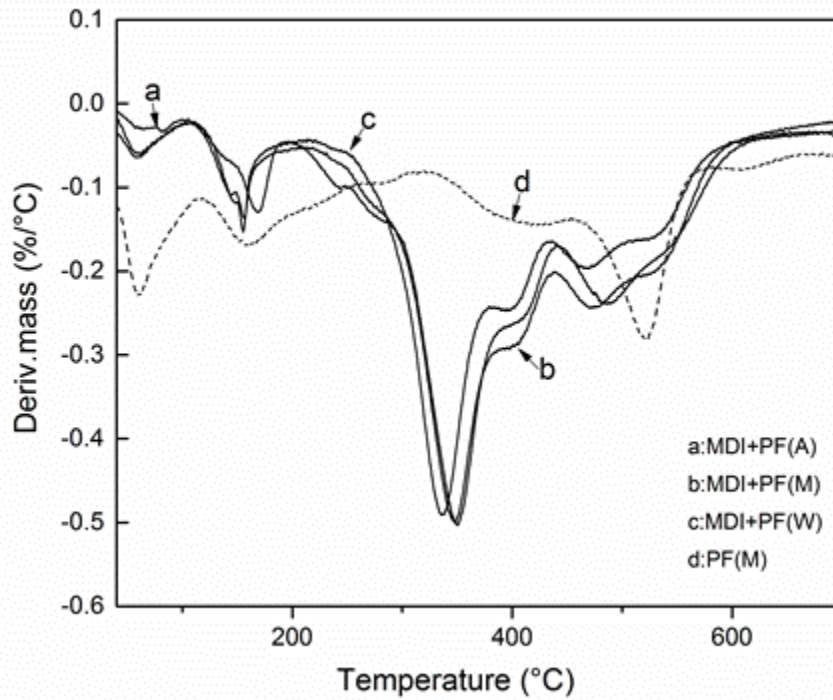


Fig. 4. DTG curves of MDI/PF co-polymer with different molecular weights

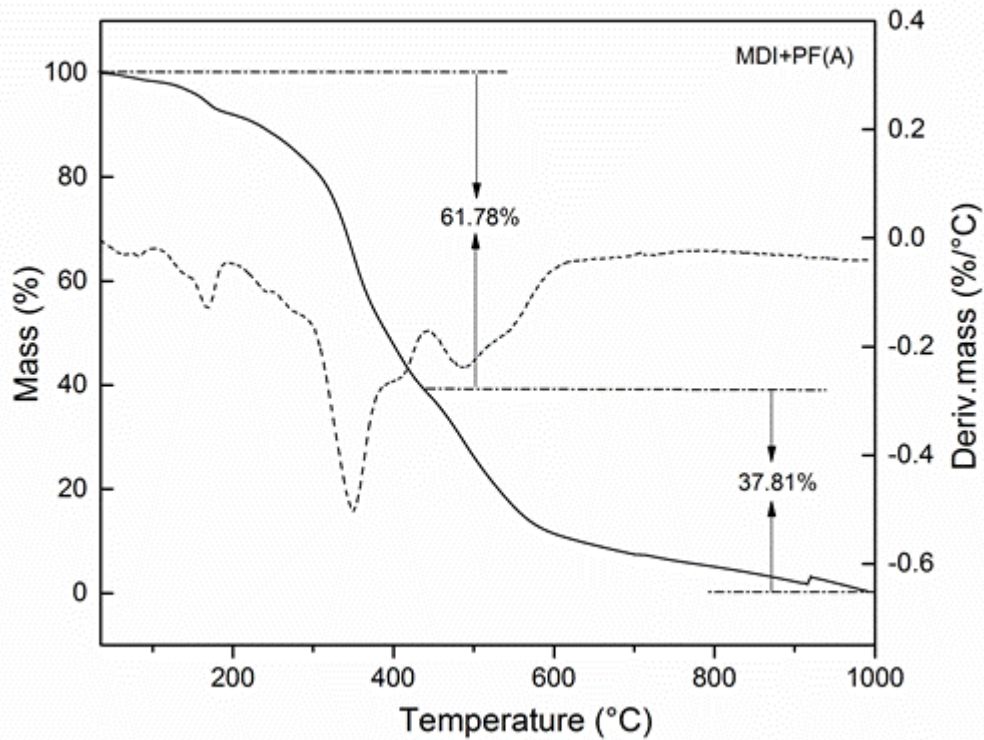


Fig. 5. TG/ DTG curves of MDI/PF co-polymer with molecular weight of A

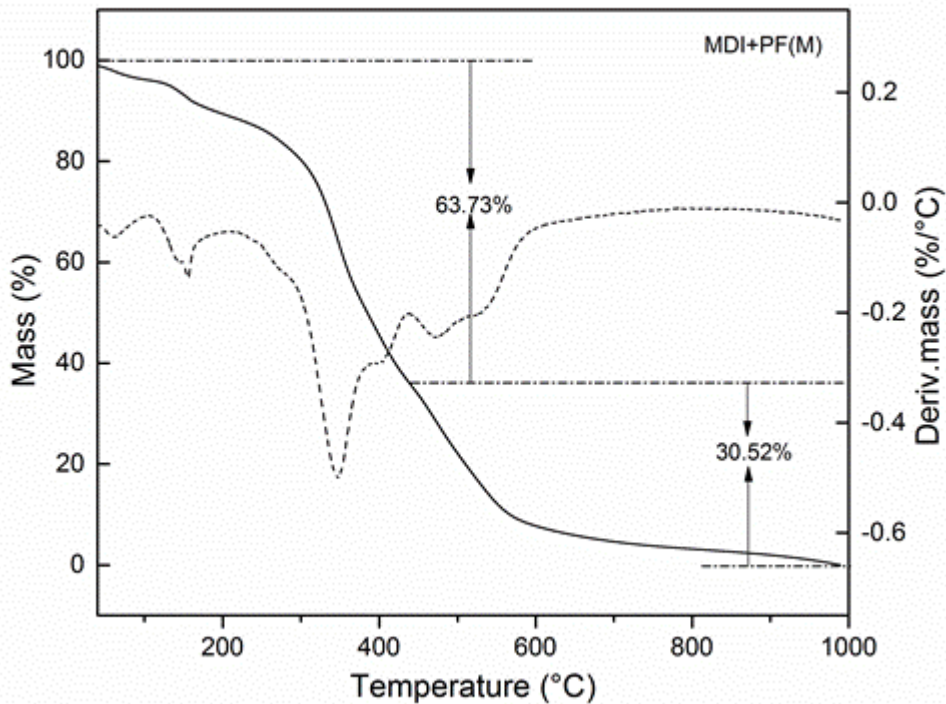


Fig. 6. TG/ DTG curves of MDI/PF co-polymer with molecular weight of M

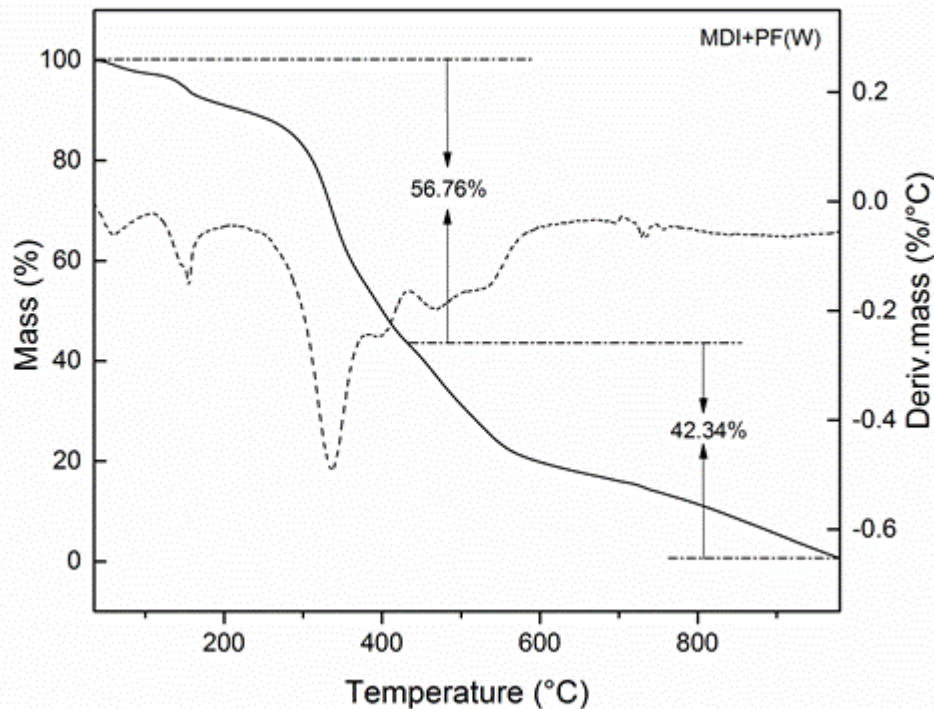


Fig. 7. TG/ DTG curves of MDI/PF co-polymer with molecular weight of W

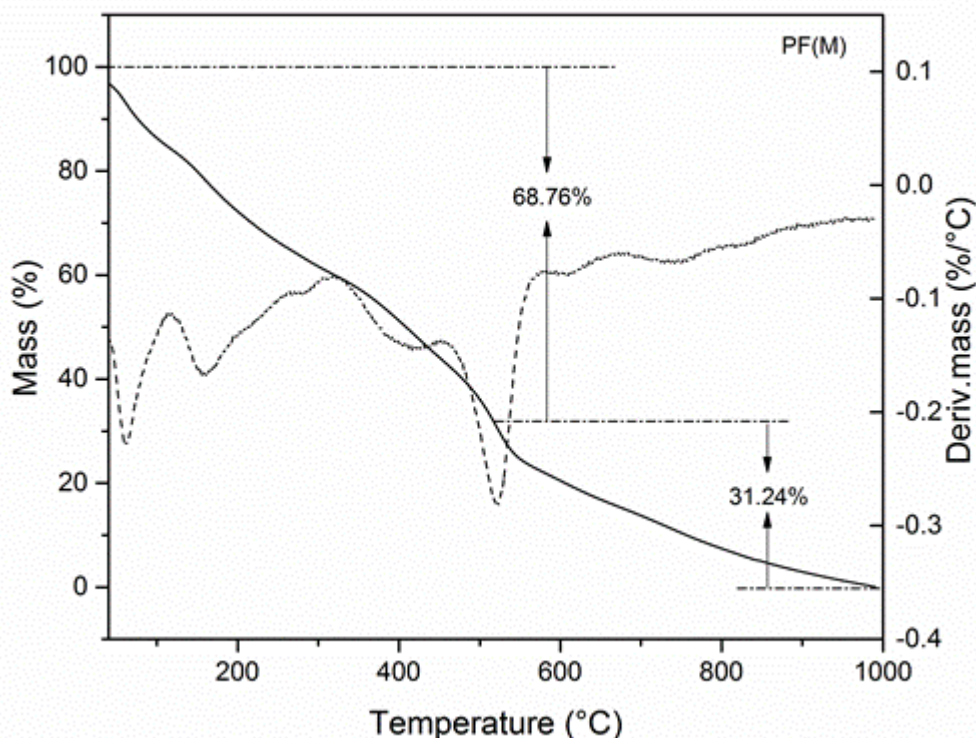


Fig. 8. TG/ DTG curves of PF resins with molecular weight of M

Figures 5 to 8 show the TG/DTG curves of co-polymer systems with different molecular weights of phenolic resins, and the control group of PF resins with molecular weight of M. In organic polymer systems, the total mass loss ratios of all the samples were approximately 100%. However, the first stage had lower mass loss ratio than phenolic resins' with molecular weight of M. This indicated that the co-polymer had better thermal properties under the temperature of 500 °C. Among all the three samples of co-polymers, during the first stage, the mass loss ratio of the sample of MDI/PF resins with the molecular weight of W was 56.76% which was significantly lower than that of the phenolic resin with molecular weight of A (61.78%) and M (68.76%). Generally, the co-polymer system of isocyanate resin with higher molecular weight of phenolic resin showed better thermal property.

XRD Analysis

X-ray diffraction techniques were used to examine the long-range order produced as a consequence of very short range interactions. Figure 9 shows the X-ray diffraction patterns of MDI/PF co-polymers with different molecular weights. The powder diffraction file exhibited broad peaks at 2θ angles around 18°, 21°, 30.3°, and 34.4°, indicating some degree of crosslinking. These peaks were assigned to the scattering from MDI/PF co-polymer system with different molecular weights. The degree of order in these materials was established in relation to the molecular weights of phenolic resins.

The evidence of crosslinking behavior of the co-polymer system was mainly from peaks at 2θ 30.3° and 34.4° . When compared with the X-ray diffraction patterns of phenolic resins in Fig. 10, the co-polymers showed clear evidence of crosslinking. From Fig. 9, it is very distinctive that with the increase of the molecular weight of phenolic resins, the co-polymer systems are more crosslinked, with the most intense peaks located at 2θ 20° , 30.3° , and 34.4° .

Through changes in the molecular weights of phenolic resins A to W, the characteristic peaks became smaller, indicating a decrease in crosslinking of the sample. The characteristic peaks disappeared completely in the samples without MDI. These results showed that the degree of crosslinking has some relationship with the molecular weights of phenolic resins. The variation of this can be explained by the extent of reaction between hydroxyl and isocyanate groups.

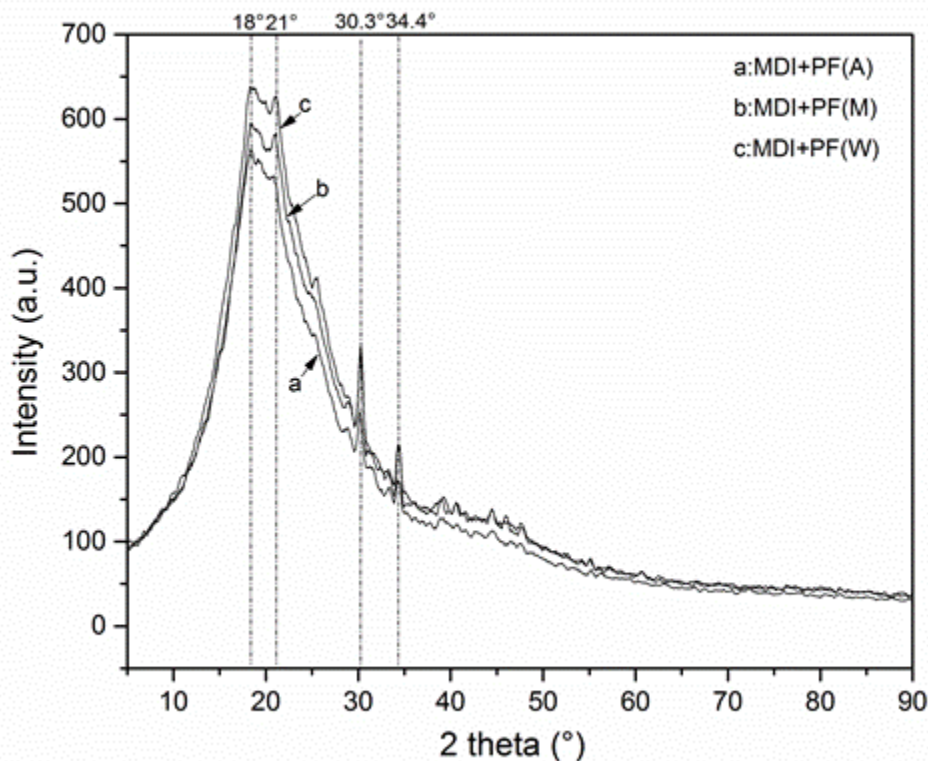


Fig. 9. XRD patterns of MDI/PF co-polymer with different molecular weights

The XRD technique was used to characterize this property in order to get more detailed information. In a crystal structure, d-spacing is defined as the distance between adjacent planes. Although it has not been confirmed that the co-polymer system employed in this study was crystalline or not, one can still use the same technique and calculation method to get the general average size of the particle which can be named d'-spacing.

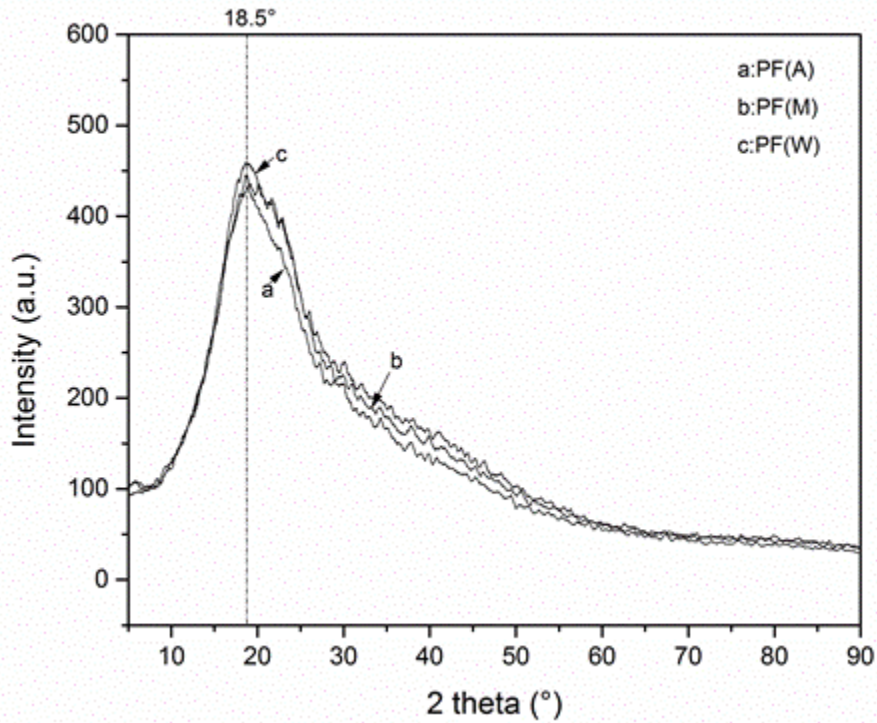


Fig. 10. XRD patterns of PF resins with different molecular weights

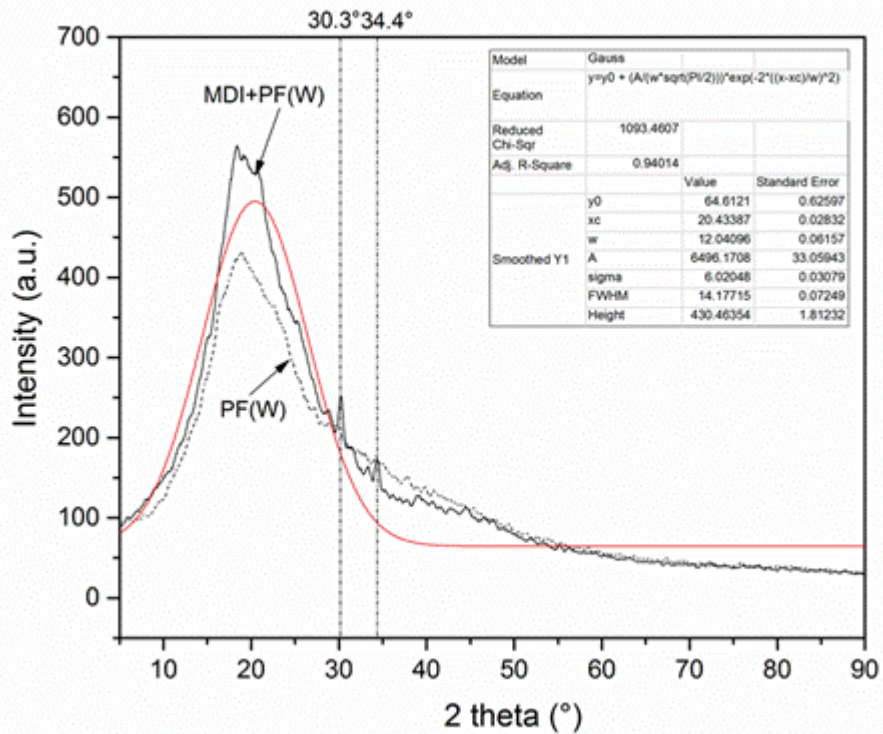


Fig. 11. Gauss fitting of XRD patterns of co-polymer and PF resin with the molecular weight of W

From Fig. 11, above, with the function of Gauss fitting, the full-width at half-maximum (FWHM) of the peaks at 2θ was 14.18. Using the equation of $\lambda = \text{CuK}\alpha = 1.540 \text{ \AA}$, the average particle size of the co-polymer system with the molecular weight of W was 0.57 nm, as calculated (The standard reference for FWHM of 0.1 degree was used in this calculation).

The d'-spacing's corresponding to the large peak(s) in the respective curves was calculated from Bragg's equation,

$$2d\sin\theta = \lambda \quad (1)$$

where 2θ is the X-ray scattering angle and λ represents the incident wavelength used.

The d'-spacing of diffraction peaks found in co-polymer system are shown in Table 2.

Table 2. Summary of X-Ray Scattering Peaks and Corresponding d'-Spacing of Copolymer

2θ (°)	$2\sin\theta$	d'-spacing (nm)
18	0.3129	4.90
21	0.3645	4.23
30.3	0.5227	2.95
34.4	0.5914	2.61

CONCLUSIONS

1. Lower molecular weight of the PF-resins used led to more –NCO residual groups observed in the copolymer system. Higher molecular weights of PF resins could promote the reaction of MDI and PF resins. The reaction between isocyanate and phenolic resin with the molecular weight of W appeared to be complete.
2. In the decomposition stage of MDI involving the breakage of urethane bonds, the reaction rates were found to be much slower than those of phenolic resins. The co-polymer systems had significantly better thermal properties than PF resins' below 500 °C. The co-polymer of isocyanate resin with the highest molecular weight of phenolic resin showed the best thermal property.
3. The co-polymer systems were a kind of amorphous material. The powder diffraction exhibited broad peaks at 2θ angles around 30.3° and 34.4°, indicating crosslinking behavior.
4. An increase in molecular weight of phenolic resins indicated more crosslinking in the co-polymer system. The average particle size of the co-polymer system with molecular weight of W was 0.57 nm.

This kind of hybrid polymer system has the potential to improve the thermal resistance, mechanical properties, as well as other properties. The relationship between these properties and the molecular weights of phenolic resins need further study.

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