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Effect of the molecular structure of phenolic novolac precursor resins on the properties of phenolic fibers

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HIGHLIGHTS

- Phenolic resins with different weight-average molecular weights and ortho/para ratios have been prepared.
- The tensile strength of the phenolic fibers increases with reducing novolac O/P ratio.
- The tensile strength of the phenolic fibers increases with increasing novolac M_w.

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ABSTRACT

A series of phenolic resins with different weight-average molecular weights (M_w) and ortho/para (O/P) ratios were prepared. The effect of the phenolic precursor resin structure on the structure and properties of the resulting phenolic fibers was investigated. The structures of the resins and fibers were characterized by nuclear magnetic resonance spectroscopy, gel permeation chromatography, melt rheometry, dynamic mechanical analysis, and thermogravimetric analysis. The results show that the O/P ratio, unsubstituted ortho and para carbon ratio (O_u/P_u), and M_w of the phenolic resins play an important role in determining the properties of the phenolic fibers. The tensile strength of the phenolic fibers increases with increasing novolac precursor O_u/P_u ratios, corresponding to low O/P ratios, at comparable resin M_w values. Also, the tensile strength of the phenolic fibers increases with increasing novolac M_w values at comparable O/P ratios. Phenolic fibers with high tensile strength and good flame resistance characteristics were generated from a phenolic precursor resin, possessing a high weight-average molecular weight and a low O/P value.

1. Introduction

Phenolic fibers (PFs) are known to have a high temperature stability, high flame resistance, outstanding resistance to corrosive environments, excellent thermal insulation, and good comfort and feel characteristics [1–6]. PFs are used in composites, gaskets, friction materials, and diverse flame- and chemical-resistant textiles and papers [1–3]. They are also used as a precursor for the production of carbon and activated carbon fibers [7]. PFs are generally prepared by crosslinking the as-spun fibers, derived from melt-spinning of novolac resins, in a solution of formaldehyde and hydrochloric acid under conventional reflux conditions [2,5,8]. Our previous study demonstrates that the tensile strength is closely related to the degree of crosslinking of the fibers [9]. The formation of low molecular weight compounds that are generated from the unstable terminal groups and inner units is reduced during pyrolysis because of the high degree of crosslinking in the phenolic fibers. This promotes the formation of graphite layers [10]. Consequently, the high degree of crosslinking between the phenolic rings in the network leads to good mechanical and flame resistance properties [11].

The high degree of crosslinking between the phenolic rings in the network is known to depend on the preparation parameters of the PFs and the structure of the phenolic precursor resins [2,8,9,12]. The influence of different parameters during the curing process, such as formaldehyde and hydrochloric acid concentrations and heating rate, on the structure and characteristics of the cured fibers, has been studied in detail [8]. However, the influence of the phenolic precursor resins has been minimally investigated.

More specifically, in the present work, the influence of the weight-average molecular weight (M_w), ortho/para ratio (O/P), and unsubstituted ortho to para carbons ratio (O_u/P_u) of phenolic resins

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on the structure and characteristics of PFs is investigated for generating highly functional phenolic fibers.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. Phenol and paraformaldehyde were supplied by Tianjin Chemical Reagent Company (China). Zinc acetate and oxalic acid were supplied by Xian Chemical Reagent Company (China).

2.2. Preparation of PFs

The phenolic novolac precursor was first prepared by reacting phenol with formaldehyde in the presence of zinc acetate and oxalic acid catalysts. Typically, 100 parts of phenol, 50–85 parts of paraformaldehyde, and 0–3 parts of zinc acetate were added in a 500 mL flask, equipped with a reflux condenser, stirrer, and thermometer. The mixture was heated and maintained at 100 °C for 3 h, and then 2.25 parts of oxalic acid was added, followed by further heating under reflux for 5 h. The mixture was then distilled under vacuum to remove water and unreacted phenol at 180 °C and −0.09 MPa for 30 min. A range of phenolic novolac precursors with different M_w values and *O*/*P* ratios were obtained by changing the concentrations of paraformaldehyde and zinc acetate.

The phenolic fibers were prepared by melt-spinning the phenolic precursor resin. The fibers were then cured in a combined solution of hydrochloric acid and formaldehyde in a 500 mL flask, under reflux conditions. The solution was heated from room temperature to boiling point at a heating rate of 4–34 °C h^{-1}. Following curing, the resulting samples were washed with water and dried at room temperature.

2.3. Sample characterization

The softening point (SP) and spinnability of the resin were evaluated by the needle insertion method [14]. About 4 g of the power samples was placed in a test tube that was immersed in a silicon oil bath. The oil bath was heated from room temperature to ~200 °C at a heating rate of 1 °C min^{-1}. SP refers to the temperature at which the iron wire falls freely to the base of the test tube.

Gel permeation chromatography (GPC) was used to determine the weight-average molecular weight (M_w), number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the novolacs. The measurements were performed on a GPC-717/1515/2414 (Waters Company USA) that consisted of an ultraviolet absorption spectrum detector using polystyrene as a standard substance and a separator column containing polystyrene with a molecular weight of 474–205 000 g mol^{-1} (HR 1.0, HR 2.0, HR 3.0). The molecular weights (PS-equivalent), as a function of the retention volume, were calibrated with a set of low-to-medium molecular weight polystyrene standards, using tetrahydrofuran (THF) as the carrier solution. A solution of novolac dissolved in THF was first prepared (about 1% by weight). For the measurement, 20 μL of the prepared solution was injected into the GPC instrument (THF flow rate: 1.0 mL min^{-1}; column temperature: 30 °C). The GPC data were processed by the Waters Breeze 2 software.

Nuclear magnetic resonance spectroscopy (NMR) spectra were acquired at 300 K, using CD_3COCD_3 solvent, on a Bruker Avance 400 MHz spectrometer. Standard pulse sequences and parameters were used to obtain the DEPT-135 spectra. About 20 mg of the sample, in a 10 mm diameter sample tube, was dissolved in about 5 mL of acetone-d_6 CD_3COCD_3, which was used as a solvent, along with tetramethylsilane as an internal standard.

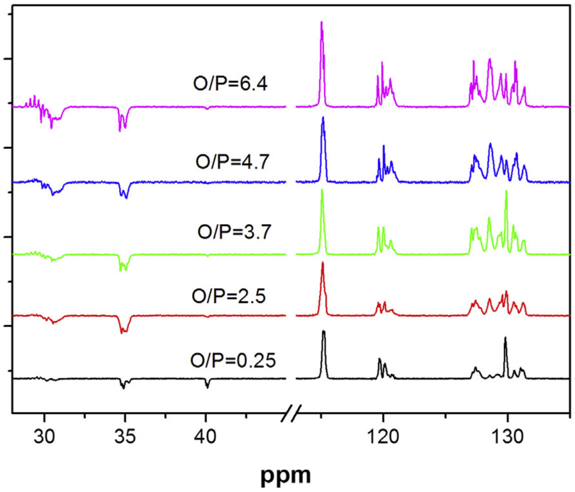

Fig. 1. The DEPT135 spectra of various novolacs.

The rheological behavior of the samples was measured by a rheometer (AR-G2, TA Company, USA) using a cooling system under a steady-state mode with a starting temperature of 200 °C and finishing temperature of 80 °C. About 0.8 g of the powder sample was compressed into a disc (diameter: 25 mm; thickness: 1 mm). When the temperature reached 200 °C, the disc-like sample was placed onto an aluminum fixture (diameter: 25 mm), and cooled to 80 °C to generate the viscosity–temperature curves.

The tensile strength of the samples was evaluated on a dynamic mechanical analysis instrument (Q800 DMA, TA Company, USA). The diameter of the fibers was estimated using microscopy (Leica DMLP, Leica Company, Germany). Fifteen fibers were tested to obtain an average diameter value.

Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TA-Q600SDT, USA). About 20 mg of the sample was placed on a platinum pan, and pyrolyzed in a stream of N_2 (99.9999%) from room temperature to 800 °C at a heating rate of 5 °C min^{-1}, or in a stream of air from room temperature to 600 °C at a heating rate of 5 °C min^{-1}.

The limited oxygen index (LOI) refers to the minimum concentration of oxygen (determined as a volume percent in a mixture of oxygen and nitrogen) required to sustain the combustion of a material. The LOI of the fibers was determined on an oxygen index-type combustion tester (LFY-606, Textile Institute of Science and Technology of Shandong Province, China) according to the Textile-Burning behavior-oxygen index method in GB/T5454-1997. The sample was assembled as a rod-shaped staple fiber of 0.2 g and 12 cm in length [11].

3. Results and discussion

3.1. Structure of the novolac resins

^{13}C NMR can be used to characterize the structure of the novolac resins. However, to accurately calculate the *O*/*P* value of the novolacs, the influence of the solvent needs to be eliminated. DEPT-135 (distortionless enhancement by polarization transfer) can be coupled with ^{13}C NMR for producing enhanced spectra by using a specific pulse sequence. It is a very sensitive analysis for random and high-ortho novolac resins [13]. By adopting the traditional ^{13}C NMR technique, the peaks of acetone-d_6 CD_3COCD_3 (lock and internal chemical shift reference at 29.8 ppm) and those of *o*–*o* linkages, observed between 29 and 31 ppm, are superimposed. In contrast, by employing the DEPT-135 technique, distinct peaks

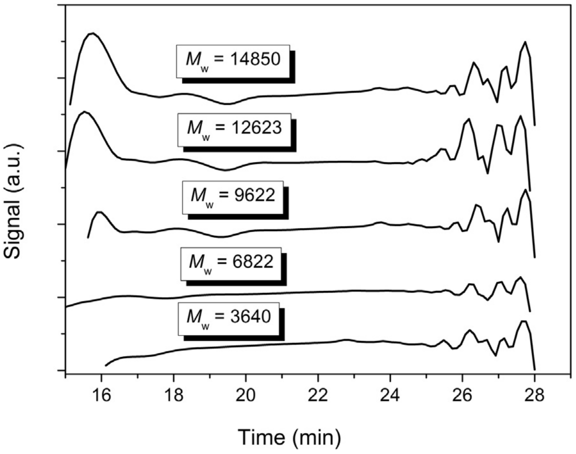

Fig. 2. The GPC chromatograms of various novolacs with similar *O*/*P* values (2.8–3.2).

corresponding to o–o (∼29–31 nm), o–p (∼34–36 nm), and p–p (∼39–42 nm) linkages can be obtained, thereby allowing accurate measurements of the peaks intensity.

Diverse structural parameters of the novolacs were evaluated from the DEPT-135 spectra. The *O*/*P* ratio of the novolac phenolic resin was calculated according to the following equation [13–16]:

$$O/P\,\text{ratio} = \frac{S_{\text{o-o}} + 0.5 \times S_{\text{o-p}}}{S_{\text{p-p}} + 0.5 \times S_{\text{o-p}}} \qquad (1)$$

where $S_{\text{o-o}}$, $S_{\text{o-p}}$, and $S_{\text{p-p}}$ are the peak intensities, associated with the o–o, o–p, and p–p bonds, respectively.

The DEPT-135 spectra of the various novolac resins are shown in Fig. 1. The main difference between the DEPT-135 spectra is the signal corresponding to the methyl group (29–42 ppm). The *O*/*P* ratios of the resins with similar M_w values of 11 000–13 000 Da, calculated according to Eq. (1), were 0.25, 2.5, 3.7, 4.7, and 6.4, respectively.

The gel permeation chromatograms of the various novolacs with similar *O*/*P* values (2.8–3.2) are presented in Fig. 2. The GPC curves indicate that a high molecular weight fraction corresponds to a high M_w. The M_w, M_n, M_w/M_n, and *O*/*P* values of these samples are shown in Table 1. The corresponding M_w values of the novolacs are 3640, 6822, 9622, 12 623, and 14 850 Da. The M_w of the samples increases with the breadth of the M_w/M_n (Table 1). In contrast, M_n did not change as drastically as M_w because the latter is relatively sensitive to the low molecular weight fraction. In principle, both the M_w and M_w/M_n of the novolacs significantly influence the softening point, melt viscosity, and the properties of the phenolic fibers, as detailed in the following section.

Table 1
Molecular weight, *O*/*P* value and melt viscosity of novolacs.

Sample	*O*/*P* value	O_u/P_u	M_n (Da)	M_w (Da)	M_w/M_n	Melt viscosity at 160 °C (cP)
A	2.8	2.98	1041	3640	3.50	7.5
B	2.8	3.05	1210	6822	5.64	13.5
C	3.1	3.10	1292	9622	7.45	29.7
D	3.2	3.13	1309	12 623	9.64	69.6
E	3.1	3.09	1319	14 850	11.26	226.3
F	0.25	6.41	1302	11 339	8.71	34.3
G	2.5	4.32	1317	11 326	8.60	30.5
H	3.7	3.94	1319	12 013	9.11	38.3
I	4.7	1.04	1305	12 114	9.28	47.8
J	6.4	0.52	1313	12 235	9.32	58.7

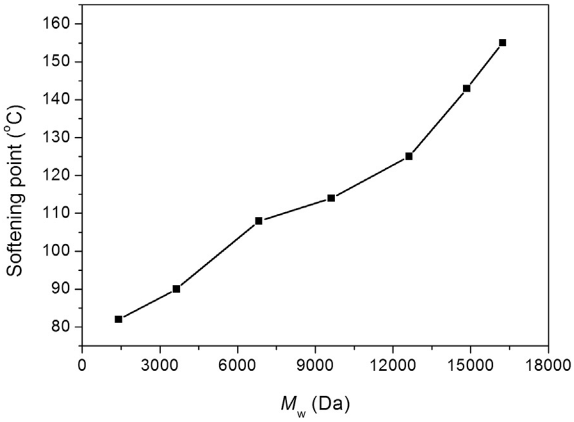

Fig. 3. The relationship between the softening point and M_w of novolacs.

3.2. Properties of the novolac resins

The relationship between the softening point and M_w of the novolacs is shown in Fig. 3. As expected, the softening point of the novolacs gradually increases with increasing M_w values—an increase in the M_w correlates to an increase in the degree of cross-linking of the resin, which leads to stronger interactions between the molecular chains, thereby resulting in a higher energy barrier for the cooperative segment jumps to cause the softening flow of the molecule.

The viscosity–temperature curves of the phenolic resins with different M_ws and similar *O*/*P* ratios (2.8–3.2) are shown in Fig. 4. A sharp decrease in the viscosity was noted at increasing temperatures. The profiles additionally featured a turning point after which the viscosity became very low (<100 cP). The respective curves of the novolacs, with M_w values of 3640, 6822, 9622, 12 623, and 14 850 Da, featured corresponding turning points at 140, 147, 153, 164, and 177 °C. These turning points corresponded to the spinning temperatures.

As shown in Table 1, the melt viscosity of the resins at 160 °C increases with increasing phenolic resin M_w values, suggesting that the viscosity is very sensitive to both M_w and M_w/M_n. In fact, the melt viscosity of the novolacs is more likely influenced by the fraction of the ultra high M_w as it can lead to a higher level of entanglement and stronger interactions between the molecular chains. Assuming that the melt novolac behaves as a Newtonian fluid, its melt viscosity can be related to the temperature using the

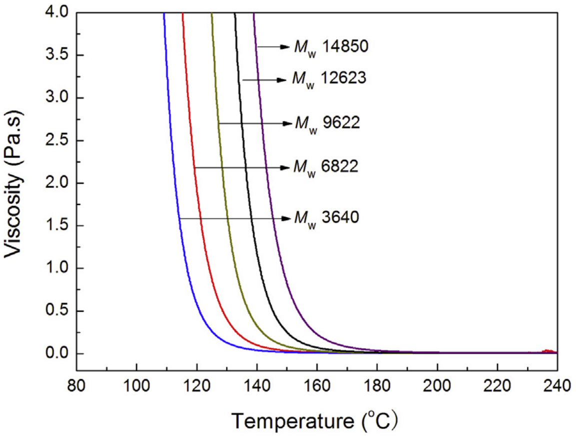

Fig. 4. The viscosity–temperature curves of novolacs.

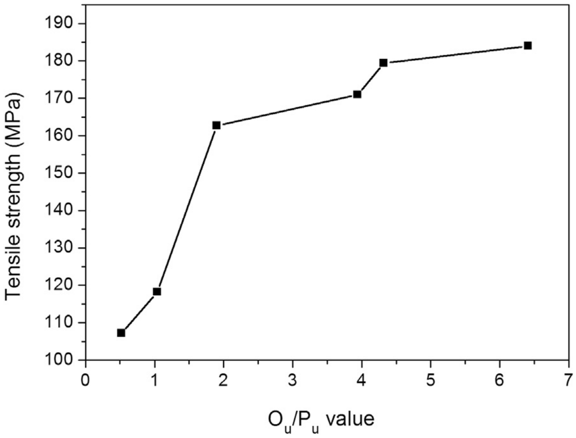

Fig. 5. The influence of O_u/P_u value of novolacs with similar M_w (11 000–13 000 Da) on the tensile strength of phenolic fibers.

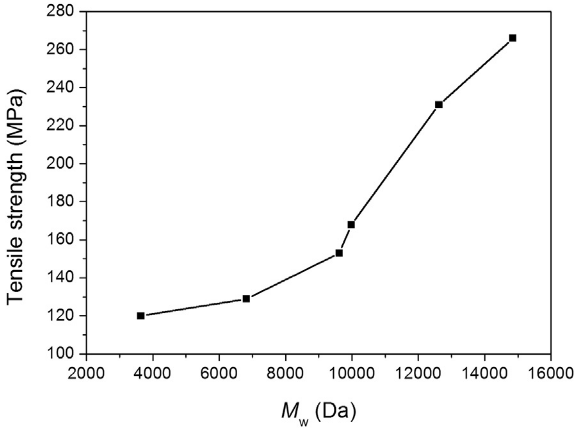

Fig. 6. The influence of M_w of novolacs with similar O/P values (2.8–3.2) on the tensile strength of phenolic fibers.

Arrhenius equation [17]. The enhanced high molecular weight fraction of the novolac induces a higher melt viscosity that considerably restricts the motion and diffusion of the molecular chains. Moreover, the ultra high M_w fraction significantly contributes towards the formulation of larger structured networks in a broader domain that further restrict the cooperative segmental motion and increase the melt viscosity.

3.3. *Effect of the novolac O_u/P_u ratios on the tensile strength of PFs*

Nanjo et al. previously reported that high-ortho novolacs, containing a high ortho-linkage content, have a fast curing property [18]. Li et al. [19] demonstrated that high-ortho novolacs exhibited higher reactivities than that of ordinary novolacs as the former novolacs contain a higher number of highly reactive para sites in the phenolic nuclei. Thus, the precursor novolacs with high O/P ratios would contain a higher amount of para-reactive sites (P_u) in the phenolic nuclei whereas those with low O/P ratios would feature a higher amount of ortho-reactive sites. The number of unreacted para (P_u) (118–122 nm) and ortho (O_u) positions (111–118 nm) per phenolic ring can easily be obtained by dividing the signal intensity of the unsubstituted ortho- and para-aromatic carbons by 1/6 of the signal intensity of the total aromatic region [13]. The O_u/P_u values of the phenolic resins are as shown in Table 1. As the O/P ratio increases from 0.25 to 6.4, the O_u/P_u ratio decreases from 6.41 to 0.52. Fig. 5 shows the influence of the O_u/P_u ratio of the phenolic resins, with similar M_ws (11 000–13 000 Da), on the tensile strength of the resulting phenolic fibers. The tensile strength of the phenolic fibers increases with increasing O_u/P_u ratios. This trend was more pronounced for O_u/P_u ratios below 1.90. The trend can be explained as follows. Phenolic fibers are known to have a three-dimensional structure with a methylene bridge between the benzene rings. The tensile strength is closely related to the degree of crosslinking of the fibers. Increased crosslinking of the functional groups, such as CH_2 methylene bridges, biphenyl ethers, and carboxyls, results in an increase in the tensile strength [8].

In the present study, curing of the spun fibers in a solution of formaldehyde and hydrochloric acid proceeded in a two-stage process [8]. In the first stage, the formaldehyde molecule reacts with the surface phenolic ring of the spun fibers to form a methylene bridge between two phenol units. In the following stage, $^{+}CH_2OH$ diffuses into the fibers and adds onto the unsubstituted para and ortho positions of the spun fibers to form the phenolic fibers. A large O/P ratio results in a small O_u/P_u ratio that corresponds to the presence of a higher number of reactive para sites in the phenolic nuclei of the spun fibers, which facilitates fast curing of the surface of the phenolic fibers. At the start of the curing process, layers are formed on the fibers, which hinder the diffusion of $^{+}CH_2OH$ into the fibers in the second stage of the curing process. This results in a low degree of crosslinking of the fibers. In contrast, a high-ortho phenolic novolac resin has a lower content of methylene bridge groups than that in random-type novolacs. Thus, a high-ortho phenolic novolac resin would generate fibers with a low tensile strength.

3.4. *Effect of the M_w of novolacs on the tensile strength of PFs*

The influence of the M_w of novolacs, with comparable O/P values (2.8–3.2), on the tensile strength of the phenolic fibers is shown in Fig. 6. The tensile strength of the phenolic fibers increases with increasing M_w values. The reaction mechanisms involved in the synthesis of novolacs and the crosslinking of the spun filaments have been established [8]. First, owing to the electrophilic nature of the reaction between phenol and formaldehyde, the carbonium ion ($^{+}CH_2OH$) reacts with the phenolic ring to produce a benzylic intermediate that rapidly reacts with another phenol to form a methylene bridge between the two phenol units. The formaldehyde molecules subsequently add onto the free para and ortho positions of the spun filaments to form the phenolic fibers. This indicates that the crosslinking groups in the phenolic fibers include both the methylene bridges, in the precursor novolacs, and the additional bridges formed during the curing reaction. Higher M_w values are indicative of a larger amount of methylene bridges on the phenolic nuclei. Moreover, the high M_w is associated with the presence of highly functional reactive sites on the phenolic nuclei. The high molecular weight fraction of novolacs can promote the formation of a stronger crosslinked network structure with HCHO during the curing reaction. The ultra high M_w fraction has a greater contribution to the development of a larger structured network in the phenolic fibers. The previous study indicated that the tensile strength of the phenolic fibers increased by increasing the degree of crosslinking of the functional groups that include CH_2 methylene bridges, biphenyl ethers, and carboxyls [8]. As a result, novolacs with high M_w values generate phenolic fibers with a large tensile strength.

3.5. *Effect of the M_w of novolacs on the thermal stability of PFs*

Thermogravimetric analysis curves of the phenolic fibers, derived from novolacs with different M_w values, in N_2 are shown in

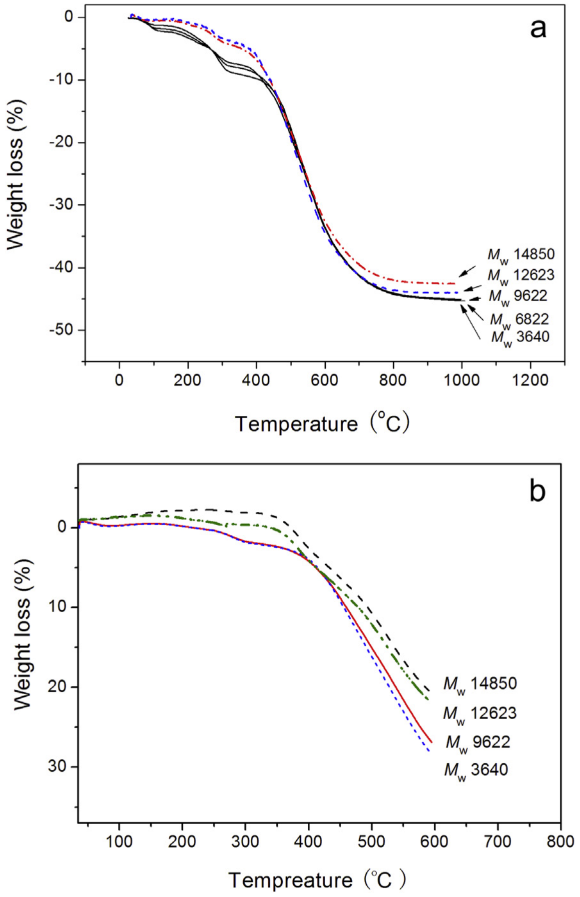

Fig. 7. TGA curves of phenolic fibers derived from novolacs with different M_ws: a) in N_2, b) in air.

Fig. 7a. The weight loss in the temperature range of 130–400 °C, corresponds to the decomposition of some small end groups, and rupture of weak bonds in the chains of the PFs [10,20]. Smaller weight losses were observed in the fibers that were prepared with novolac precursors with higher M_w values. The weight loss, corresponding to the decomposition of phenol, cresol, and xylenol molecules in the fibers, in the temperature range of 400–1000 °C, also decreased with increasing novolac precursor M_w values. This is reasonable as the phenolic fibers, derived from the higher M_w novolac precursors, have a higher degree of crosslinking. The high degree of crosslinking in the phenolic fibers limits the formation of low molecular weight compounds, generated from the unstable terminal groups and inner units during the pyrolysis of the fibers.

Fig. 7b shows the TGA curves of the phenolic fibers, derived from novolacs with different M_w values, in air. The total weight loss decreases with increasing novolac precursor M_w values. The TGA curves of the fibers differ in the range of 100–350 °C. The TGA curves of the fibers, derived from novolacs with M_w values of 9622 and 3640 Da, show a continuous weight loss whereas those derived from novolacs with M_w values of 12 623 and 14 850 Da show a slight weight increase. Beyond 400 °C, the weight of all the samples decreases sharply. This can be explained as such: the oxidation of phenolic fibers begins by attacking the methylene bridge to form a peroxide bond [2,5,11]. Some of the methylene links are converted to carbonyls that possess a higher resistance to oxidation. The peroxide subsequently decomposes at elevated temperatures with the evolution of heat. The observed weight increases in the range of 100–350 °C for the fibers derived from the novolacs with M_w values of 12 623 and 14 850 Da indicate that the methylene links are converted to carbonyls. The fibers, derived from the novolacs with M_w values of 12 623 and 14 850 Da, contain more methylene bridges between the phenol units, thereby enhancing the oxidation resistance property of the fibers.

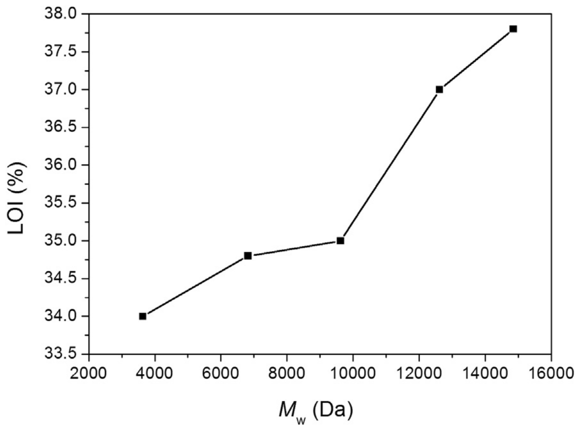

Fig. 8. The influence novolac M_w on LOI of phenolic fibers.

The measured LOI values of the fibers were used to assess the flame resistance of the phenolic fibers. Fig. 8 shows the effect of the M_w of the phenolic resins, bearing similar O/P ratios (2.8–3.2), on the LOI of the phenolic fibers. The LOI of the phenolic fibers increases with increasing phenolic resin precursor M_w values—the maximum LOI value of 3.8 was achieved with the highest novolac M_w.

4. Conclusion

The O/P ratio, O_u/P_u ratio, and M_w of phenolic precursor resins significantly influence the properties of the resulting phenolic fibers. At comparable novolac M_w values, the tensile strength of the phenolic fibers increases with increasing novolac O_u/P_u ratios that translate to low O/P ratios. At comparable novolac O/P ratios, the tensile strength of the phenolic fibers increases with increasing novolac M_w values. Phenolic fibers with a high tensile strength and good flame resistance can be prepared from a phenolic precursor resin with a high weight-average molecular weight and a low O/P value.

Acknowledgments

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