Novolac 鉬改質酚醛樹脂的製備及其在鑽石研磨工具的應用特性

林俊德[1]、李訓清[2]、林平和[3*]

桃園創新技術學院化妝品應用系[1，3*]

萬能科技大學奈米材料應用研發中心[2]

摘　要

本試驗製備出的鉬改質酚醛樹脂（Mo-PF），在製備過程中鉬酸鹽與酚醛樹脂（PF）反應後形成具有 Mo-O 鍵結的低交聯度鉬酚醛樹脂，然後再進一步與六亞甲基四胺（hexamethylenetetramine）混合後，經由 190 ^{o}C 熱固化後形成熱固性鉬改質酚醛樹脂。Mo-PF 樹脂與 PF 樹脂藉由 FTIR、DSC、DMA、TGA、SEM 及抗彎曲強度測試後，可觀察到 Mo-PF 的熱性能及機械強度都明顯高過 PF 樹脂。由於 Mo-PF 樹脂結構中形成的 Mo-O 鍵結，因此 Mo-PF 樹脂在 10%熱重量損失溫度及抗彎曲強度分別為 503 ^{o}C、76.5 MPa，其熱性能及機械強度高過 PF 樹脂的（439 ^{o}C、53.7 MPa）。另一方面，藉由 Mo-PF 及 PF 樹脂做為黏結劑分別製作鑽石研磨工具，從氧化鋁陶瓷研磨試驗中觀察鑽石研磨工具表面的研磨狀態，其試驗結果的比較及觀察 Mo-PF 具有良好的耐熱性能及研磨品質。

關鍵字：鉬酚醛樹脂、鉬酸銨、鑽石研磨工具

*Email：lin101@tiit.edu.tw　TEL:03-4361070 ext 2301

PREPARATION OF NOVOLAC MOLYBDENUM MODIFIED PHENOLIC RESINS AND USED AS A BINDER IN DIAMOND GRINDING TOOLS

Chun-Te Lin[1]，Hsun-Tsing Lee[2]，Pin-Ho Lin[3*]

[1，3*]Department of Applied Cosmetology, Taoyuan Innovation Institute of Technology, Chung-Li, Tao-Yuan

[2]Nanomaterials application R&D center, Vanung University,

Chung-Li, Tao-Yuan

Abstract

Novolac molybdenum modified phenolic resins (Mo-PF) were successfully prepared. In the process of preparation, molybdate reacted with phenolic resins (PF) to form a low cross-linked Mo-PF with new Mo-O bonds, and it was confirmed by the FTIR spectrum. The Mo-PF can be further cured with hexamethylenetetramine at 190°C. The structure and characterization of PF and Mo-PF were performed by using FTIR, DSC, DMA, TGA, SEM, mechanical strength tester. The thermal resistance, flexural strength, and hardness of Mo-PF are respectively higher than those of PF. This is due to the presence of Mo-O cross-linking bonds in Mo-PF. The thermal decomposition temperature at 10% weight loss and flexural strength of Mo-PF are 503°C and 76.5MPa respectively, which are much higher than the corresponding values of 439°C and 53.7MPa for PF. Furthermore, in order to identify the applied properties of Mo-PF resin, it was compared with PF in the performance as a binder for diamond grinding tools through the basic grinding experiments of Al_2O_3 ceramics. Mo-PF is a better binding resin than PF so the grinding tool made from the former resin has better grinding quality

than that made from the latter resin.

Keywords：Molybdenum-phenolic resin, Ammonium molybdate, Diamond grinding tools

*Email：lin101@tiit.edu.tw TEL:03-4361070 ext 2301

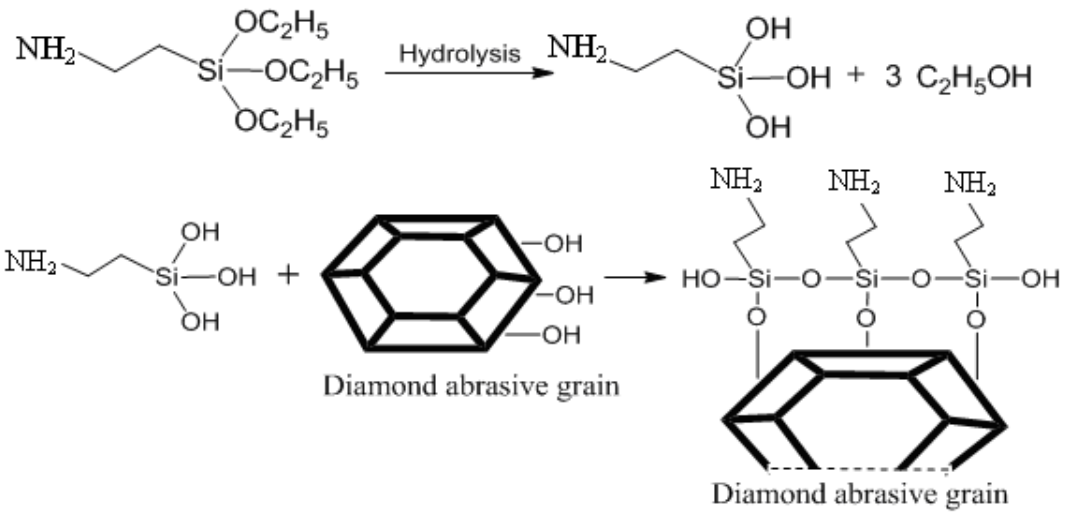
1. Introduction

Phenolic resin is the first synthetic polymeric material, and is generally synthesized from phenol and formaldehyde in the presence of a catalyst. Phenolic resin can be classified into two categories as resole and novolac resins according to the phenol/formaldehyde ratio used during the synthesis process [1-2]. Nowadays, phenolic resin is irreplaceable materials in many industries because of the high flame retardation, char yield after pyrolysis, chemical resistance, electrical insulation, thermal resistance, mechanical strength, adhesive property and dimensional stability [2-3].

However, the thermo oxidative resistance and inherent brittleness of the phenolic resin still can be improved. Therefore, the modification of phenolic resin by using organic or inorganic materials has been studied by many laboratories and researchers [1,4-5]. The modifications can improve the thermal resistance, mechanical strength, electric insulation property and absorbance of neutral radiation of the phenolic resins [4,6]. In order to enhance the physical properties of phenolic resin at most, we have modified the phenolic resins by using molybdate to form a metal modified Mo-PF with new Mo-O bonds. Furthermore, the effects of molybdate on the thermal and mechanical properties of phenolic resin have been investigated. The Mo-PF resin is also used as binders for diamond grinding tools in this study.

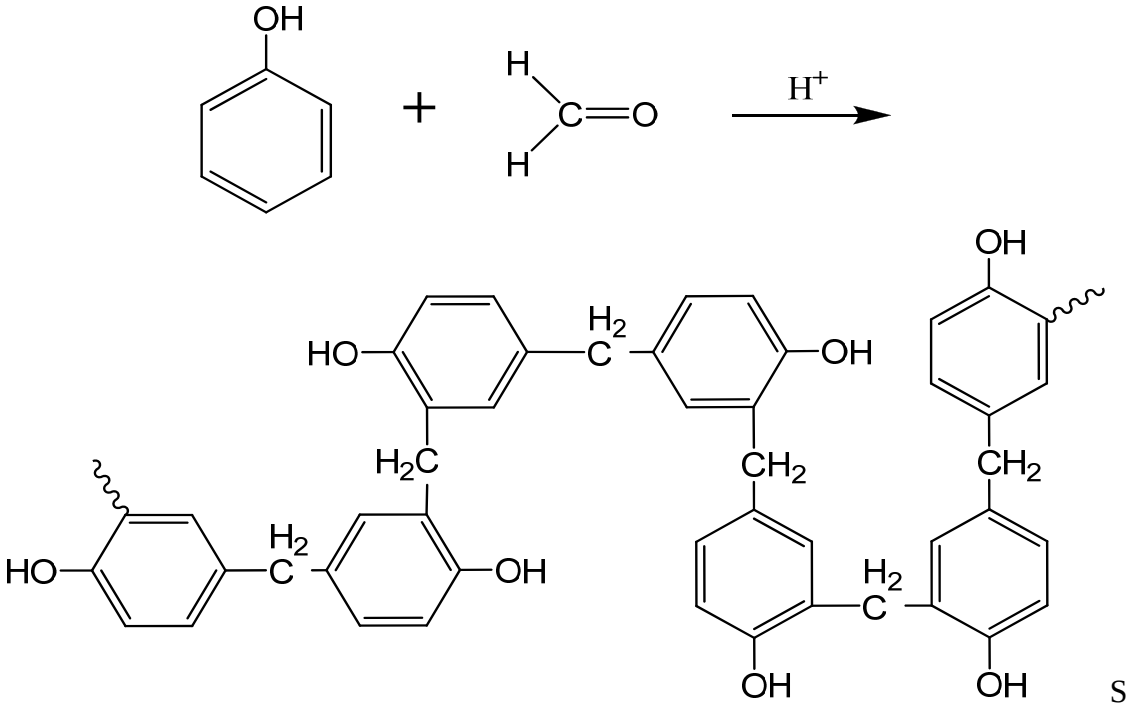
2. Experimental section

Phenol and formaldehyde (37%-formalin) were purchased from Nippon Shiyaku Chemical Co., Japan. Ammonium molybdate was purchased from Osaka Chemical Co., Japan. Oxalic acid were purchased from Shimakyu Chemical Co., Japan. Hexamethylenetetramine was supplied by Chang-chun Resins Co., Taiwan. Synthetic diamond grains (YK-J, 140-170) were purchased from Fine Abrasives Taiwan Co., LTD.The diamond grains (10g) and a solution of APTES(3-Aminopropyl triethoxysilane) (0.2g) in ethyl alcohol (60ml) were placed in a flask reactor. The reaction proceeded with stirring and reflux heating at 90°C for 4 hours. Then, APTES-modified diamond grains were obtained through evaporating ethyl alcohol at 90°C and drying at 150°C. The reaction scheme for the preparation of diamond grains is shown in Scheme 1.

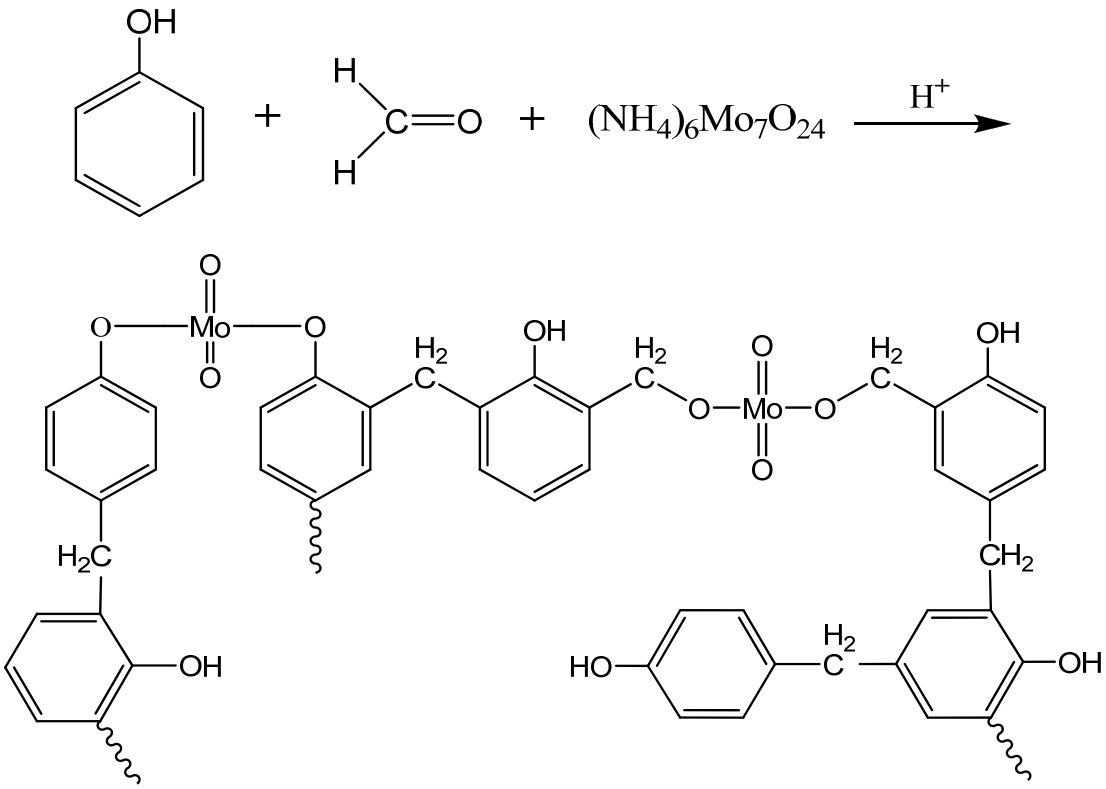


Scheme 1. Reaction scheme for the preparation of APTES-modified diamond grains

PF resin was synthesized in a 0.5L four-neck and round-bottom flask reactor equipped with a thermometer, a reflux condenser, and a stirrer. Certain amounts of phenol (19g), formalin (13ml) and oxalic acid (0.25g) were stirred and gradually heated to 110°C during 1 hour, and then kept heating for 4 hours at reflux in the flask reactor. At the end of the reaction, PF resin was washed with boiling water to remove the impurities and unreacted phenol. Subsequently, water was removed under vacuum at 120°C and the solid parts were further dried in a steel plate at 170°C for 2 hours. Finally, the PF resins were obtained. The synthesis route for PF resins is shown in Scheme 2. The synthesis procedure of Mo-PF resin is similar to that of PF. In the flask reactor, certain amounts of phenol, formalin and oxalic acid (0.38g) were stirred and gradually heated to 110°C during 1 hour. Then, Ammonium molybdate (1.8g) was added into the reactor and the mixture was stirred at 110°C for 1 hour. Thereafter, the mixture was heated at 150°C for 5 hours at reflux. The Mo-PF resin was obtained. The synthesis route for Mo-PF resins is shown in Scheme 3.



Scheme 2. Synthesis route for the PF resin



Scheme 3. Synthesis route for the Mo-PF resin

The PF or Mo-PF was mixed with hexamethylene tetramine (10 % based on PF moiety) and grinded to powdery state. The powdery mixture (1.7g) was charged into a tetragon metal mold (length 40 mm, width 10 mm, thickness 3 mm). Then, the mold was placed in a manual press machine, gradually heated to 190°C during 1 hour, and held at that temperature for 1 hour. After cooling the mold to room temperature, a stiff bulk of cured specimen was removed from the metal mold. The preparation of diamond grinding tools is similar to the above-mentioned process. The PF or Mo-PF (2.7g) was mixed with hexamethylenetetramine (0.27g) and grinded to powdery state. Then, the diamond grains (2.3g) were mixed with the mixture to form a homogeneous molding mixture. The molding mixture (0.66g) was charged into a tetragon metal mold (length 10mm, width 10mm, thickness 3mm). Then, a piece of diamond grinding tool was removed from the metal mold through the above mentioned thermo-forming procedure in metal mold.

3. Results and discussion

3.1. Chemical analysis

The FTIR spectra of PF and Mo-PF are shown in Figure.1. The peaks at 3328-3367 and 3014 cm^{-1} are respectively due to the O-H and C-H stretching vibrations of the phenolic ring. The peaks at 2919, 2845, 1479 and 1439 cm^{-1} are attributed to C-H_2 stretching vibrations [7]. The C=C stretching vibration of phenolic ring appears at 1611 and 1595 cm^{-1}. The phenyl-OH stretching vibration is at 1509 and 1230 cm^{-1}, and the in-plane bending vibration of phenolic O-H is at 1360-1363 cm^{-1} [7-8]. The peaks at 819 and 756 cm^{-1} correspond to the characteristic absorption-peak of respective para and ortho CH substitutions on the phenolic ring [8]. Therefore, the formation of PF can be confirmed by the FTIR spectra.

There are some differences between the spectra of Mo-PF and PF. In the spectrum of Mo-PF, the OH stretching and in-plane bending vibrations of phenolic ring are at 3367 and 1363 cm^{-1} respectively. On the other hand, in the spectrum of PF, the above-mentioned two peaks are at 3328 and 1360 cm^{-1} respectively. Moreover, since C=C groups in the phenolic rings were not consumed or produced during the synthesis of Mo-PF from PF, the stretching of these groups at 1611 cm^{-1} is adopted as an internal

reference peak to compare the relative intensities between the peaks of Mo-PF and PF spectra. In the spectrum of Mo-PF, the peak height ratios of the peaks at 3367 and 1363 cm^{-1} to the peak at 1611 cm^{-1} are designated as A_{3367}/A_{1611} and A_{1365}/A_{1611} respectively and are 1.588 and 0.776 correspondingly. On the other hand, in the spectrum of PF, the peak height ratios of A_{3328}/A_{1611} and A_{1360}/A_{1611} are 1.747 and 0.867 respectively. So, relative to the internal reference peak of C=C stretching, both peaks of the OH stretching and in-plane bending vibrations of phenolic ring of the Mo-PF spectrum are smaller than those of the PF spectrum. In addition, the phenyl-OH stretching vibration peaks of Mo-PF at 1509 and 1228 cm^{-1} relative to the internal reference peak of C=C stretching (A_{1509}/A_{1611}= 1.494 and A_{1228}/A_{1611}=1.447) are smaller than those (A_{1509}/A_{1611}= 1.867 and A_{1230}/A_{1611}= 1.689) of PF. These spectrum differences indicate the consuming of -OH groups during the synthesis of Mo-PF from PF. Moreover, the two peaks at 1363 and 938 cm^{-1} associated with the asymmetric vibration of Mo-O bonds [9-11] and the bending vibrations of Mo-O bonds of Mo-PF respectively, are not observed in the spectrum of PF. Therefore, differences between the two spectra of Mo-PF and PF confirm the formation of Mo-O bonds in Mo-PF due to the reaction between PF and molybdate. The formation of Mo-O bonds in Mo-PF resins results in the consumption of -OH groups in PF.

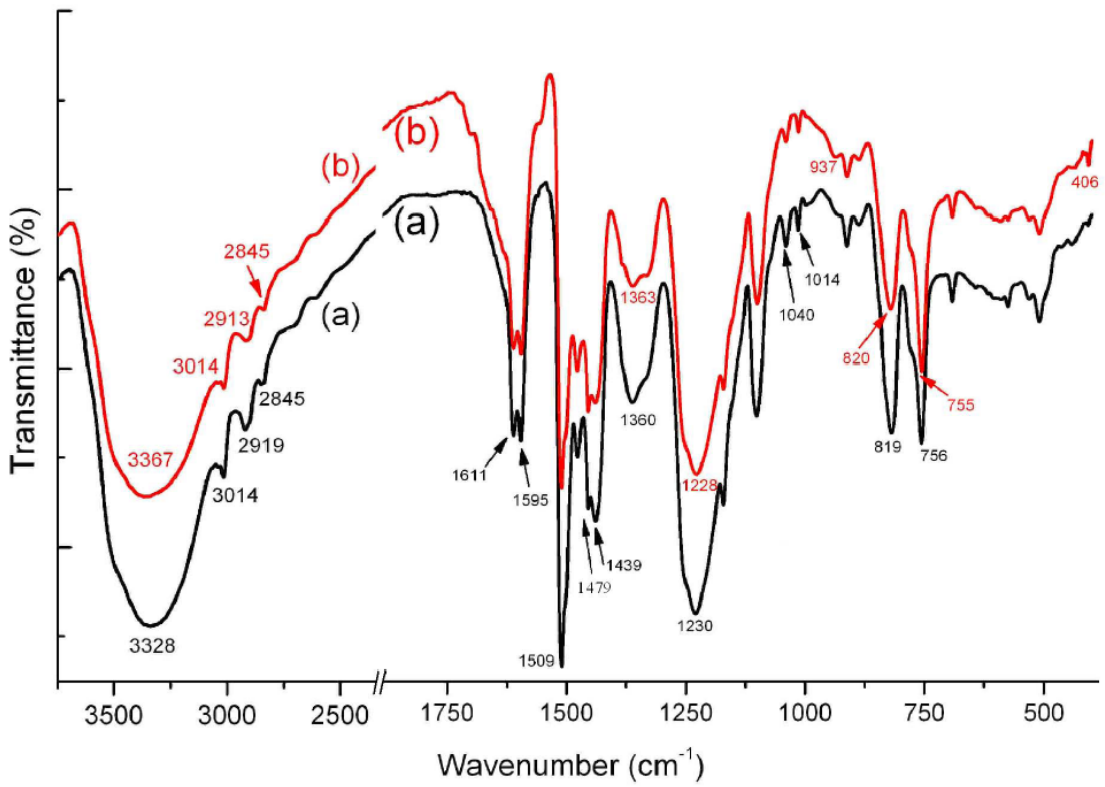


Figure 1. FTIR spectra of PF (a) and Mo-PF (b)

3.2. Thermal properties

The PF and Mo-PF can respectively undergo cross-linking reaction with hexamine. The cross-linking temperatures of PF/hexamine and Mo-PF/hexamine mixtures were separately evaluated by DSC measurement and are shown in Figure 2 and Table 1 as 145 and 148°C respectively. The temperature ranges of cross-linking reaction for PF/hexamine and Mo-PF/hexamine mixtures are 123-171 and 126-175 ^{o}C respectively. These results indicate that the cross-linking temperature of PF is increased by treating with molybdate. When PF was reacted with ammonium molybdate, the resulting Mo-O bonds caused an increase of cross-linking density in Mo-PF, which restricted the thermal motion of Mo-PF polymer chains. The hindered Mo-PF polymer chains were more difficult to react with hexamethylenetetramine and resulted in a higher cross-linking temperature.

DMA is used to evaluate the thermo-mechanical properties of PF and Mo-PF which were all pre-cured with 10wt% hexamine at 200°C. The results are shown in

Figure. 3a-b and Table 1. Each tan δ curve of the two films has one peak centered at about 162 and 237 ^{o}C respectively**.** These peaks are the glass transition temperatures of these films, because their storage moduli drop by 1-2 orders during the transition. For cured PF resin, the glass transition begins at about 120°C and ends at around 200°C. The polymer chains of cured PF start to undergo thermal motion and induce glass transition at a wide range of temperature. This indicates a complicated structure or morphology of the cured PF. For cured Mo-PF resin, the temperature span of glass transition is similar to that of cured PF. However, the glass transition of cured Mo-PF is less obvious and centers at higher temperature than that of cured PF as shown in their tan δ curves. This is due to the higher cross-linking density of cured Mo-PF. There are two kinds of cross-linking networks in the cured Mo-PF. One is the cross-linking caused by hexamethylenetetramine as in cured PF. The other is the presence of Mo-O bonds in the Mo-PF as shown in the FTIR spectra. Therefore, the glass transition temperature of PF resin can be more raised by treating with molybdate.

Thermal resistance of cured PF and Mo-PF are shown in Figure 4 and Table 1. The decomposition temperatures at 10% weight losses are designated as Td-10 respectively. The Td-10s of PF and Mo-PF are 439 and 503°C respectively. The Td-10 of Mo-PF is higher than that of PF. Moreover, the residual masses at 800 ^{o}C of PF and Mo-PF are 59.0 and 72.2% respectively. The increase trend of residual masses for these two specimens is also similar to that of Td-10s. Thus, thermal resistance of PF can be improved by treating with molybdate. The thermal resistance of a compound is related to its composition, structure and cross-linking density. Treating PF with ammonium molybdate can form Mo-O bonds and cause an increase of cross-linking density which promotes the thermal resistance simultaneously.

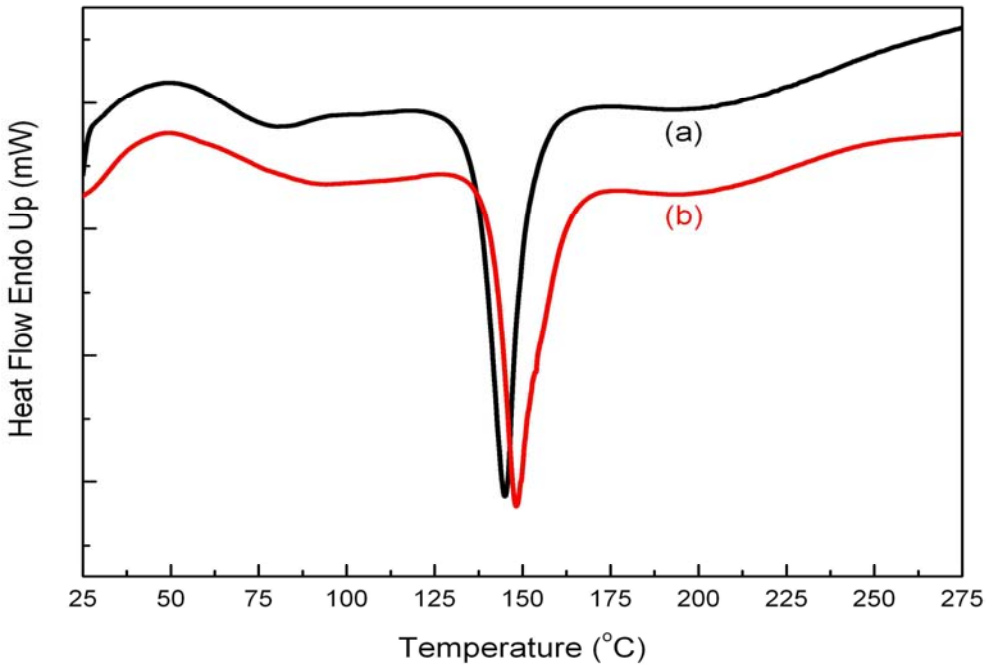


Figure 2. DSC curves of PF (a) and Mo-PF (b)

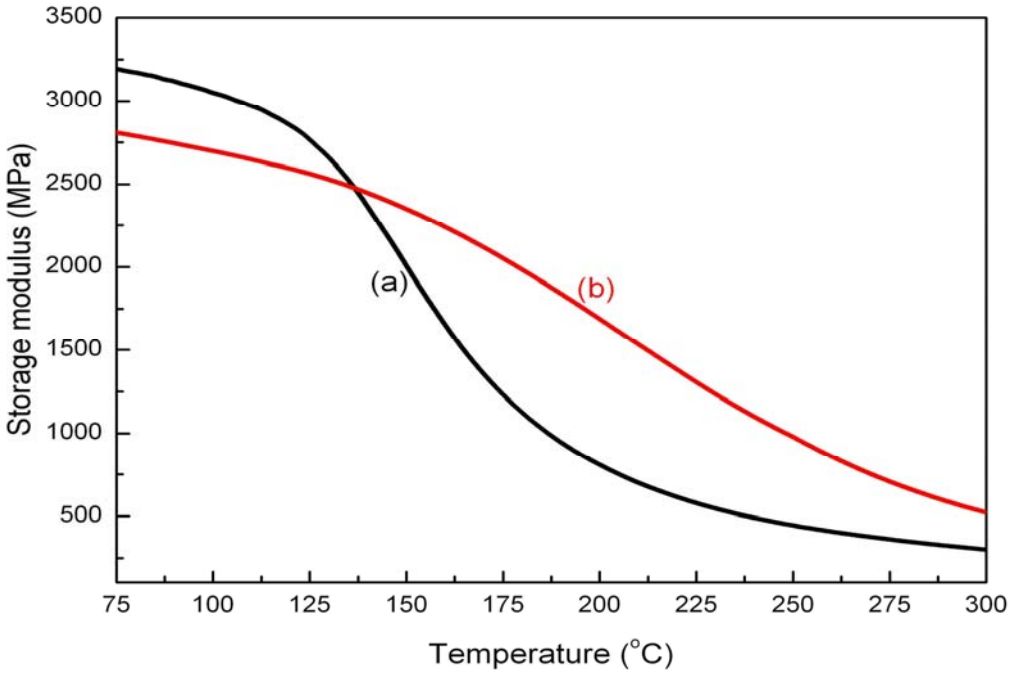


Figure 3a. Storage moduli of PF(a) and Mo-PF(b) at various temperatures

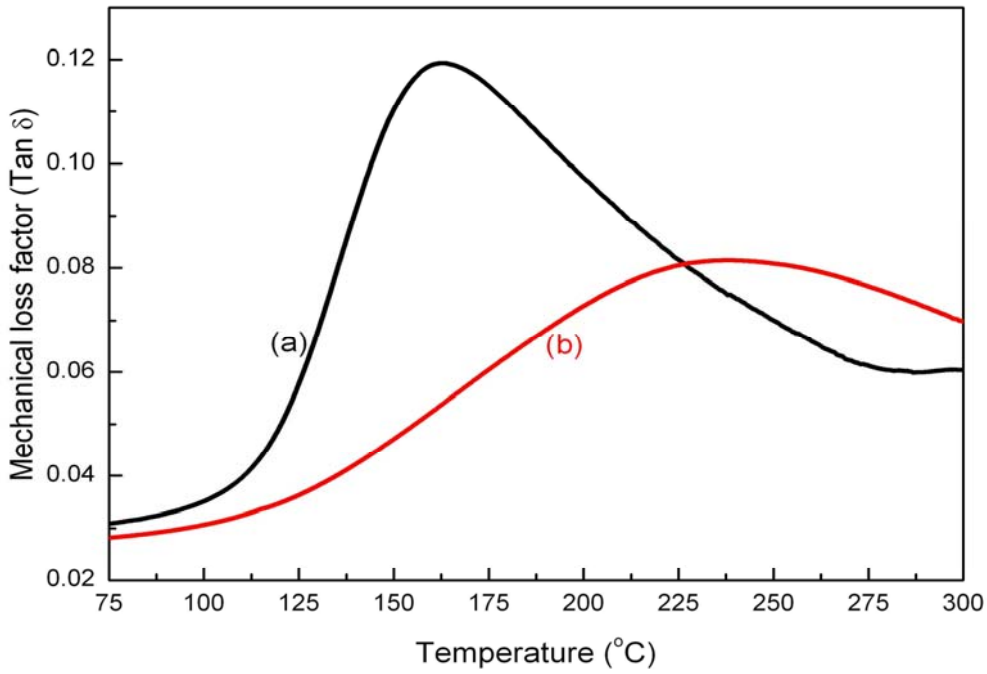


Figure 3b. Mechanical loss factor (tan δ) of PF(a) and Mo-PF(b) at various temperatures.

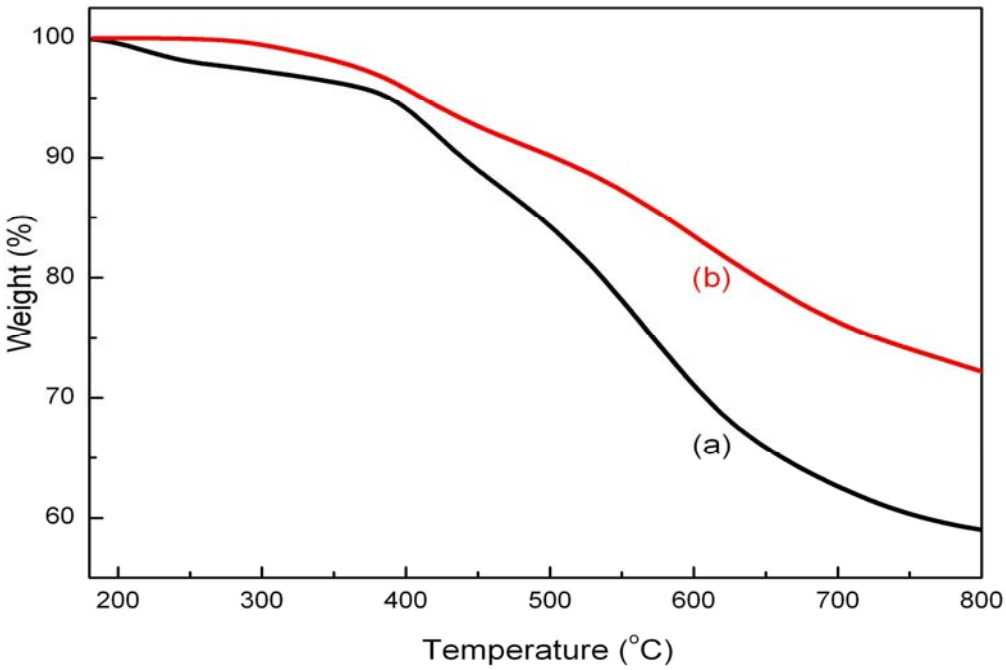


Figure 4. TGA curves of PF (a) and Mo-PF (b)

Table 1. The thermal properties of PF and Mo-PF

Specimens	PF	Mo-PF
Cross-linking temperature peak (^{o}C)	145	148
Cross-linking temperature range (^{o}C)	123-171	126-175
Glass transition temperatures (^{o}C)	162	237
Td-5 (^{o}C)	381	411
Td-10 (^{o}C)	439	503
Residual mass at 800 ^{o}C (%)	59.0	72.2

3.3. SEM observation of the fracture surface

Scanning electron micrographs of the bending fractural surfaces of the cured PF and Mo-PF are shown in Figure 5a-b. The PF shows a smooth and ripples-full morphology that somewhat implies the brittle property of PF. The Mo-PF shows a dendritic morphology which is rougher than that of PF. This implies that Mo-PF is tougher than PF.

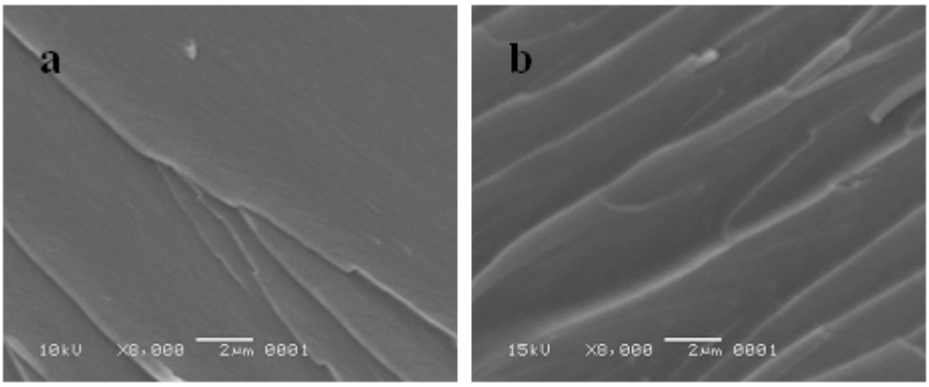


Figure 5. SEM images of PF (a) and Mo-PF (b)

3.4. Mechanical strength

The mechanical properties of cured PF and Mo-PF were examined by measuring their flexural strength, flexural modulus and hardness. The results are listed in Table 2.

Flexural strength is the minimum required stress applied on the surface to break a specimen. The flexural strength of PF and Mo-PF are 53.7 and 76.5 MPa respectively. The flexural strength of Mo-PF is higher than that of PF. Thus, the flexural strength of PF resin can be enhanced significantly by treating with molybdenum. This behavior can be explained by the structural change. The reaction between PF and molybdate formed many Mo-O linkages and subsequently enhanced the flexural strength of Mo-PF resin. The flexural moduli of PF and Mo-PF are 4.4 and 4.9GPa respectively and are shown in Table 2. The variation sequence and its reason for the flexural moduli resemble those for the flexural strength. As for the hardness measurement, the results for PF and Mo-PF are 74 and 87 respectively as shown in Table 2. The hardness of Mo-PF is higher than that of PF. The variation sequence and its reason for the hardness also resemble those for the flexural strength.

Table 2. The mechanical strength of PF and Mo-PF

Specimens	PF	Mo-PF
Flexural strength (MPa)	53.7	76.5
Flexural modulus (GPa)	4.4	4.9
Hardness (Shore D)	74	87

3.5. Performance as a binder for diamond grinding tools

In order to compare Mo-PF with PF in the performance as a binder, diamond grinding tools were prepared by diamond grains with Mo-PF and PF separately. The resin-bound diamond grinding tools which are shown in Figure 6a-b were used to grind the Al_2O_3 fine ceramics. The surface morphology of the Tool-A (with PF binder) and Tool-B (with Mo-PF binder) after grinding experiments is shown in Figure 6a-d. As shown in Figure.7a-b, Tool-A exhibits significant damage and rupture after grinding experiments. There are many exposed diamond grains and voids originated from the drop of diamond grains on the grinding surface of Tool-A. There is much heat release and mechanical friction in the interface between grinding tool and ceramics during

grinding experiments. The PF resin matrix was consumed and damaged gradually by this heat release and mechanical friction. Then diamond grains exposed and dropped off easily due to the low binding strength of PF. The exposed PF was worn and leveled off again. Tool-B also shows the damage and rupture morphology as presented in Figure 7c-d. The extent of damage and rupture for Tool-B is less than that for Tool-A. The Mo-PF resin matrix in Tool-B has higher thermal resistance, mechanical property and binding strength than PF resin matrix in Tool-A. So the diamond grains are more strongly bound by the resin matrix and harder to drop off in Tool-B than those in Tool-A. Moreover, the Mo-PF resin matrix in Tool-B is more abrasion resistant and harder to be leveled off than the PF resin matrix in Tool-A. So Tool-B has a rougher morphology than Tool-A after grinding experiments.

In addition, the photographs of Ceramics-A and Ceramics-B work-pieces that had been grinded by Tool-A and Tool-B respectively, are shown in Figure 8a-b. The grinding surface on Ceramics-B shows smoother than that on Ceramics-A. This indicates that Tool-B has better grinding quality than Tool-A. The reason for the better grinding quality of Tool-B is due to the higher thermal resistance, mechanical property and binding strength of Mo-PF resin matrix therein as compared to the PF in Tool-A. In Tool-B, the Mo-PF is harder to be worn away and the bound diamond grains are harder to drop off also. So Mo-PF is a better binding resin than PF and Tool-B has better grinding quality than Tool-A.

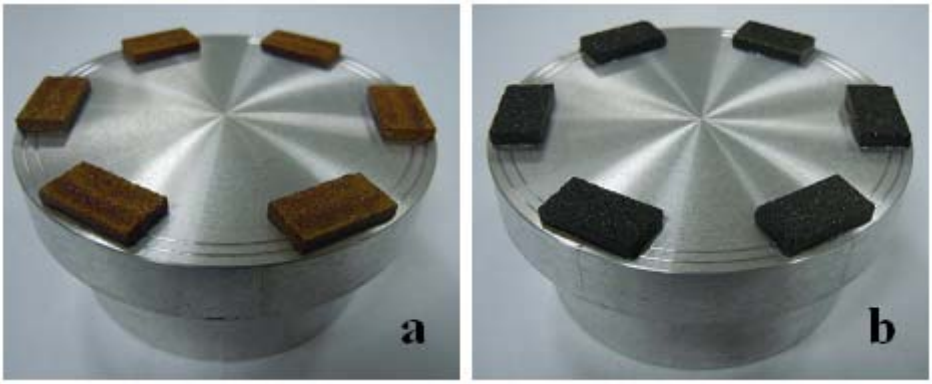


Figure 6. Tool-A(a) and Tool-B(b) of Resin bonded diamond grinding tools

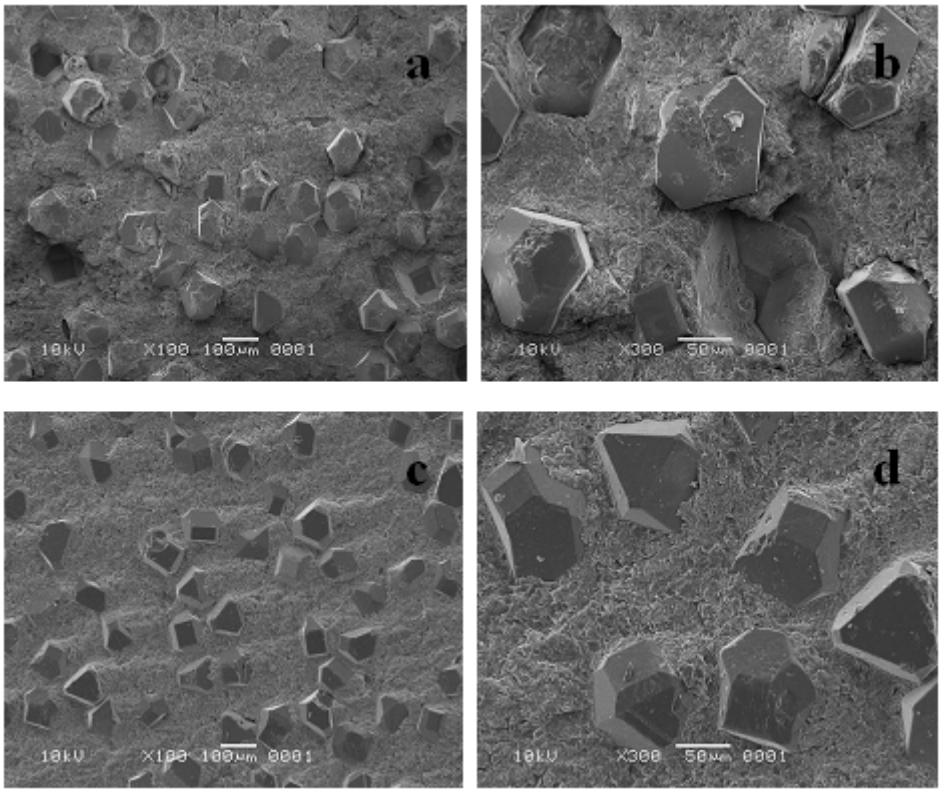


Figure 7. SEM images of grinding tool-A (a, b) and grinding tool-B (c, d) after grinding experiments

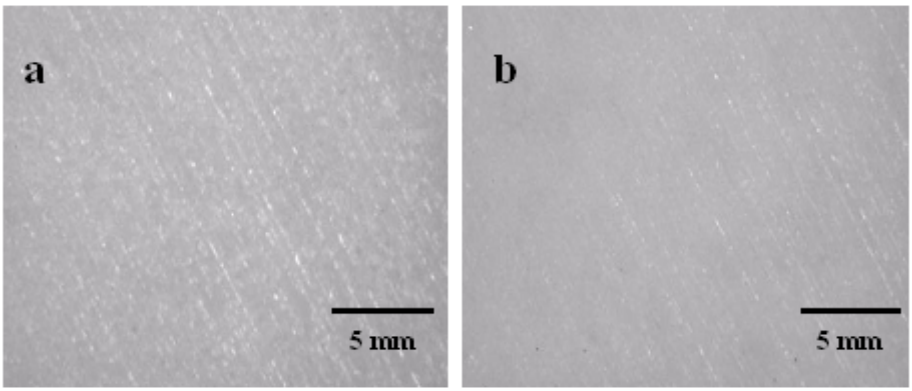


Figure 8. Ceramics-A(a) and Ceramics-B(b) work-piece after grinding experiments

4. Conclusion

Novolac molybdenum modified phenolic resins (Mo-PF) were obtained by firstly reacting phenolic resin (PF) with molybdate. The thermal resistance, flexural strength and hardness of Mo-PF are enhanced significantly. The glass transition temperature, thermal decomposition temperature at 10% weight loss and flexural strength of Mo-PF are 237 ^{o}C, 503 ^{o}C and 76.5 MPa respectively, which are 75 ^{o}C, 64 ^{o}C and 22.8MPa higher than the corresponding values of PF. Mo-PF have such a superior performance because molybdate reacted with phenolic hydroxyl groups of PF resin to form cross-linked Mo-O bonds. In addition, Mo-PF is a better binding resin than PF as evaluated by the grinding experiments which were performed with their corresponding diamond grinding tools. Therefore, Mo-PF can also be used as a binder of grinding or cutting tools with high thermal and mechanical properties.

Reference

[1] Shafizadeh JE, Guionnet S, Tillman MS, Seferis JC. Synthesis and Characterization of Phenolic Resole Resins for Composite, Applications Journal of Applied Polymer Science, 1999; 73: 505-514.

[2] M. Lopez, M. Blanco, A. Vazquez, N. Gabilondo, A. Arbelaiz, J.M. Echeverria, I. Mondragon, Curing characteristics of resol-layered silicate nanocomposites, Thermochimica Acta 2008; 467:73-79.

[3] Liu L, Ye Z, Effects of modified multi-walled carbon nanotubes on the curing behavior and thermal stability of boron phenolic resin, Polymer Degradation and Stability 2009; 94: 1972-1978.

[4] Abdalla M, Ludwick A, Mitchell T. Boron-modified phenolic resins for high performance applications. Polymer 2003; 44(24): 7353-7359.

[5] Zhang W, Liu C, Ying Y, Dong W. The preparation and characterization of boron-containing phenolic fibers. Materials Chemistry and Physics, 2010; 121: 89-94.

[6] Gao J, Xia L, Liu Y. Structure of a boron-containing bisphenol-F formaldehyde resin and kinetics of its thermal degradation. Polymer Degradation and Stability 2004;

83: 71-77.

[7] Poljansek I, Krajnc M. Characterization of Phenol-Formaldehyde Prepolymer Resins by In Line FT-IR Spectroscopy, Acta Chimica Slovenica, 2005; 52: 238-244.

[8] Kristkova M, Filip P, Weiss Z, Peter R. Influence of metals on the phenol-formaldehyde resin degradation in friction composites. Polymer Degradation and Stability 2004; 84: 49-60.

[9] Qiang Min, Zhang Shuan-gqing, Lin Huishan, et al, Analysis and application of thermosetting molybdic acid-modified phenolic resin, NAIHUO CAILIAO, 2005, 39(2): 119-122.

[10] Nirmalya Ballav, Molybdenum blues based conducting nanocomposites of polypyrrole, poly*N*-vinylcarbazole and of their binary combination, Materials Science and Engineering B 2005; 123: 115-122.

[11] Li-Ngee Ho, Tasuku Ikegawa, Hiroyasu Nishiguchi, Synthesis and characterization of molybdenum incorporated mesoporous aluminophosphate, Applied Surface Science 2006; 252: 6260-6268.