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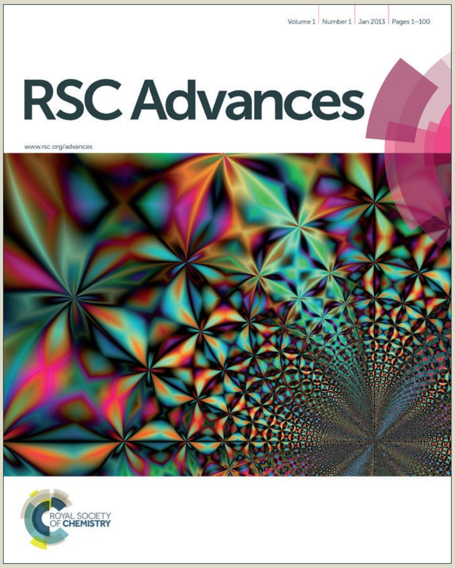

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Preparation of self-promoted hydroxy-containing phthalonitrile resins by in situ reaction

Jianbo Wang,[a] Jianghuai Hu,[a] Ke Zeng,*[a] Gang Yang*[a]

ABSTRACT

In situ reaction of hydroxy to phthalonitrile system was carried out by a simple nucleophilic displacement of a nitro-substituent from 4-nitrophthalonitrile in a dipolar aprotic solvent, one-pot reaction. The hydroxy-containing phthalonitrile system (blends-HPBD) was prepared by mixing 4-hydroxyphenoxy phthalonitrile(HPPH) and 1,3-bis(3,4-dicyanophenoxy)benzene(BDB) followed by heating. The curing behaviors were studied by differential scanning calorimetry and dynamic rheological analysis, the results indicated that the HPBD exhibit large processing windows(~75°C) and low complex viscosity (0.1–1Pa·s) at moderate temperature, respectively. Fourier transform infrared spectroscopy (FT-IR) showed that polytriazine, polyindoline and phthalocyanine structures have been formed during polymerization, and the introduction of HPPH facilitated curing reaction. Additionally, the prepared HPBD polymers showed outstanding thermal stability, high modulus and high glass transition temperature (Tg). After 300°C cured, the Tg of HPBD resin was up to 410°C. Postcuring effects on thermal and dynamic mechanical properties were evaluated using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

1. Introduction

Phthalonitrile (PN)-based polymers[1–20] have been emerged as ideal materials for the last 30 years. They are easily processed into various shaped structures by cost effective manufacturing techniques and offer a unique combination of physical properties for advanced composite. These properties include high thermal and oxidative stability, low water absorption, and the absence of a Tg before the thermal decomposition temperatures. Many potential uses including adhesive,[1] electronic,[2–4] and structural applications[5–7] can be envisioned for a polymeric material such as a PN resin compared to metals due to its significant strength-to-weight[8] and performance advantages.

The polymerization of the neat resins is extremely sluggish and requires several days at elevated temperatures before a vitrified product is obtained.[9] The polymerization reaction of phthalonitrile can be initiated with many different types of curing additives such as organic amines,[9] strong organic acids,[10] organic acid/amine salts,[11] metallic salts,[12] and metals[13]. During the past decades, systematic studies have been conducted at Naval Research Laboratory (NRL) on phthalonitrile resins in terms of cure behavior, processabilities and effects of various linkages between the terminal phthalonitrile units on the properties of the cured resins.[14-22] They mainly focused on commercially available aromatic diamine curing additives such as 1,3-Bis(3-aminophenoxy)benzene (m-APB). Formulation of the resins at the NRL is achieved typically by physically mixing a bisphthalonitrile monomer and a curing additive below the melting temperatures (Tms) of the bisphthalonitrile monomer or adding to the melting monomer under vigorous stirring.[23] Until now, phthalonitrile

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polymers with excellent combination of properties, good processability, and phthalonitrile-based composites have been successfully developed by NRL.[5,6,24] However volatilization of diamine[23] slowdown downs the curing especially at high temperature. To overcome this problem, we need stable and less reactive curing reagents to get the anticipated product. Thus, try to find curing agents that did not volatilize at elevated cure reaction temperatures and that were less reactive relative to m-APB was a key to promote the processability of phthalonitrile-based composites.[23]

On the other hand, there are still some problems for using phthalonitrile materials. The high temperature of melting transition is a common shortcoming for phthalonitrile monomers(usually >200°C).[14,16-18] For example, the melting point of 4,4-bis(3,4-dicyanophenoxy) biphenyl phthalonitrile monomer is 230°C,[23] and the processing window (temperature between the melting point and the polymerization temperature) is only 20°C when curing with amine catalyzers, which brings difficulties for processing. More importantly, the processing mode of the phthalonitrile resins described previously, is mainly based on bisphthalonitrile monomers/curing additives composition systems referred to as binary composition systems. In these systems, to ensure an uniform cure rate within phthalonitrile resins, evenly molecular dispersion of a trace percent of curing additives into bisphthalonitrile monomers is required and can be achieved merely under extreme conditions (e.g. vigorous stirring).[24] Therefore, the development of a self-catalyzed phthalonitrile monomer with low melting temperature would be interesting in the view of both science and industrial applications.

In our laboratory, the previous investigations have demonstrated that amino or hydroxy-containing phthalonitrile derivatives (APN or HPN) showed a self-promoted cure behavior even in the absence of curing additives which are required for conventional binary composition systems.[25-26] Therefore, curing of the phthalonitrile derivatives containing amino or hydroxy groups offers a new route to the fabrication of phthalonitrile-based polymers or resins possessing excellent mechanical and thermal properties. Liu et al.[27] synthesized phthalonitrile oligomer containing biphenyl ethernitrile cured with 4-aminophenoxy phthalonitrile. Zhou et al.[28-29] prepared amino-containing (in ortho, meta, and para positions) self-catalyzed phthalonitrile resins.

In this paper, self-promoted hydroxy-containing phthalonitrile systems were prepared by in situ reaction. And hydroxy was introduced into the self-promoted phthalonitrile-based system by this way. Therefore, the blending problem of phthalonitrile monomers/curing additives under extreme conditions (e.g. vigorous stirring) was solved. Meanwhile, the phthalonitrile system, which was, the blends of 1,3-bis(3,4-dicyanophenoxy) benzene(BDB) and self-promoted phthalonitrile, 4-hydroxyphenoxy phthalonitrile(HPPH), exhibited good processability, thermal and dynamic mechanical properties. In addition, the polymerization mechanism and postcuring effects were also investigated.

2. Experimental

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2.1 materials

Resorcinol(99.5%),Dimethylsulfoxide(DMSO,AR) was supplied by Chengdu Kelong Chemical Reagent Co., Ltd, Chengdu,China.4-nitrophthalonitrile (99%) was purchased from Hong Kong's Ming Tai Prosperity Chemical Co., Ltd. Potassium carbonate(99.0%) was obtained from Chengdu Kelong Chemical Reagent Co., Ltd. All the solvents were used without further purification.

2.2. Synthesis of self-promoted hydroxy-containing phthalonitrile systems

To a 500 mL, three-necked flask was added resorcinol, 4-nitrophthalonitrile and DMSO. During the course of the reaction, the pulverized potassium carbonate was added in three portions. While stirring, the resulting mixture was heated at 40°C for 10h under an inert atmosphere. After cooling, the product mixture was poured into 2400ml water. The off-white solid was collected by suction filtration and washed with water until the filtrate was neutral, and dried in vacuum oven(-0.09MPa) at 80°C for 16h.Using this procedure, different compositions of HPPH and BDB—HPBD-18,HPBD-28-were synthesized by controlling the feed ratio. The detailed synthesis data are listed in Table1.

Table 1 the specific synthetic feed parameters and yield

	4-nitrophthalonitrile	resorcinol	DMSO	K_2CO_3	Yield
HPBD-18	58.87g	22.02g	330ml	83.00g	87.54%
HPBD-28	51.95g	22.02g	300ml	83.00g	87.64%

HPBD-24 was obtained through HPBD-18 and HPBD-28 blended with equal weight ratio.

2.3 Preparation of polymers

The HPBD were melted in a 100 mL reaction kettle equipped with a stirrer and degassed for 10min under the vacuum conditions(-0.09MPa) at 180℃.Poured the prepolymer into a mold with dimensions of 35 mm × 15 mm × 8 mm and then cured in a nitrogen-circulating oven with curing procedure of 180°C for 2 h, 200°C for 5h, 250°C for 10h, and 300°C for 6h. Postcured samples were prepared in a muffle furnace at elevated temperatures: 325°C&5h; 350°C&5h; and 375°C&5h. The cured polymers were machined into rectangular specimens (30 mm × 12.5 mm ×3.2 mm) for DMA experiments.

2.4. Characterizations

FT-IR spectra of HPBD and phthalonitrile resins were recorded on a Nicolet- 460 FT-IR spectrometer in KBr pellets between 4000 cm^{-1}and 400 cm^{-1} in air.^{1}H NMR spectra were obtained using a Bruker AV II300 nuclear magnetic resonance(NMR) spectrometer at a proton frequency of 300 MHz and the corresponding proton frequency using DMSO-d_6 as solvent. Differential scanning calorimetric (DSC) study was performed on TA Instruments Q200 DSC from 50°C to 300°C at a heating rate of 10°C/min with nitrogen flow rate of 50 mL/min. Rheological behaviors of the blends were investigated using TA Instruments Rheomerter AR-2000 with a frequency of 1 Hz and a heating rate of 3°C /min^{-1}.Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen and air atmosphere respectively with flow rate of 60 mL/min. Dynamic mechanical analysis (DMA) was recorded using TA Instruments Q800

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dynamic mechanical analyzer at a frequency of 1 Hz from 50°C to 450°C with a heating rate of 5°C/min. The mechanical properties of the HPBD resins were investigated by JEOL JSM-7500F field-emission scanning electron microscope (SEM). The specimen was coated with Au prior to observation.

3. Results and discussion

3.1. Preparation

HPBD system with varying contents of HPPH ingredient were synthesized by a nucleophilic displacement of a labile nitrosubstituent from 4-nitrophthalonitrile as illustrated in Scheme1. The reaction took place in DMSO solution in the presence of alkaline substance K_2CO_3 as catalyst. ^{1}H NMR of HPBD-18 was given in Fig.1 proving the success of synthesis of HPBD and the content of HPPH in HPBD system.The content of HPPH was calculated by using the ^{1}HNMR integral area of HPBD.

$$W_{HPPH}(mol\%) = \frac{S_e}{S_e + S_k/2} \qquad (I)$$

According to formula (I), the content of HPPH was calculated(S_e and S_k represent integral area e and k in ^{1}HNMR, respectively). The detailed data were listed inTable2.

Scheme 1 General synthetic scheme for HPBD

Figure.1 ^{1}HNMR of HPBD-18

Table 2 the molar ratio of HPPH in HPBD system

	S_e	$S_k/2$	HPPH content (mol%)
HPBD-18	0.11	0.5	18
HPBD-24	0.16	0.5	24
HPBD-28	0.20	0.5	28

3.2. Curing Behaviors of HPBD

Curing behavior of HPBD system were studied by DSC. As is shown in Fig.2, all HPBD systems showed a larger processing window, and the processing window (temperature between the melting point and the polymerization temperature) of HPBD-18 blends was up to 75°C. Obviously, larger processing window is favorable to processing phthalonitrile monomers into void-free resins. The DSC results also indicated that BDB can be cured into polymers with HPPH.[30] In other words, HPBD system can self-promoted through heat treatment. Compared to the curing agent of aromatic amines,[23-24,36] HPPH exhibited a slower reactivity. However, an advantage of the slower reactivity is that a larger processing window is available.[24] Moreover, an extremely sluggish curing behavior is favorable in fabricating thick composite components by resin infusion methods (RIM) or resin transfer molding (RTM).[30]

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The rheological behaviors play an important part in determining the processabilitiy of materials.[31] Therefore, the variation of the complex viscosity of the HPBD was determined as a function of temperature from 175°C to 325°C. The results, presented in Fig.3, revealed that the complex viscosity of the blends were affected by the HPPH content. The HPBD-28, HPBD-24 and HPBD-18 exhibit an abrupt complex viscosity increase at 240°C, 260°C, and 280°C, respectively. The data showed that the higher the HPPH content, the faster the viscosity increase. This result was expected since the blends richer in HPPH have a greater tendency to react or cure at a faster rate. A minimum melt viscosity of around 0.1Pa·s was observed for all the blends at temperatures above 175°C. The low melt viscosity of the blends at the higher temperatures is evidence of their good melt stability. Based on the above results, the HPBD display good processabilitiy for low complex viscosity at moderate temperature.

Figure.2 DSC thermograms of HPBD system.

Figure.3 Complex viscosity (η*) as a function of temperature for the various HPBD systems

We further investigated the cure behavior by analysis of the FTIR spectra of HPBD resins. Figure4a showed the FTIR spectra of HPBD-18 resin obtained after being heated at 200℃ for 5h. It was obvious that the characteristic absorption bands at 2229 cm^{-1} (Fig.4a) was evidently weakened. Meanwhile, in Fig.4b, the peaks at around 1009cm^{-1} and 1521 cm^{-1} were belonged to the characteristic absorptions of the NH stretching and bending vibration in phthalocyanine ring[32] and stretching vibration in triazine ring,[33] respectively. Moreover, the peak at around 1720cm^{-1} was attributed to the characteristic absorption of isoindole ring.[34] Additionally, there was still a weak absorption peak attributed to the -CN groups (Fig.4b) at around 2229cm^{-1}, and it became weaker gradually with increase in HPPH content. Thus, it can be concluded that curing reaction was happened between BDB and HPPH. However, the nitrile groups were not participated in the curing reaction completely, which can be ascribed to the formation of triazine ring and phthalocyanine during polymerization. Only half of the nitrile groups contributed to the triazine ring structure formation because of the high steric hindrance. Based on these results, it could be concluded that HPPH could facilitates polymerization of phthalonitrile systems and the possible polymerization mechanism of HPBD is shown in Scheme 2.

Figure.4 FT-IR spectra of HPBD resins, (a)HPBD resin cured at 200℃, (b)HPBD resins.

Scheme2 Possible reaction mechanism of HPBD system.

3.3. Thermal stability

The thermal and thermo-oxidative properties of HPBD resins cured with HPPH were evaluated by TGA as shown in Fig.5, and the results are summarized in Table3. $Td_{5\%}$

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and $Td_{10\%}$ are defined, respectively, as the temperature at which 5% and 10% weight loss occurs. Whether in a nitrogen atmosphere or in an air atmosphere, as seen from Table3, 5wt% and 10wt% weight loss temperature decrease obviously with the increase ratios of HPPH. These data showed the dependence of the thermal and thermo-oxidative stability on the HPPH content in the blends. The decrease in blend stability with an increase in the HPPH content was attributed to the weak bonds(-OH) of HPPH, it could be destroyed in the heating process. With the HPPH increasing, the weak bonds(-OH) became more intense, leading to the possible degradation of HPBD resins. Basically, the various HPBD resins all possessed excellent thermostability with the temperatures corresponding to the weight loss of 5wt%, all exceeding 475˚C, and char yields are all above 72% when heated to 800˚C in a nitrogen atmosphere. These results should also be attributed to the crosslinking reaction between the BDB and HPPH. The TGA plots of HPBD resins involved several stages which imply oxidation degradation of different molecular segments in air atmosphere.[35] Small solid samples of HPBD resins heated in air showed weight retention of 95% at around 480˚C for all samples with catastrophic decomposition occurring between 500˚C and 800 ˚C. Based on the above results, it could be concluded that the HPBD polymers cured with HPPH show outstanding thermal stabilities and the thermal decomposition temperature was reduced regularly with the increase of HPPH content.

Figure.5 TGA curves of HPBD resins cured with different ratios of HPPH in nitrogen and air atmosphere

Table 3 Thermal properties of HPBD reins cured with HPPH

	HPBD	$Td_{5\%}$（˚C）	$Td_{10\%}$（˚C）	Char yield (%) at 800˚C
In N_2	HPBD-18	493.0	530.0	74.54
	HPBD-24	477.0	525.0	72.17
	HPBD-28	475.0	524.5	72.00
In air	HPBD-18	489.0	533.0	-
	HPBD-24	485.5	535.0	-
	HPBD-28	481.5	527.0	-

3.4. Dynamic mechanical properties

The dynamic mechanical properties of the cured HPBD polymers were evaluated to ascertain the modulus and the loss factor (Tg). Plots of the storage modulus (G') and damping factor (tan δ) were presented in Figure.6 (a) and (b), respectively. After curing to a maximum temperature of 300˚C, as seen from Fig.6a, all the HPBD polymers exhibited a high storage modulus at 50˚C, which decreased gradually along with increasing temperature. The high modulus should be ascribed to the aromatic and crosslinked microstructure. The decrease of modulus with increasing temperature was due to stress relaxation of the polymer network. Moreover, it could be shown that the storage modulus of HPBD-24 resin was up to 3.1GPa at 50˚C ,which is superior to the modulus of 5wt% ODA cured BDB resin (2.9GPa),[36] amino-containing self-catalyzed

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phthalonitrile resins (4-aminophenoxy-phthalonitrile, ~1.7GPa).[37]

The maximum of tanδ curve represents Tg which is a particular important parameter for polymer materials, because it generally determines the upper limit of application temperature. The tanδ versus temperature plots for HPPH cured resins were presented in Fig.6b. As seen, Tg increased gradually with the content of HPPH increased from 18mol% to 28mol%. It could be seen that the Tg of HPBD-28 resin was up to 410℃ which was superior to the Tg of 5wt% ODA cured BDB resin (320°C) and 5wt% and 10wt% APPH cured BDB resins (320°C and347°C, respectively)[35]. For the state-of-the-art high temperature resin, PMR-15, the maximum postcure temperature is 316°C, and the corresponding Tg is 340°C. Clearly, the low softening point of PMR-15 resin would restrict its usage in structural applications that require stability at temperatures in excess of 340°C.It has been reported that the shift of the maxima of the modulus as well as tanδ to higher temperatures can also be explained by a higher degree of crosslinking of polymers.[38-39] The greater Tg of HPBD polymers should be also attributed to the higher crosslinking structure when BDB cured with HPPH, and the more of HPPH leads to higher Tg.

Figure.6 Dynamic mechanical properties of HPBD resins, (a) storage modulus versus temperature and (b) tanδ versus temperature

3.5. Postcuring effects

As mentioned above, the samples (HBPD resin cured with HPPH) were prepared with the curing procedure at 180°C for 2h, 200°C for 5h, 250°C for 10h, 300°C for 6h. In order to explore postcuring effect especially different postcuring temperatures on properties, the samples were then gradually postcured at 325°C for 5h, 350°C for 5h, 375°C for 5h. After postcuring, the thermal properties were evaluated and the TGA curves were displayed in figure7, and the data were collected in Table4. As is shown in figure7, all of the HPBD resins exhibited higher char yield after postcuring in a nitrogen atmosphere. In addition, whether in a nitrogen atmosphere or in an air atmosphere, the resins exhibited much higher thermal decomposition temperatures ($Td_{5\%}$ and $Td_{10\%}$) which indicated that thermal stabilities could be further improved via postcuring at elevated temperature process. This behavior was attributed to the corresponding increase in the curing degree and crosslinking density.

Dynamic mechanical analysis (DMA) was performed to explore the postcuring effects on mechanical properties. Figure8 shows the DMA curves of postcured HPBD resins. After curing to a maximum temperature of 375°C, it can be found that the storage moduli of the HPBD resins with various content HPPH were 2.7GPa, 3.4GPa, 3.5GPa at 50°C, respectively, and it decreased with the increase of temperature gradually due to stress relaxation of the polymer network. However, the moduli of the resins still remain 1.3GPa, 1.2GPa and 1.6GPa respectively at 450°C. Moreover, no viscoelastic transition characteristic of a Tg was observed in the tanδ plot of the HPBD resins indicating that a stable crosslinked polymer network had been formed on curing

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process and that the polymer remained in the glassy state to at least 450˚C. These data also showed that a higher cure temperature was needed to complete the cure of the phthalonitrile resins.

We further investigated the postcuring effect by analysis of the DMA of HPDB-24 resin at different postcured temperature (Fig.9a and b).With the cured temperature increased, the storage moduli of HPBD-24 resin elevated steadily. After curing to a maximum temperature of 375˚C, HPBD-24 resin exhibited a Tg in excess of 450˚C and maintained 35% of its initial modulus up to 450˚C. Thus, the results revealed that postcuring at elevated temperatures is favorable to improving cross-linking degree and thermal stability of phthalonitrile resins.[20,21,23]

To sum up, the phthalonitrile resins show higher thermal and mechanical properties after postcuring as proved by TGA and DMA, and it also demonstrates that the higher curing temperature is necessary to improve the curing degree of phthalonitrile resin.

Figure.7 TGA thermograms of polymers HPBD with postcuring at 375˚C: under nitrogen(a) and under air (b).

Table 4 Thermal properties of HPBD reins after cured at 375˚C

	HPBD	$T_{d5\%}$（˚C）	$T_{d10\%}$（˚C）	Char yield (%) at 800˚C
In N_2	HPBD-18	514.5	549	74.59
	HPBD-24	504.5	538	74.65
	HBPD-28	503	538.5	75.06
In air	HBPD-18	505.0	536.0	-
	HBPD-24	508.5	542.0	-
	HBPD-28	501.5	536.0	-

Figure.8 DMA curves of HPBD resins, (a) modulus versus temperature and (b) tan δ versus temperature.

Figure.9 DMA plots for HPBD-24 samples postcured at elevated temperatures (a) modulus versus temperature and (b) tan δ versus temperature.

In addition, SEM were used to evaluate the microstructure of the cured resin. The morphology of the HPBD-28 polymer section with different magnification times were showed in Fig.10. No voids can be observed for the HPBD-28 polymer under a magnification of 2000 times (Fig.10c) which proves the void-free structure of HPBD-28 polymer and it also guarantees the excellent thermal and mechanical

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properties. Moreover, the addition polymerization mechanism of the monomer is one of the most important factors for preparing void-free components.

Figure.10 SEM images of resin HPBD-28 after postcured at 375 °C.

4. Conclusion

In situ reaction of hydroxy to phthalonitrile systems was successfully carried out by a simple nucleophilic displacement of a nitro-substituent from 4-nitrophthalonitrile in a dipolar aprotic solvent, one-pot reaction. Based on the DSC investigations and the rheometric studies, HPBD exhibit large processing windows(~75°C)and good processabilitiy for low complex viscosity(0.01Pa·s) at moderate temperature. FTIR spectra indicated that HPBD have formed the phthalocyanine ring, isoindole ring, and triazine ring in the process of polymerization. Dynamic mechanical analysis revealed that HPPH cured resins exhibited excellent mechanical properties and glass transition temperature. More of the HPPH can lead to higher modulus and Tg, and better thermal stability was achieved with postcuring at elevated temperatures. Moreover, HPBD resins were proved to form the void-free structure which guaranteed the excellent thermal and mechanical properties. Thus, it is a good candidate for applications such as structural components, high temperature adhesives and packing materials in aerospace and microelectronic industries.

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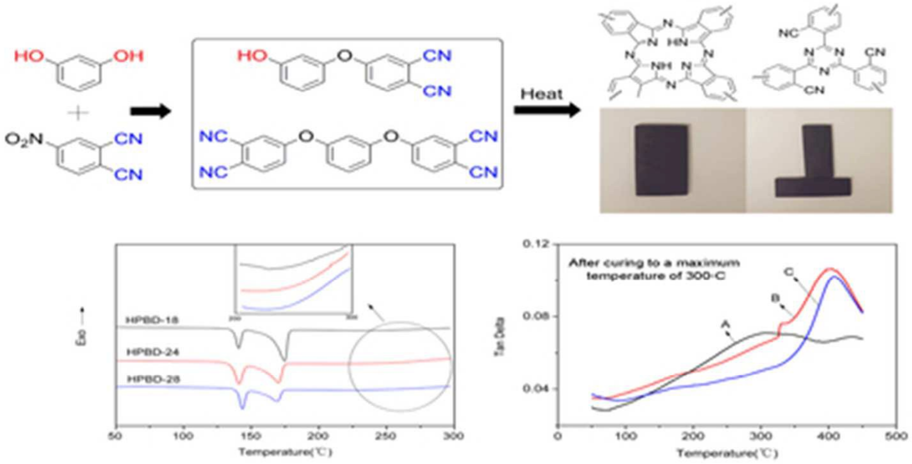

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$$W_{HPPH}(\mathrm{mol\%}) = \frac{S_e}{S_e + S_k/2} \qquad \text{(I)}$$

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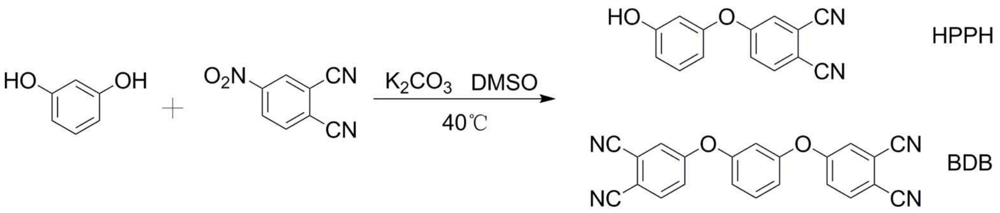

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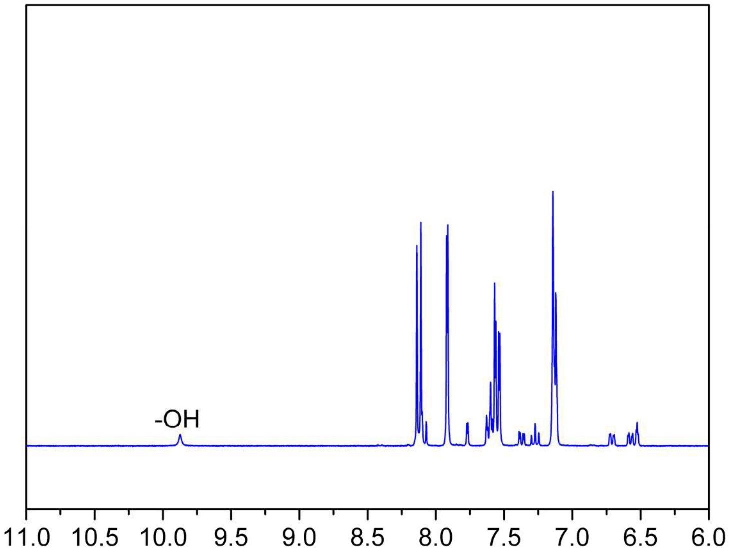

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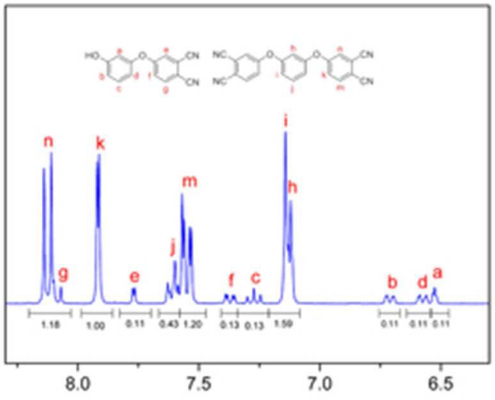

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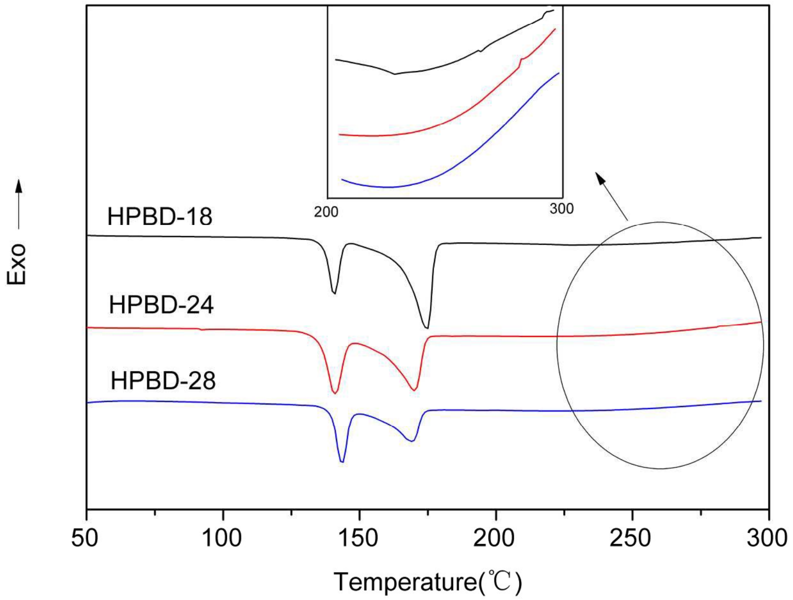

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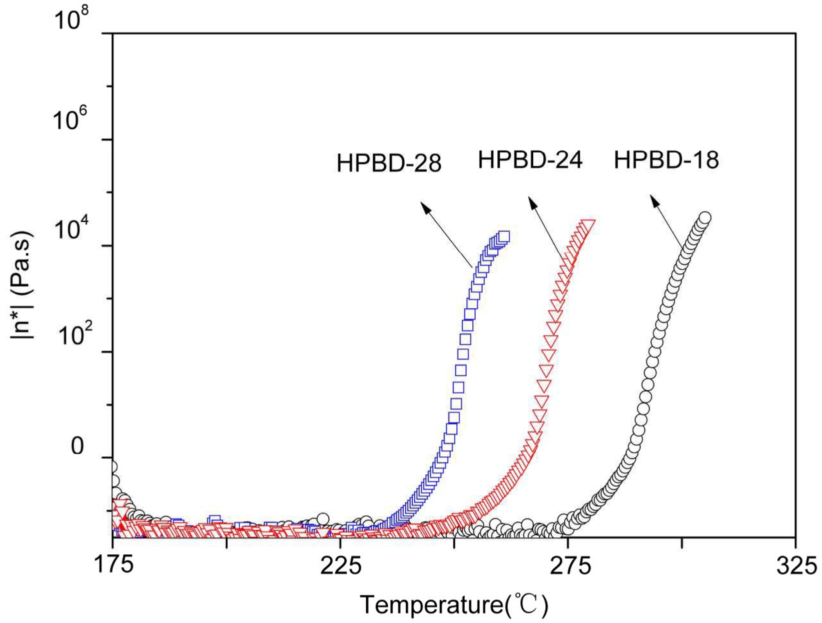

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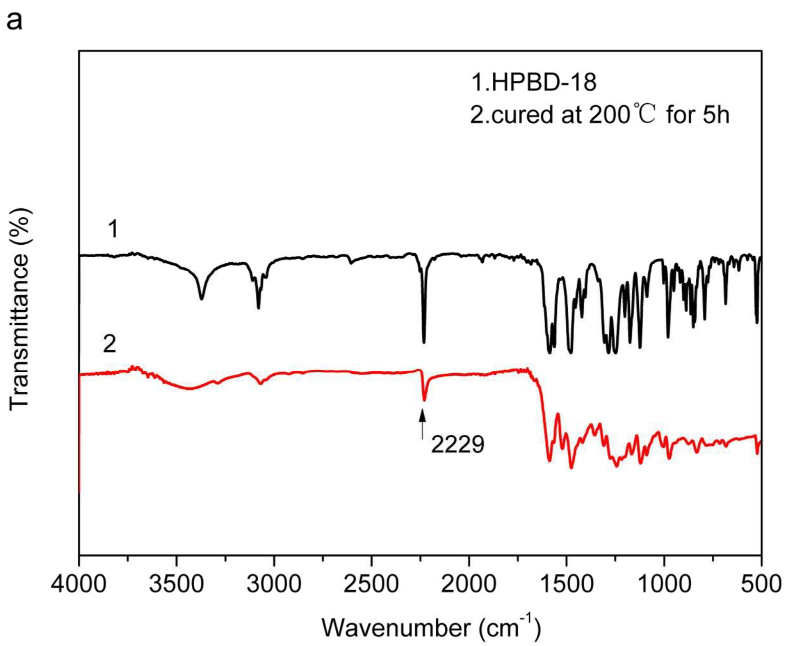

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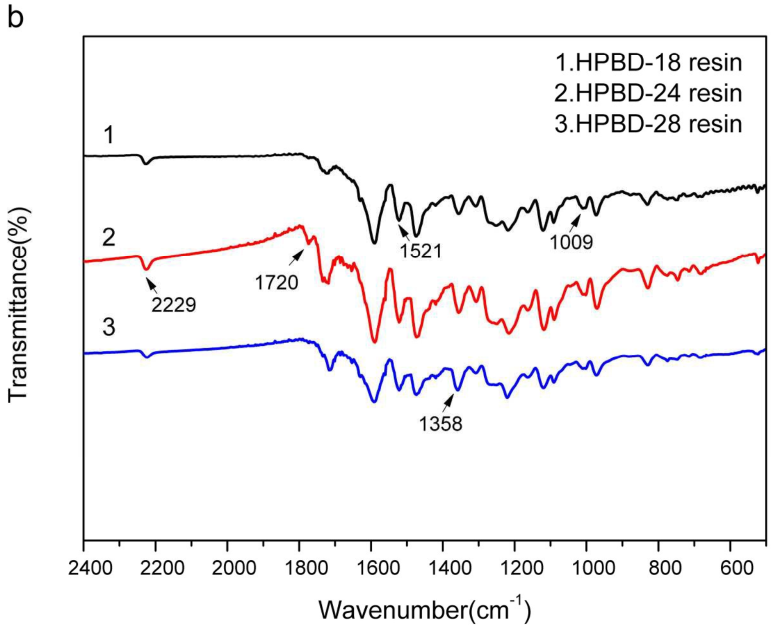

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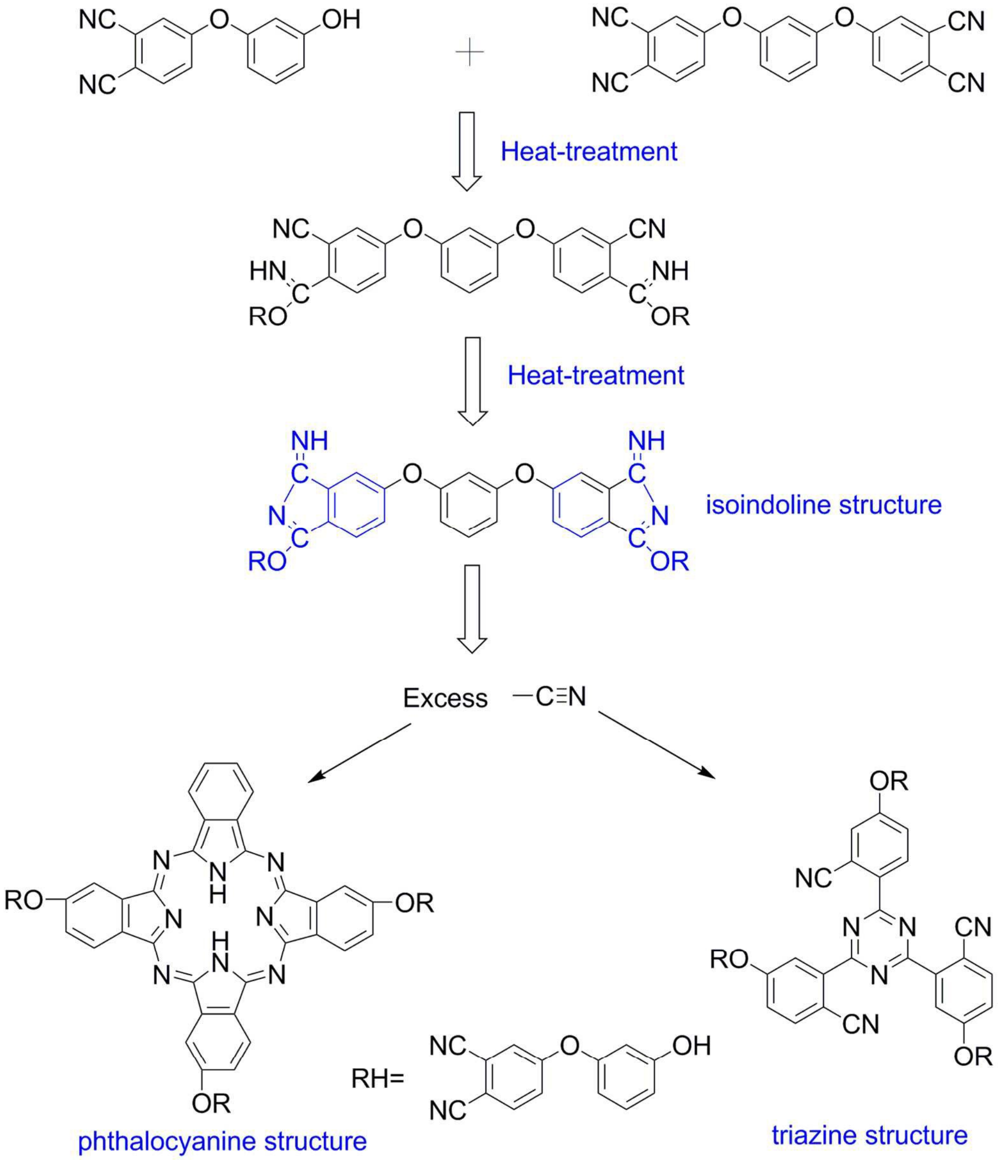

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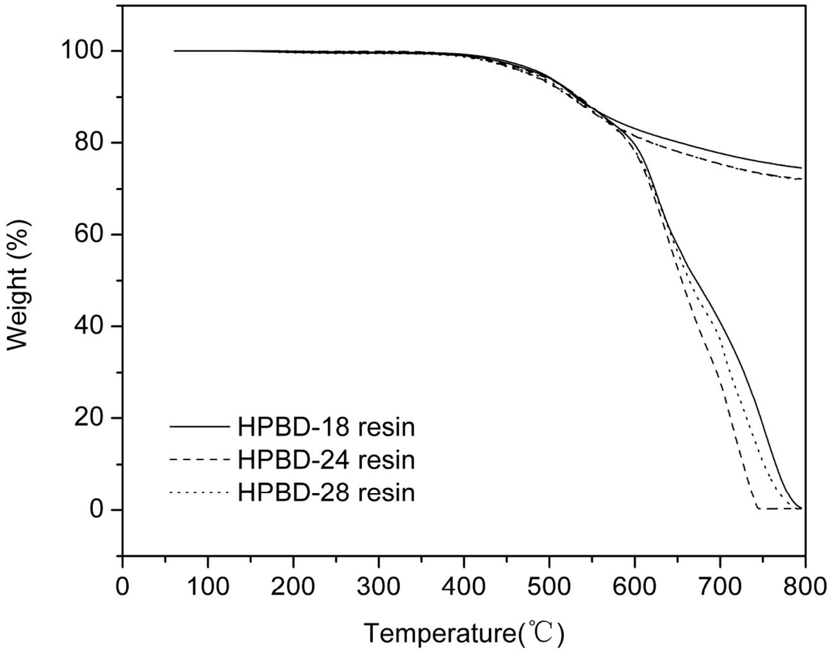

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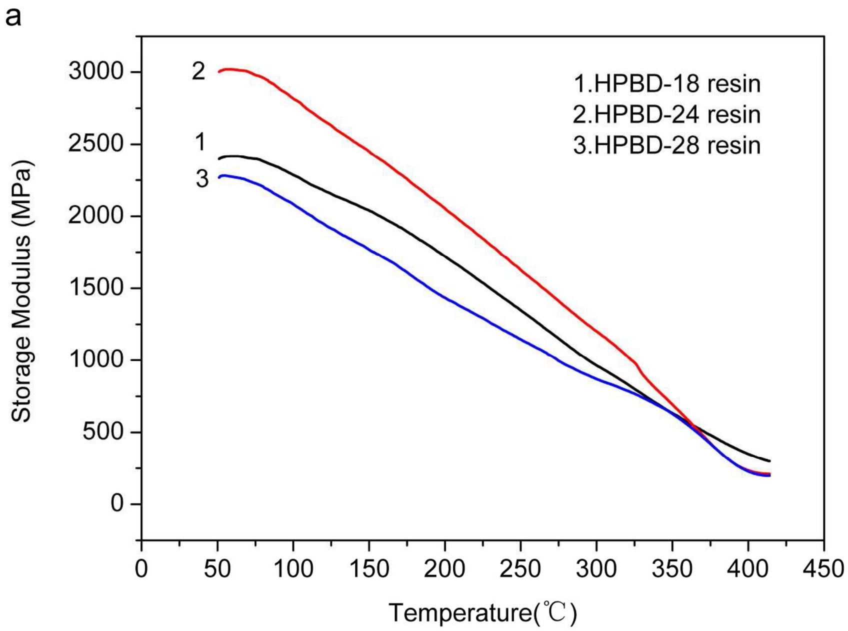

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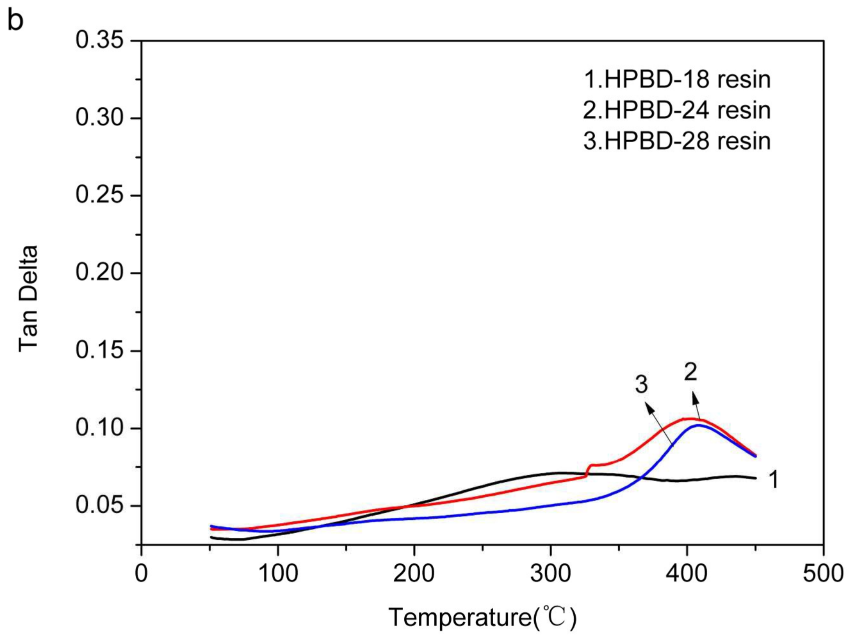

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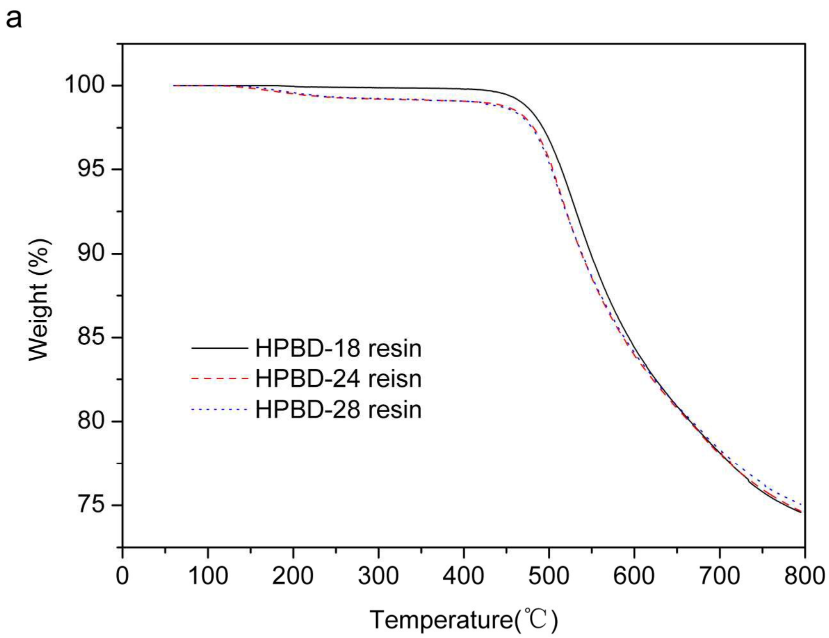

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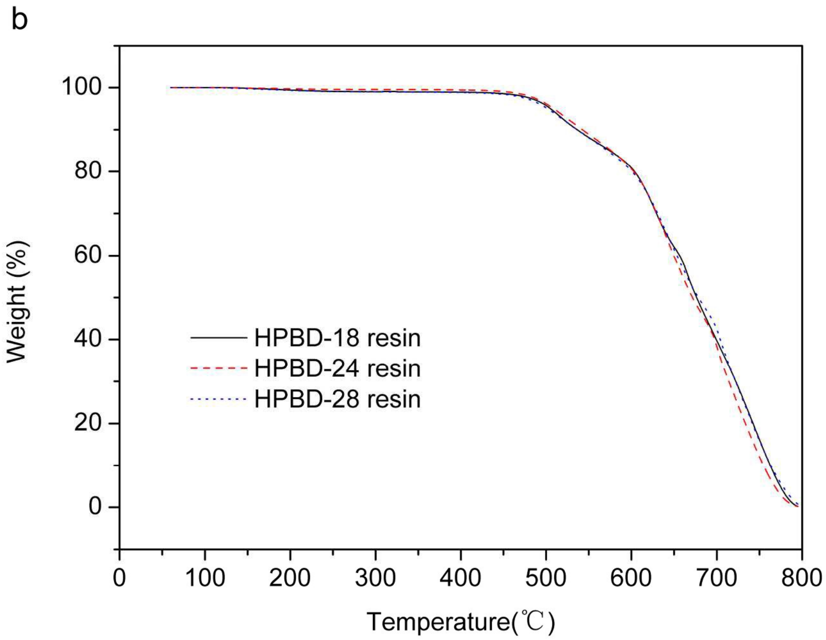

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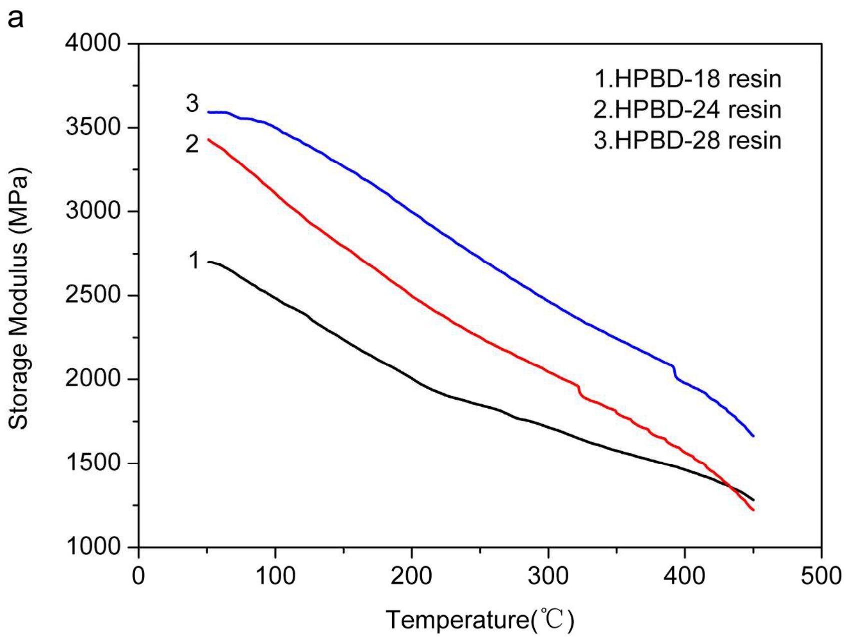

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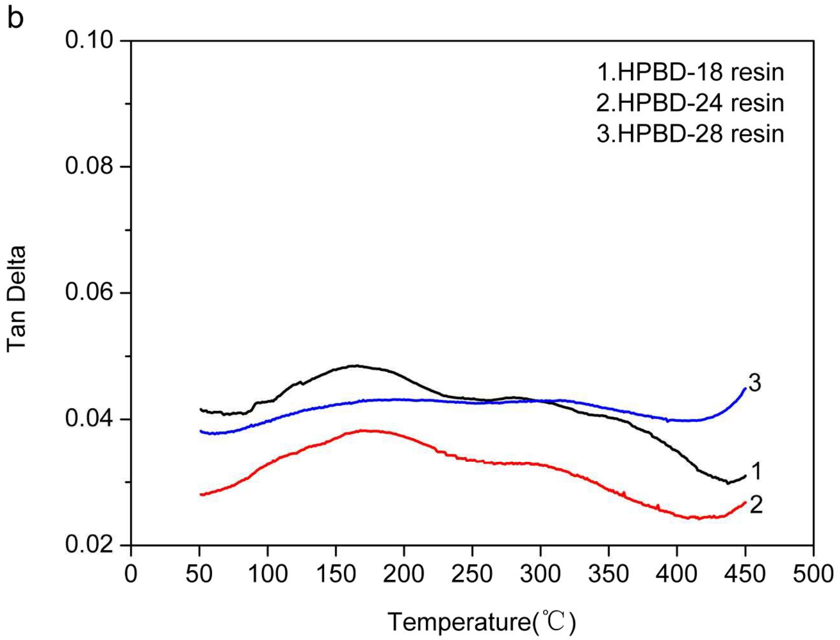

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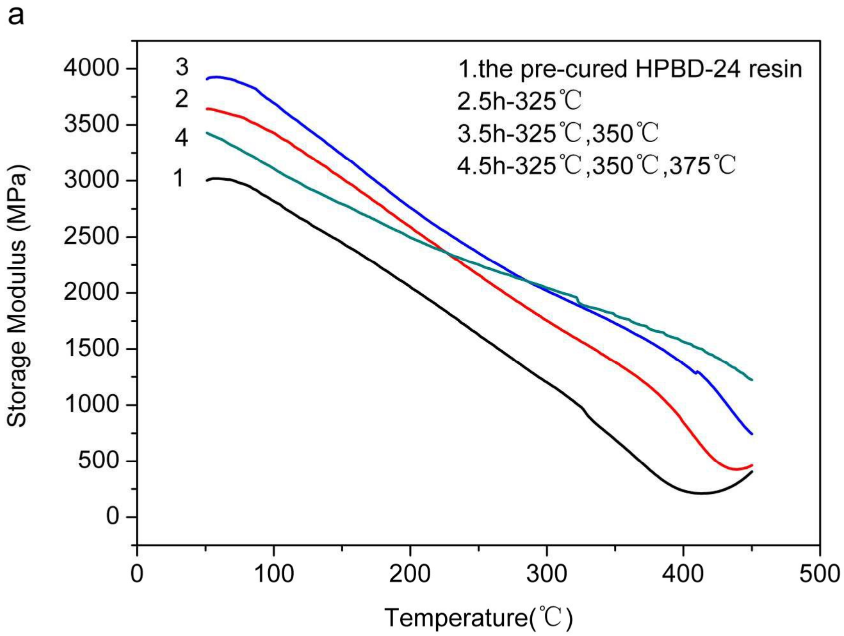

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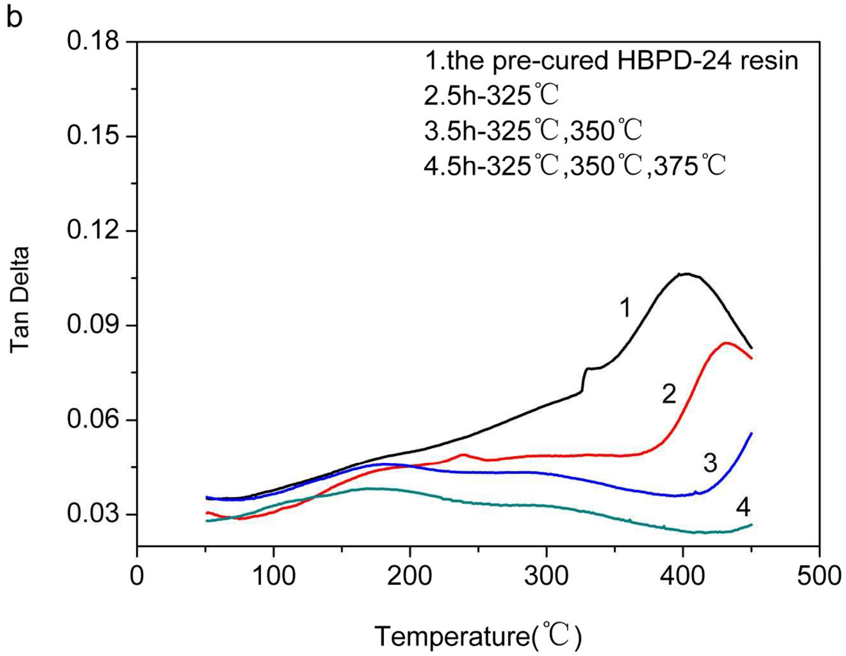

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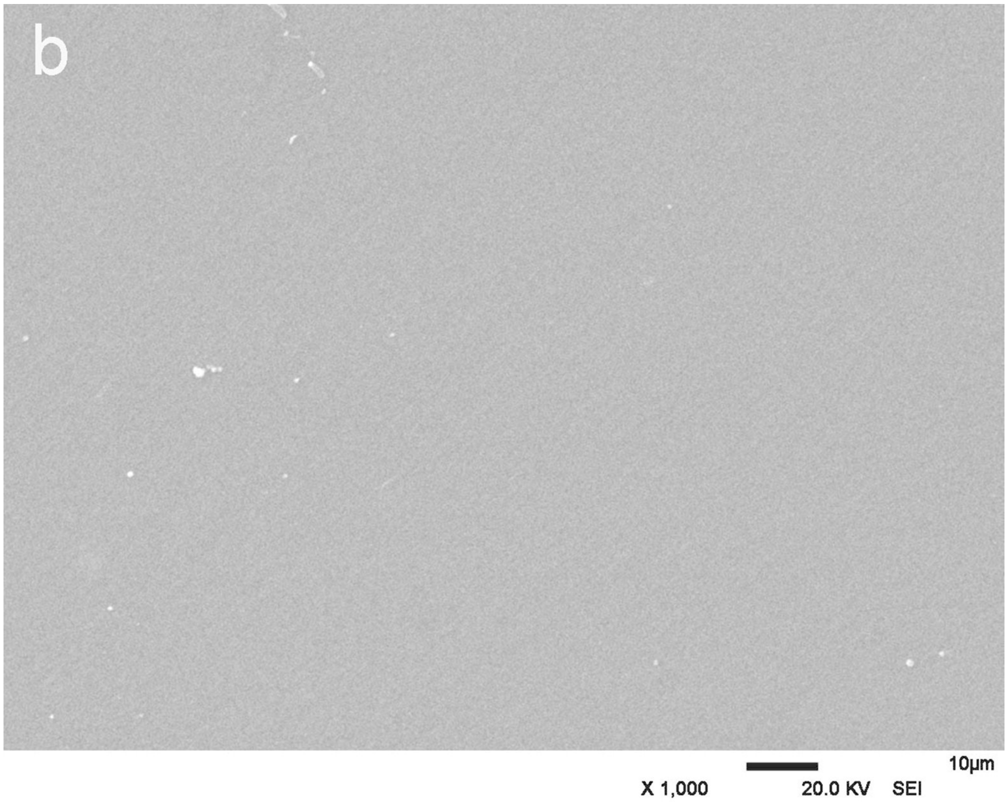

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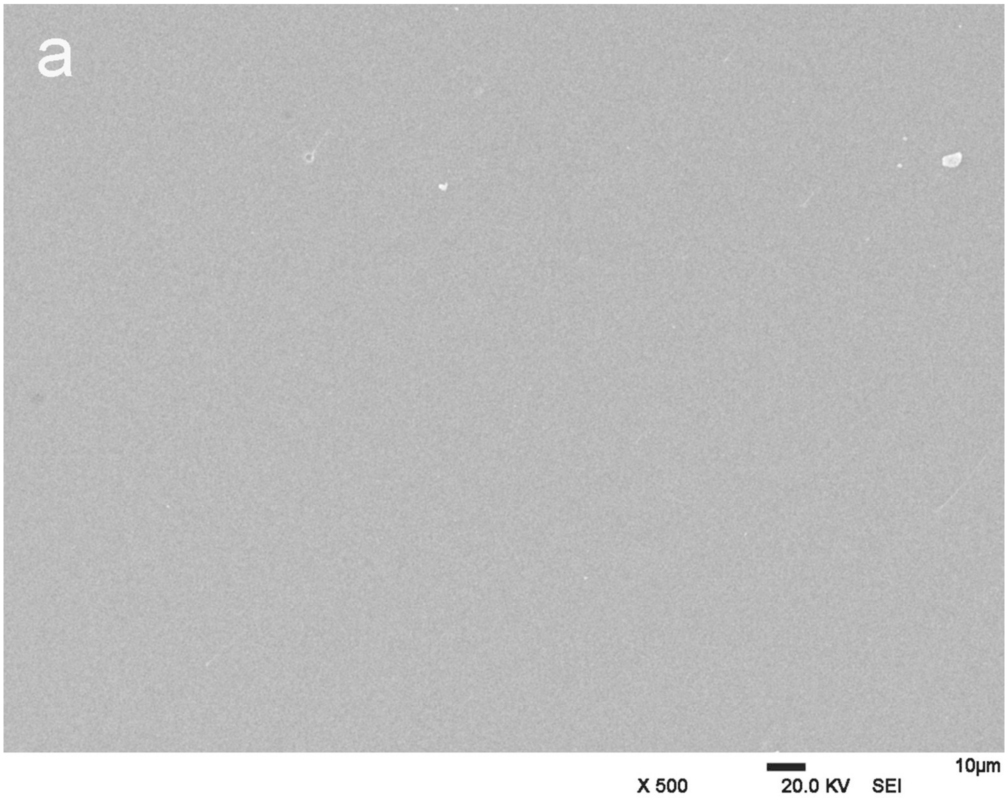

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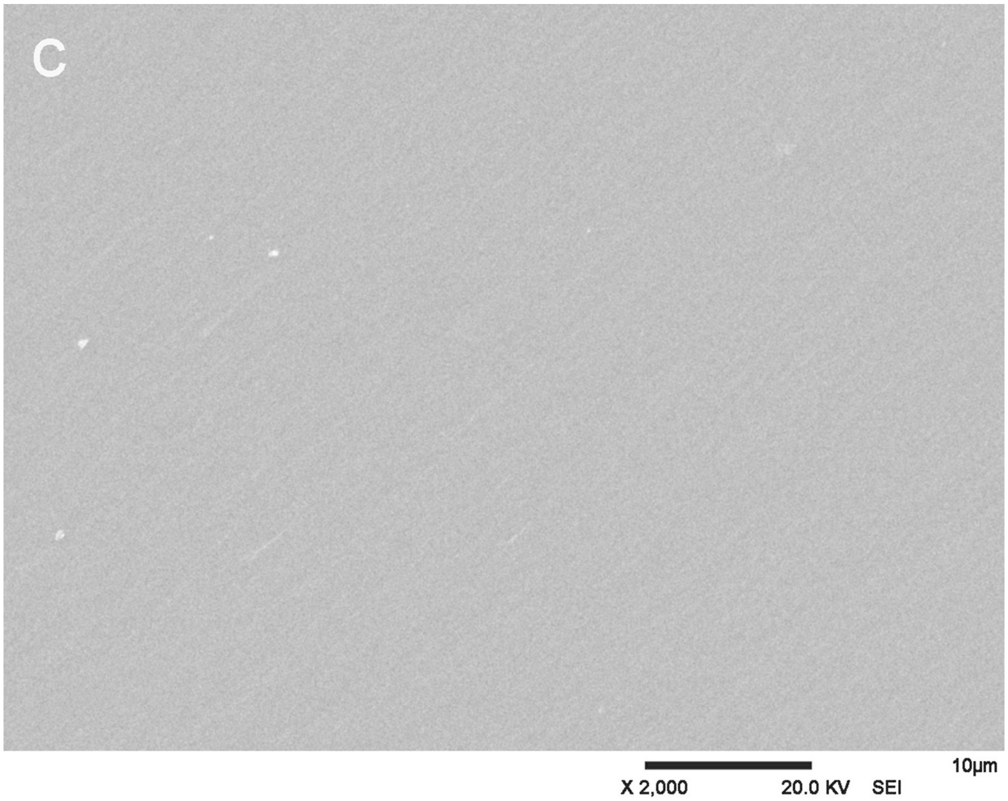

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