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The effect of free dihydroxydiphenylmethanes on the thermal stability of novolac resin

Ping Zhang [a], Shujuan Wang [a], Xiaoting Zhang [a], Xinli Jing [a, b, c, *]

[a] *Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, People's Republic of China*
[b] *MOE Key Laboratory for Non equilibrium Synthesis and Modulation of Condensed Matter, Xi'an, Shaanxi, 710049, People's Republic of China*
[c] *Xi'an Key Laboratory of Sustainable Energy Material Chemistry, Xi'an, Shaanxi, 71049, People's Republic of China*

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ABSTRACT

Phenolic resins (PRs) play an important role in aerospace due to their low cost, outstanding chemical resistance, mechanical properties, thermal properties and ablative properties. However, the industrially produced PRs are often mixtures of polyphenolic compounds with different structures and molecular weights, among which the low molecular weight components are detrimental to the properties of PRs, especially the thermal stability. In this paper, the dihydroxydiphenylmethane (DHDM) contents in several typical industrial novolac resins (NRs) were measured by liquid chromatography and gel permeation chromatography, and the effect of DHDM content on the viscosity, curing process, glass transition temperature (T_g) and thermal stability of NRs was investigated. The results showed that a significant reduction in viscosity and T_g was observed for the NRs with higher DHDM content. The existence of DHDMs reduced the gel point and crosslinking density of the cured NRs by hexamethylenetetramine, leading to a significant decrease in the 5% weight loss temperature, the maximum weight loss temperature, as well as the char yield at 800 °C. Therefore, in addition to the free phenols, we should pay more attention to the DHDMs existed in the NRs. This study provides an important insight for NR manufacturers that the DHDM contents should be reduced through the proper control of process parameters to further expand their wider application scope.

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1. Introduction

Thermal protection system (TPS) materials are used to protect space vehicles from high temperatures during atmospheric entry. Among many materials used for exploration vehicles, the phenolic impregnated carbon ablator (PICA) is the primary material which was developed at NASA Ames Research Center and showed high ablation performance. The European Space Agency is currently supporting the development of a light weight carbon/phenolic resins (PRs) ablator that can be used for sample return mission. Actually, as the first synthetic polymer, due to the low cost of raw material, excellent electrical properties, thermal stability, chemical resistance, dimension stability and ablation resistance, PRs are widely used in a broad range of applications such as adhesives, carbon foams, molding compounds, coatings, and fiber-reinforced composites et al. Especially, PRs and their composites play an important role in the application of structural materials resistant to instantaneous high temperature and ablation [1], such that they have been widely used as the thermal protection structure materials for high-performance solid rocket engine nozzles, space shuttle wings and intercontinental missile reentry systems. During atmospheric entry, low-density carbon/PRs ablative materials undergo thermal degradation and ultimately recession. With the continuous and in-depth exploration of the universe, the harsh working environment of spacecraft puts forward more stringent requirements on the properties of PRs. However, the low thermal decomposition temperature and residue weight at high temperatures for traditional PRs limited their application [2]. Theoretically, if all carbon atoms in the PRs are participated in the char formation at high temperatures, the char yield of PRs at high temperature is approximately 80%. In fact, the collapse of the polymeric network to form polyaromatic domains as well as the volatilization of small carbon oxides occur during pyrolysis, the ultimately char yield of typical PRs at high temperature is generally 55–65% [3]. Therefore, a large number of modification methods have been emerged in the

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* Corresponding author. Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, People's Republic of China.;
E-mail addresses: xljing@mail.xjtu.edu.cn, rgfp-jing@mail.xjtu.edu.cn (X. Jing).

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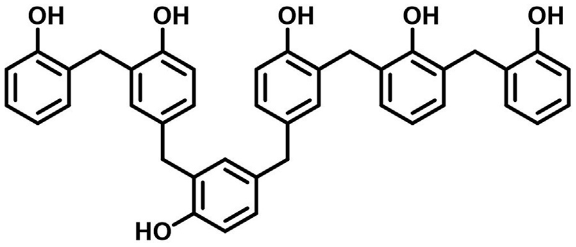
past decades to improve the thermal stability of PRs, such as blending with other thermal-resistance resins, introducing functional groups with high carbon content, or adding heteroatoms. As reported in Ref. [4], the char yield of aryl-boronic acid modified PR reached up to 76% (800 °C, nitrogen atmosphere).

Although a great deal of effort has been devoted to modify the thermal properties of PRs, an important issue has been overlooked for a long time, which is the low molecular weight components existed in the industrial PRs. Generally, PRs are divided into thermoplastic (novolac resin, NR) and thermosetting (resol) [5]. As a main difference between those two resins, NR is synthesized from phenol and formaldehyde under acid condition and then is cured with hexamethylenetetramine (HMTA). NR has a linear structure, composed of phenolic rings and methylene linkages (Scheme 1). The wide molecular weight distribution for PRs is the result of the addition-condensation polymerization between phenol and formaldehyde. The characteristics of condensation polymerization resulted in the fact that the actual PRs consist of various polyphenolic compounds with different molecular weights [6], such as phenols, bisphenols, trimers, tetramers and so on. It is generally known that the free phenols have adverse effects on the properties of PRs. Thus during the industrial production, people try to control the free phenol contents of PRs [7,8]. Up to now, the free phenol content in resol is approximately 5%, whereas that in NR can be controlled below 0.5% by distillation or water washing. Many researches have been done to analyze the composition of NR. For example, Mechin et al. [9] separated and identified 42 kinds of phenolic compounds in NR using high-performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR). Bruze et al. [10] quantified 14 kinds of phenolic monomers and dimers in 14 kinds of NR. However, these studies did not draw much attention to bisphenols. Li et al. [11] did pay particular attention to dimers, and the contents and structures of dimers in NR were separated and identified by chromatography. However, the separated dimer content was in the order of milligrams, and the effect of dimers on the NR properties was not illuminated.

It can be seen clearly from the thermogravimetric analysis (TGA) curve of NR8063 (Fig. S1) that an obvious weight loss below 300 °C was observed, while the reason of which confused us for a long time. After a long period of exploration, we realized that the weight loss below 300 °C was caused by the volatilization of free dihydroxydiphenylmethanes (DHDMs) in NR, as shown in Scheme 2. The results indicated that the effect of DHDMs on the properties of NR cannot be ignored. Our preliminary results revealed that the DHDM content in NR is as high as 10%, and it can be easily volatilized below 300 °C, resulting in a low thermal decomposition temperature and char yield at high temperature [12].

On this basis, the aim of this work is to explore the effect of DHDMs on the curing process and thermal properties of NR. To the best of our knowledge, it is the first time that this problem is addressed. Firstly, the DHDM species and contents in several typical commercial NRs were analyzed, and the method of removing DHDMs from NRs was established. Considering NR8063 as an example, the effect of DHDMs on the curing process, thermal stability and pyrolysis process was then investigated. It is worth noting that the thermal stability of NR and its cured resin is fundamentally improved after removing DHDMs. We anticipate that the comprehensive performance of NR, especially the thermal stability, can be further enhanced combining with other modification methods.



Scheme 1. The possible structure of NR.

2. Experimental

2.1. Materials

Ethanol and xylene were supplied by Tianjin Fuyu Fine Chemical co. LTD. Phenol, HMTA and acetone were supplied by Tianjin Fuchen Chemical Reagent Factory, Tianjin Tianli Chemical Reagent co. LTD and Tianjin Chemical Reagent No.6 Plant, respectively. 2,2′-DHDM, 2,4′-DHDM and 4,4′-DHDM were supplied by Tokyo Chemical Corporation. The above chemicals were all analytical pure reagents and used as received without further purification. Three types of novolac resins (NR8063, NR2123, and NR3490) were supplied by Shandong Shengquan Chemical co. LTD, Xinxiang Bomafengfan industry co. LTD and Jiangmen Yikun Resin Material Technology co. LTD, respectively. All of them are industrial grade NRs.

2.2. Extraction of DHDMs from NRs

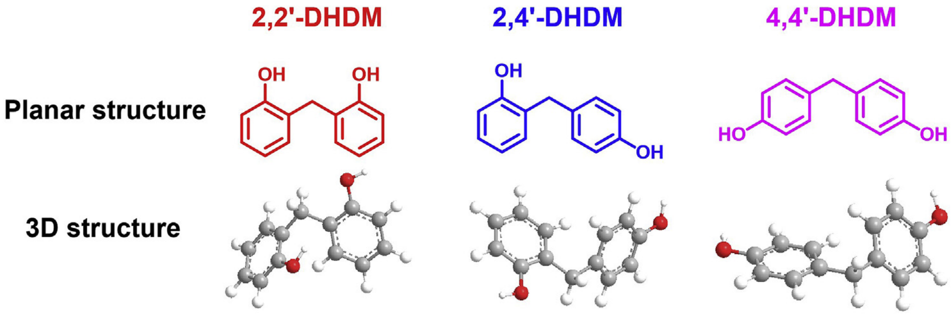
First, NR (50 g) and xylene (100 g) were added into a 250 mL round bottom flask equipped with a reflux condenser, and the mixture was stirred at 120 °C for 60 min under a nitrogen atmosphere. Then the supernatant was poured into an Erlenmeyer flask while it is hot. After repeating the above extraction process for 5 times, the final DHDM content in NR was 0.49%. This sample nearly free of DHDMs was used to compare with the NR containing more DHDMs. The quantitative determination of the DHDM species and contents in NR was carried out by liquid chromatography (LC) using standard curve method (Fig. S2 and Table S1). The samples with different DHDM contents were designated as NR-0, NR-2, NR-4 and NR8063, respectively (Fig. S3 and Table S2). For example, the NR-4 indicates that the total DHDM content in NR8063 is about 4 wt%.

2.3. Preparation of the cured NRs

A 60 wt% ethanol solution of NR was first obtained, and then a certain amount of HMTA was added. The solution was dried at room temperature for more than 12 h to remove most of the ethanol. The mixture of NRs and HMTA was poured into PTEF molds and cured at 170 °C for 2 h in a vacuum oven.

2.4. Characterization

NMR spectra were acquired using a Bruker (Avance III, Bruker Corporation, Darmstadt, Germany) 400 MHz spectrometer with deuterated acetone-d6 as solvent and tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) was performed using a Waters GPC 2410 (Waters Corporation, Milford, MA, USA) consisting of PLgel 5 μm MIXED-D gel column (300 × 7.5 mm, two) and refractive index detector with a flow rate of 2.0 ml/min at 40 °C, and tetrahydrofuran was used as a carrier solvent. A linear calibration curve with polystyrene (PS) standards was made to determine the molecular weight and polydispersity of the resin. LC was performed using Waters C18 (2.1 × 50 mm, 3 mm) chromatographic column with the same degree of flow in the binary system of methanol and water (the volume ratio of methanol to water was 38:62) at 30 °C and ultraviolet detector was used to detect at



Scheme 2. The structures of DHDMs.

270 nm. Differential scanning calorimetry (DSC) analyses were performed on a NETZSCH DSC 200 PC (Selb, Germany) under nitrogen atmosphere at a rate of 10 K/min from 30 to 800 °C. TGA was carried out using a NETZSCH TG 209C under nitrogen atmosphere at a rate of 10 K/min from 30 to 800 °C. Rheology analysis was performed using MCR501 rotary rheometer produced by Anton Paar. Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) analysis was performed using Frontier PY-2020S tubular furnace cracker, and gas was analyzed by GC/MS-QP2010 of Shimadzu of Japan.

3. Results and discussion

3.1. The DHDM species and contents in NRs

Before investigating the DHDM species and contents in NRs, the structures of NRs were analyzed firstly for better understanding the relationship between the structures of DHDMs and NRs [13]. Fig. 1 showed the ^{13}C NMR spectra of three different kinds of NRs. The ^{13}C NMR signals appeared at 29.5, 34.7 and 40.0 ppm corresponded to the methylene carbons of ortho-ortho' (*o-o'*), ortho-para' (*o-p'*) and para-para' (*p-p'*) linkages, respectively. The *o-o'*, *o-p'* and *p-p'* methylene contents in NRs were statistically estimated by integrating the peak areas according to the method described by Nomoto et al. [14], as shown in Table 1. The *o-o'* and *p-p'* methylene contents in NR3490 were 48.5% and 3.6%, respectively, indicating that NR3490 was a kind of high ortho-position phenol-formaldehyde resin. The *o-o'*, *o-p'* and *p-p'* methylene contents in NR2123 or NR8063 were relatively average, indicating that the methylene linkages between phenol rings were in a random manner. The *o-o'*, *o-p'* and *p-p'* methylene contents in NRs were consistent with the types and contents of DHDMs contained in NRs.

The average molecular weight is an important characteristic of oligomers and polymers. The molecular weights and molecular weight distributions of NRs were obtained from the GPC chromatograms, as shown in Fig. 2. The retention time at about 21 min was assigned to the solvent of tetrahydrofuran. The retention time at about 20 min indicated that a small amount of free phenols still remained in NRs, among which the free phenol content in NR8063 was the least. The peaks ranging from 18.9 to 19.3 min corresponded to the three types of DHDM isomers (Scheme 2). The hydrodynamic volumes of these three DHDMs were ranked from large to small in the order of 4,4'-, 2,4′- and 2,2′-DHDM [15], and their corresponding retention time was 18.9, 19.0 and 19.3 min, respectively. Thus there were slight differences in the peak position and strength among the three NRs in this time interval as shown in Fig. 2. The retention time at about 18.5 min corresponded to the trimers in NR. Similarly, the hydrodynamic volumes of trimer isomers were different, but the peaks of different types of trimer isomers were overlapped and cannot be distinguished clearly, appeared as a wide peak. The average molecular weights of NRs were obtained from GPC curves using PS as calibration standards and shown in Table 1. The problem of using PS calibration standards for NRs was the lower number-average molecular weights (M_n), whereas the weight-average molecular weights (M_w) were more spread. The M_n of all NRs were below 1000 g/mol (regardless of the deviation), indicating that on average less than 10 phenolic units were existed in each NR chain. The polydispersity indexes (PDI) of the three kinds of NRs were ranged from 1.50 to 4.89.

The contents of these three types of DHDM isomers in NRs were quantified by LC, as shown in Fig. 3 and Table S3. The separation efficiency of LC was greatly influenced by the mobile phase [16]. As the polarity of water is higher than that of methanol, the proportion of methanol in mobile phase was higher, and the retention time of samples was longer, accordingly the distance among the peaks will be farther. Furthermore, the high proportion of methanol will result in leading and tailing peaks. In this work, the same flow degree in the binary system of methanol and water (the volume ratio of methanol to water was 38:62) was chosen. As shown in Fig. 3, the three types of DHDM isomers in NRs were separated thoroughly. The 4,4′-, 2,4′- and 2,2′-DHDM were eluted according to their polarities. The retention times of 4,4′- and 2,4′-DHDM were very close, which were 5.5 and 6.1 min, respectively, while that of 2,2′-DHDM was 11.6 min. It can be seen from Table S3 that the DHDMs types and contents in different kinds of NRs were different. For NR8063 and NR2123, 4,4′-DHDM was dominated, while higher 2,2′-DHDM content was contained in NR3490. The results were basically consistent with the results obtained from ^{13}C NMR spectra. In addition, NR8063 had the highest DHDM content (9.68%) and the lowest free phenol content among the three kinds of NRs. As a result, NR8063 was chosen as an example to study the effect of DHDMs on the processibility and thermal stability of NRs.

3.2. The effect of DHDMs on the viscosity, curing process and T_gs of NRs

For resin matrix, processibility is the ability to meet the requirements of production processes, thus optimizing the processibility of NR can give full play to its advantages in the field of composites. The rheological behavior of NRs has a significant impact on their application and curing process, especially the viscosity is a key parameter reflecting the pros and cons of NRs. NRs with low viscosity had good fluidity and permeability, while that for NRs with high viscosity had poor penetration of the resin with fiber, resulting in the poor laying and self-adhesion of the prepregs. NRs with higher viscosity can be obtained after removing the DHDMs. The complex viscosities versus temperature curves for NR8063 and NR-0 were shown in Fig. 4. The viscosity of NR-0 was clearly higher than that of NR8063 in the temperature range from

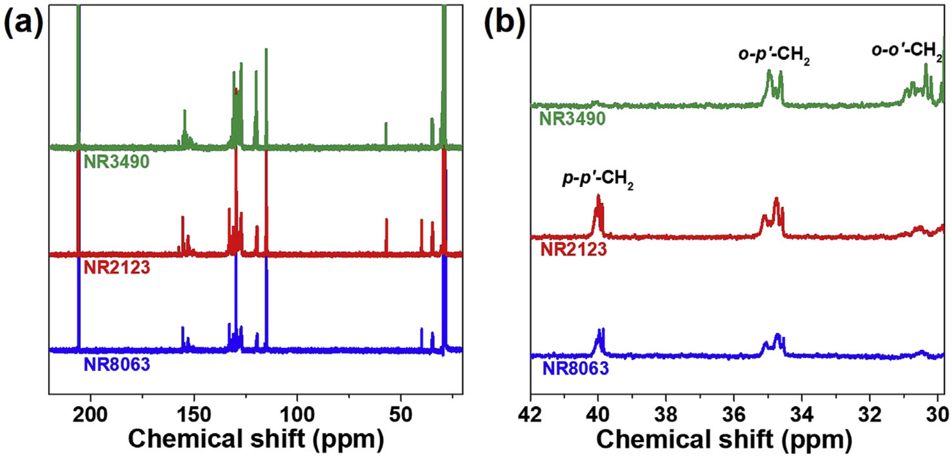


Fig. 1. ^{13}C NMR spectra of NR3490, NR2123, and NR8063, measured in acetone-d_6: (a) full spectra; (b) partial spectra.

100 to 170 °C, indicating that DHDM acted as a plasticizer improving the fluidity of NR.

The NRs with different DHDM contents were then cured by HMTA at 170 °C for 2 h in the vacuum oven. The gelation occurred very quickly for the NR with a small amount of DHDMs to yield a denser crosslinking network (Fig. S4 and Fig. S5). It can be seen from Fig. S6 that the cured NR-0 exhibited higher crosslinking density and glass transition temperature (T_g) than that of the cured NR8063 [17].

The T_g of NRs is greatly influenced by their molecular weight distribution, especially the low molecular weight components (such as DHDMs). As the possibility of participating in the curing reaction for the low molecular weight components in NRs was lower than that of the high molecular weight components [18], NRs with few DHDMs showed higher T_gs. As shown in Fig. 6(d), at the same HMTA content, the T_gs of the cured NRs decreased with increasing DHDM contents. For example, the T_g of NR8063 with the DHDM content of 9.68% was 75.5 °C, while that without DHDMs was 90.4 °C. It is concluded that the free DHDM acted as a plasticizer leading to a decrease in the T_g of NRs. Generally, the higher crosslinking density led to the higher T_gs of the cured resins [19]. It can be seen from Fig. 5(d) that the T_gs of the cured NRs increased with increasing HMTA contents. The DSC curves of the cured NRs (Fig. 5(b) and (c)) showed the endothermic peaks above 200 °C because of the second curing process above 200 °C. Therefore, the presence of DHDMs had a significant effect on the T_gs of NRs and cured NRs, and it was very necessary to decrease the DHDM contents during the synthesis of NRs.

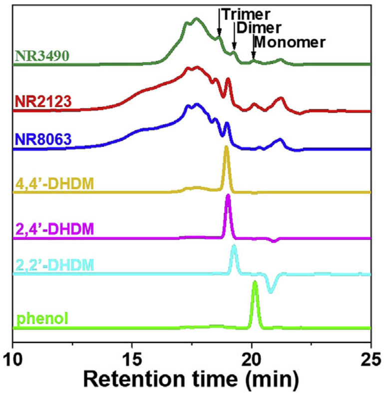


Fig. 2. GPC curves of free phenol, different kinds of NRs and DHDMs.

3.3. The effect of DHDMs on the thermal stability of NRs

As mentioned above, PR is an important matrix resin used in ablative composites. However, the low thermal decomposition temperature and char yield at high temperatures of traditional PRs can't meet the requirements for application [20]. We believe that the DHDM existed in the NRs is one of the most important reasons for the lower thermal decomposition temperature and char yield of NRs and their cured resins. Thus one goal of this work is to explore the effect of DHDMs on the thermal stability of NR and its curing products. Also we hope to provide a guidance for the optimization of the processing parameters and the control of the quality of NRs.

Table 1
The types and contents of methylene linkages obtained from ^{13}C NMR spectra, as well as the average molecular weights obtained from GPC curves for NR3490, NR2123, and NR8063.

NR	o-p' (%)	o-o' (%)	p-p' (%)	$\overline{M_n}$[a] (g/mol)	$\overline{M_w}$[b] (g/mol)	PDI[c]
NR8063	51.5	14.4	34.1	792	3876	4.89
NR2123	49.5	25.6	24.9	740	2447	3.31
NR3490	47.9	48.5	3.6	556	834	1.50

[a] Number-average molecular weight.
[b] Weight-average molecular weight.
[c] Polydispersity index.

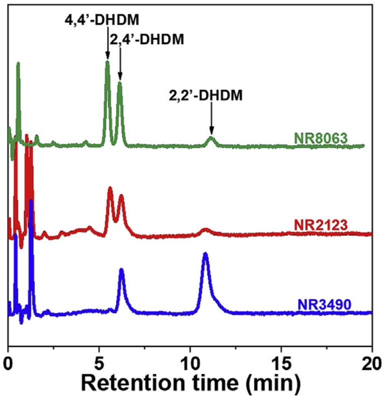


Fig. 3. Liquid chromatograms of NR3490, NR2123, and NR8063.

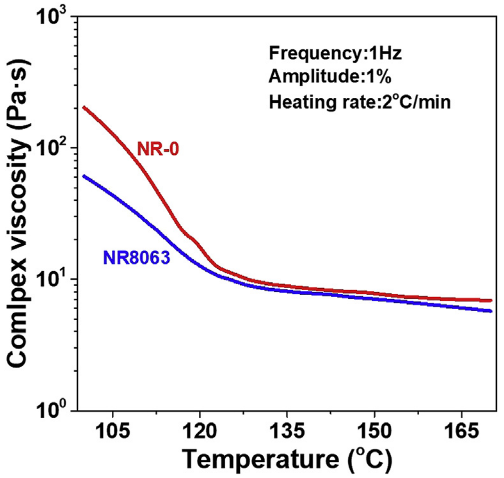


Fig. 4. The complex viscosities versus temperature curves of NRs with different DHDM contents, obtained from rheology analysis.

Firstly, the thermal stability of phenol, three kinds of DHDM isomers and NR8063 (Fig. 6) were studied, and the TGA results were summarized in Table 2. The volatilization of the three kinds of DHDM isomers largely depended on their boiling points, and the DHDMs with higher boiling point showed higher thermal decomposition temperatures, such as the 5% and 10% weight loss temperature (so-called $T_{5\%}$ and $T_{10\%}$, respectively), the maximum weight loss temperature (T_{max}) and the complete weight loss temperature ($T_{100\%}$). TGA results indicated that the free phenols and DHDMs began to volatilize at temperatures far below their boiling points and were completely volatilized below 300 °C. Thus it can be concluded that the weight loss below 300 °C for NR8063 corresponded to the volatilization of free DHDMs, and it is suggested that NR was chemically stable at this temperature, which will be demonstrated subsequently.

The effect of DHDMs on the pyrolysis process of NR was studied using Py-GC/MS, and the pyrolysis temperature of 200, 300 and 400 °C were chosen. During the Py-GC/MS test, the samples reached the setting temperature almost instantaneously, and they did not experience a slow heating process. Thus Py-GC/MS can directly reflect the temperature sensitivity of samples [21], and it is also useful to explore the thermal pyrolysis of NRs at different temperatures [22].

The Py-GC/MS results of DHDMs at 200, 300 and 400 °C were shown in Fig. S7. At 200 °C, only the volatilization of DHDMs occurred. At 300 °C, a small amount of free phenol was observed in volatiles, while the volatilization of DHDMs was still dominate. The results showed that the pyrolysis of DHDMs took place at 300 °C. When DHDMs were analyzed by Py-GC/MS at 400 °C, their rapid volatilization induced the pyrolysis hard to take place, so few phenols could be formed and detected.

Then the pyrolysis of NRs with different DHDM contents was investigated by Py-GC/MS, as shown in Fig. 7(a)–(c). At 200 °C, in addition to the impurities, only DHDMs were detected in the volatile of NR8063 and NR-0. It is worth noting that the DHDM content (9.68 wt%) in NR8063 was much higher than that in NR-0 (0.49 wt

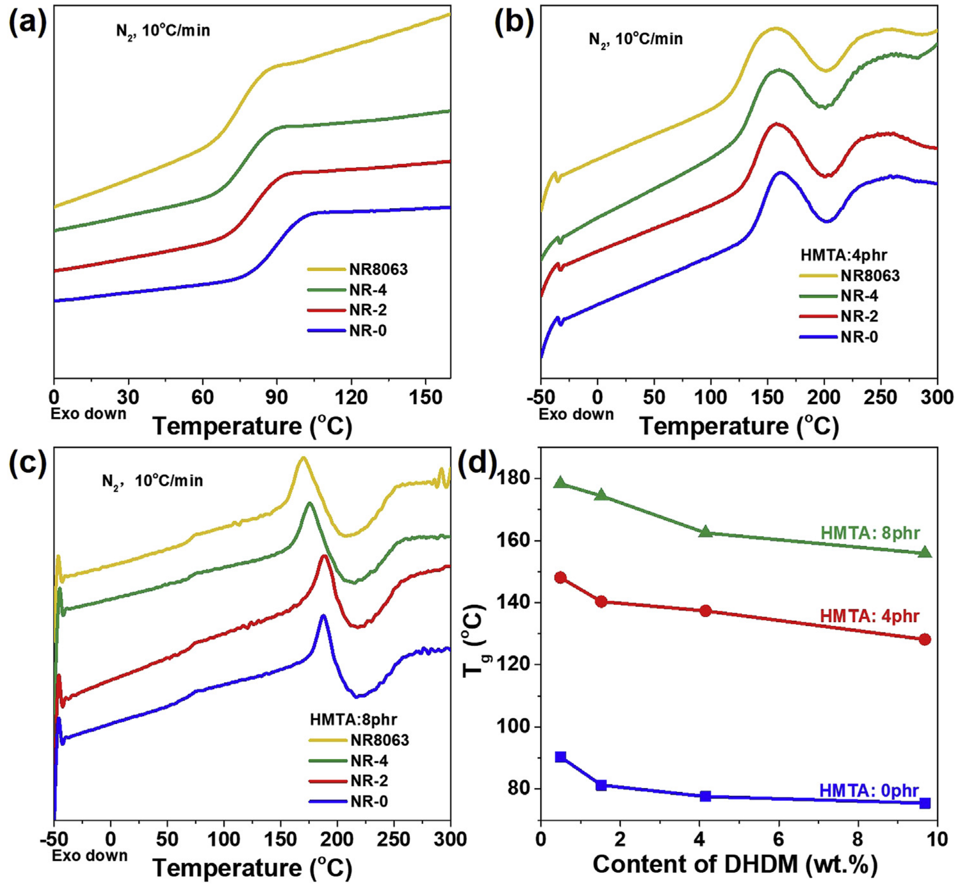


Fig. 5. DSC (2nd heating) curves of NRs with different DHDM contents and different HMTA contents: (a) pure NRs; (b) NRs cured by 4 phr HMTA; (c) NRs cured by 8 phr HMTA; (d) T_gs of the NRs and cured NRs obtained from DSC curves.

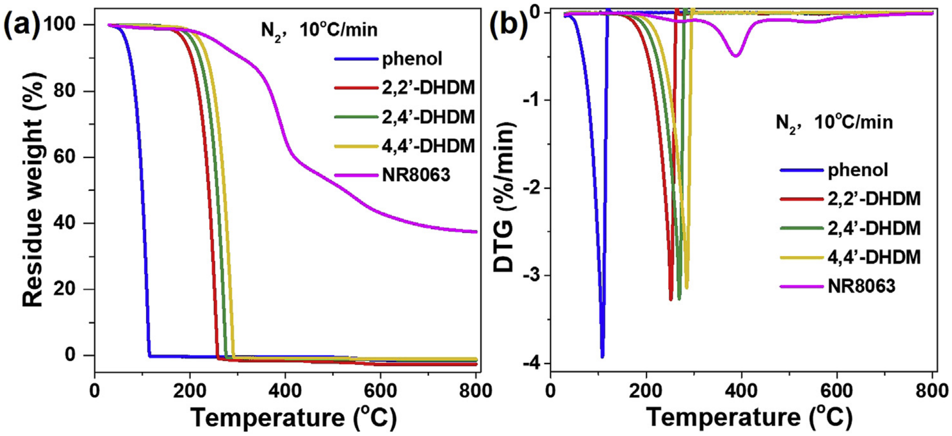


Fig. 6. TGA (a) and DTG (b) curves of phenol, DHDMs and NR8063 under a nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C.

Table 2
The results of thermogravimetric analyses of phenol, DHDMs and NR8063, obtained from TGA and DTG curves.

Sample	m.p.[a] (°C)	b.p.[b] (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	$T_{100\%}$ (°C)	R^{o}_{800C} (%)
Phenol	40–42	181.9	65.8	74.3	107.8	115.0	0
2,2′-DHDM	118–119	362.5 ± 22.0	189.2	203.3	252.5	257.7	0
2,4′-DHDM	119–120	376.0 ± 22.0	206.2	220.5	269.0	275.3	0
4,4′-DHDM	162–163	390.0 ± 22.0	221.7	235.7	285.3	290.8	0
NR8063	/	/	225.8	309.2	271.5 388.0 549.2	/	37.5

[a] Melting point.
[b] Boiling point.

%), indicating that NRs were chemically stable at 200 °C. At 300 °C, the pyrolysis of NR8063 occurred, and small amounts of free phenols and cresols were produced. For NR-0, there was little difference between the Py-GC/MS curves at 200 and 300 °C. The results indicated that DHDMs were the weak links in NRs, which were prone to pyrolysis when heating. On the other hand, after removing DHDMs, the NR-0 with high molecular weight showed better thermal stability, and the pyrolysis of NR-0 did not occur even at

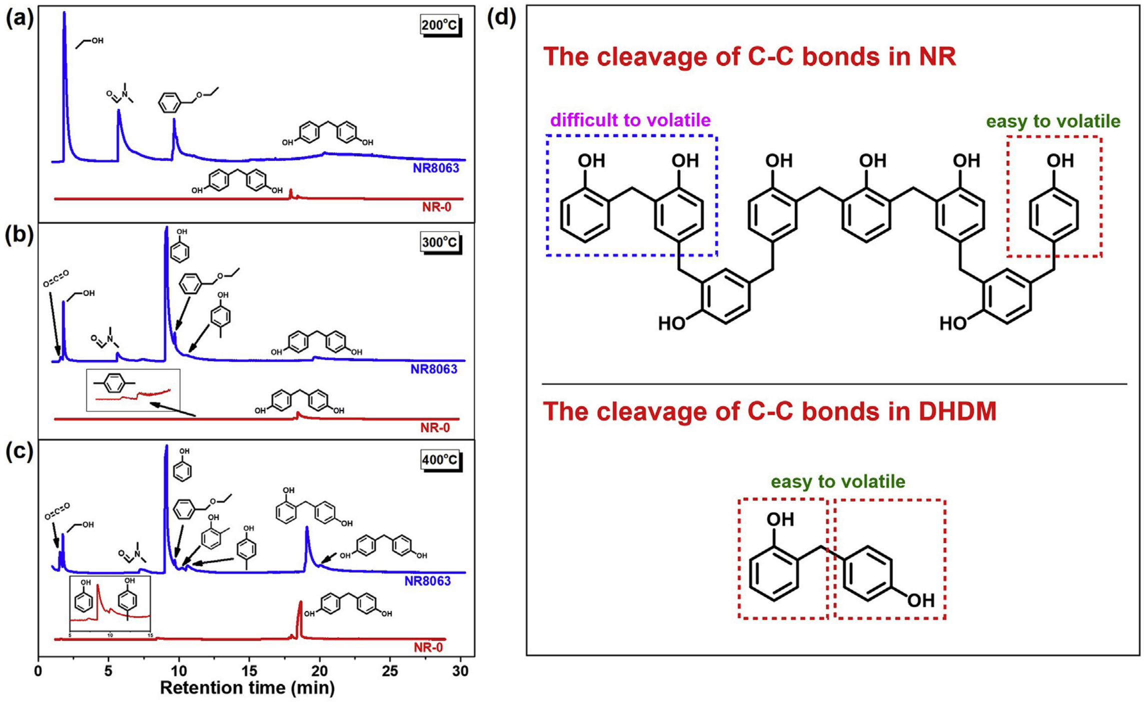


Fig. 7. Py-GC/MS chromatograms of NR-0 and NR8063 at (a) 200 °C, (b) 300 °C and (c) 400 °C; (d) The formation of monophenols and bisphenols from the pyrolysis of C–C single bonds.

300 °C. The cleavage of covalent single bonds happened easily comparing to double bonds in the benzene ring during the thermal pyrolysis of NR, among which the cleavage of C—C single bond resulted in the formation of monophenols and bisphenols. It was proved that the C—C single bonds in the different positions of NR molecular chain were broken at nearly the same probability, in our unpublished works through the molecular dynamic study based on reactive force field. So, the lower molecular weight NR chains tended to form more monophenols, especially DHDMs. The formation mechanism of monophenols and bisphenols resulted from the cleavage of C—C single bonds was shown in Fig. 7(d).

At 400 °C, even the NR-0 with few DHDM and high molecular weight began to pyrolyze [23], while the detected phenols and DHDMs were derived from the volatilization of DHDMs originally existed in NR-0 and the pyrolysis of NR-0 chains. And the DHDMs in the NR samples tended to be pyrolyzed rather than volatized since DHDMs were blocked by the NR chains. The amount of phenolic compounds produced during the pyrolysis of NR8063 is higher than that of NR-0. Therefore, the Py-GC/MS results indicated that the presence of DHDMs significantly reduced the thermal stability of NR, especially the initial stage of pyrolysis.

TGA was used to further study the effect of DHDM contents on the thermal stability of NRs (Fig. 8), and the thermal characteristic data were summarized in Table 3. The higher DHDM contents in NRs resulted in the lower $T_{5\%}$, $T_{10\%}$, T_{max} and char yield at 800 °C (R_{800}). For example, the R_{800} of NR-0 containing little DHDMs was 42.79%, while that of NR8063 was 37.45%. As some xylene still remained in NR-4, NR-2 and NR-0 during the removal of DHDMs, a significant decrease in $T_{5\%}$ was observed, thus $T_{10\%}$ was used to evaluate the thermal stability of NRs with different DHDM contents at the initial stage of pyrolysis. The results were in good consistence with the Py-GC/MS results that the DHDMs existed in NR reduced the thermal stability of NR. Compared to the Py-GC/MS test, the TGA tests were carried out at a low heating rate (10 °C/min), and it was beneficial to study the volatilization during heating.

According to the DTG curves (Fig. 8(b)), the pyrolysis process can be divided into three stages. The first stage occurred below 300 °C, resulting from the volatilization of low molecular weight components. In the second stage (300—483 °C), the methylene linkages in NR chains were pyrolyzed, as a result, the phenol and its derivatives were produced. In the third stage (483—600 °C), further pyrolysis of NR chains occurred to release carbohydrates, hydrocarbons and water [24,25]. For NR8063 with the highest DHDM content, a significant weight loss in the first stage was observed, and the weight loss clearly reduced after removing the DHDMs. The main weight loss of NR8063 occurred in the second stage ranging from 300 to 483 °C, resulting from the pyrolysis of the methylene linkages. It can be seen that the weight residue of NR8063 decreased from 90.81 to 43.10% with increasing temperatures from 300 to 600 °C, while that of NR-0 decreased from 94.21% to 49.20%. As analyzed by Py-GC/MS, the volatilization of DHDMs mainly took place below 300 °C, the weight losses during the second and third stages for the NRs with different DHDM contents showed little difference [26].The above results revealed that removing DHDMs significantly improved the thermal stability of NRs.

To demonstrate the generality of our results, the thermal stability of three different kinds of industrial NRs were studied. As shown in Fig. S8 and Table S6, the NRs with different molecular weights, PDI, as well as different DHDM species and contents almost showed similar thermal pyrolysis processes. According to the DTG curves, the weight loss processes for the three kinds of NRs can be divided into three stages, only the temperature range of each stage existed a small difference. As the volatilization of DHDMs occurred in the first stage, the weight loss for the three kinds of NRs in this stage was related to the types and contents of DHDMs. The weight loss of the second and third stages were related to the molecular weight and molecular weight distribution of the NRs. NR3490 mainly contained 2,2′-DHDM, the boiling point of which was the lowest among the three DHDMs, and the weight-average molecular weight of NR3490 was also the lowest among the

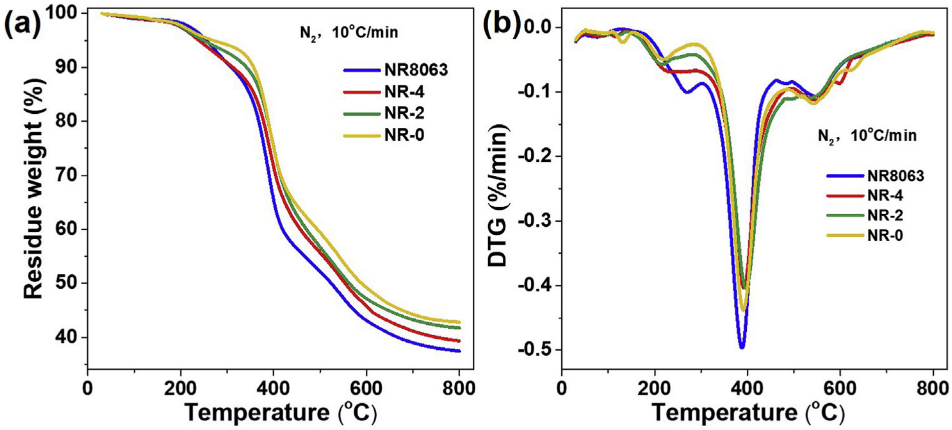


Fig. 8. TGA (a) and DTG (b) curves of NRs with different DHDM contents under a nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C.

Table 3
Thermal characteristic data of NRs with different DHDM contents, obtained from TGA and DTG curves.

Resin	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	R_{800} (%)	Weight loss (%)		
				First stage (222—300 °C)	Second stage (300—483 °C)	Third stage (483—600 °C)
NR8063	256.0	309.3	37.45	8.22	37.39	10.87
NR-4	239.7	312.7	39.33	7.90	33.90	12.22
NR-2	249.5	341.8	41.73	6.16	34.62	11.63
NR-0	270.5	357.0	42.79	4.57	33.54	12.32

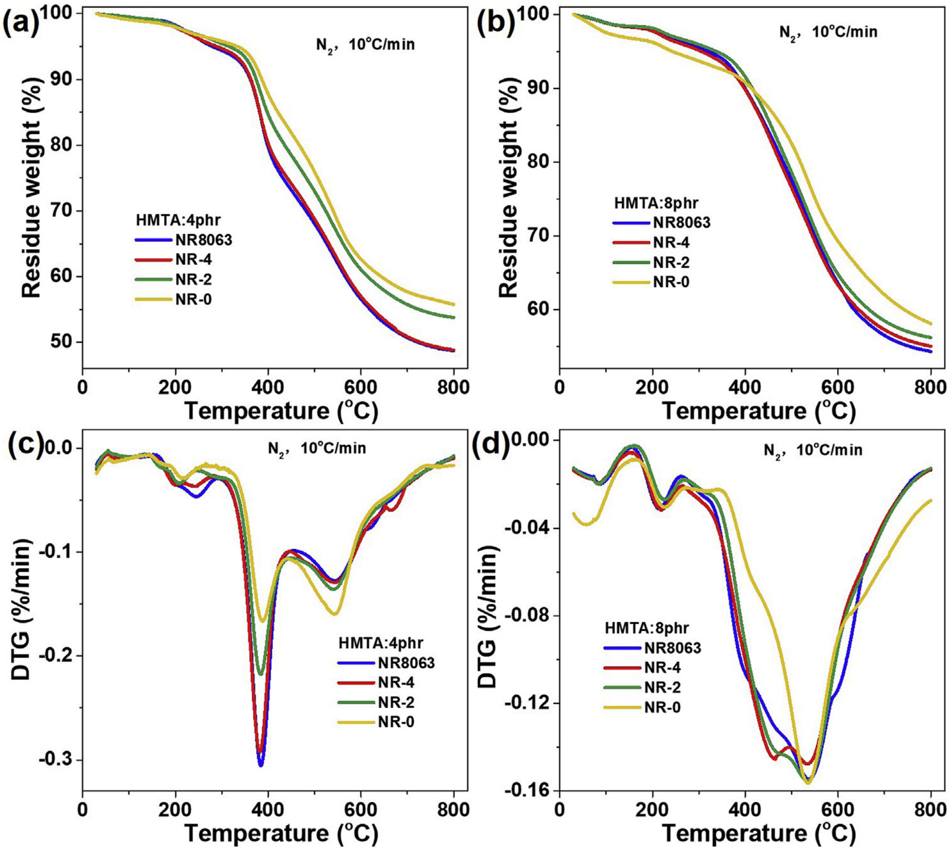


Fig. 9. TGA and DTG curves of NR8063 with different DHDM contents and cured by different amount of HMTA: (a) TGA curves of NRs cured by 4 phr HMTA; (b) TGA curves of NRs cured by 8 phr HMTA; (c) DTG curves of NRs cured by 4 phr HMTA and (d) DTG curves of NRs cured by 8 phr HMTA.

three kinds of NRs, thus NR3490 showed lower thermal stability. The results indicated that the conclusion obtained from NR8063 are also suitable for other industrial NRs.

In addition, the heating rate during TGA tests was 10 °C/min, which was different from the actual thermal pyrolysis environment. Therefore, the NR-0 without DHDMs was used to study the effect of heating rates in the thermal stability. As shown in Fig. S9 and Table S7, reducing heating rate only sped up the reaction progress without changing the reaction mechanism. When the heating rate was 2 °C/min, the $T_{5\%}$ and $T_{10\%}$ of NR-0 were 315.9 and 337.9 °C, respectively, decreased by 2.4 and 32.3 °C, respectively. There was little difference in the char yield at 800 °C for the NRs with different heating rates.

3.4. The effect of free DHDMs on the thermal stability of the cured NRs

The thermal stability of NR is critical for the performance of the cured resin, ultimately influencing the practical value for their application in the fields of aeronautics and aerospace [27]. The thermal stability of NRs with different DHDM contents that were cured with different amount of HMTA was studied.

As clearly revealed in Fig. 9 and Fig. 10, the thermal stability of NR was significantly improved after curing. At the same HMTA content, the cured NR-0 with the lowest DHDM content showed the highest thermal decomposition temperature and char yield at 800 °C. The trend was similar to that of the uncured NR. After cured by 4 phr

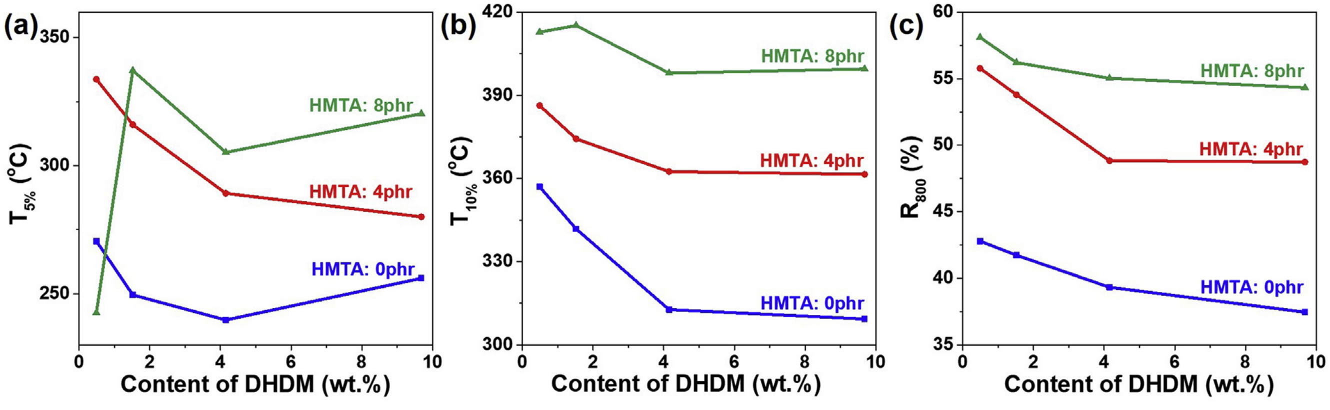


Fig. 10. Thermal characteristic data of NRs and cured NRs with different DHDM contents and different amount of HMTA: (a) $T_{5\%}$; (b) $T_{10\%}$; (c) R_{800}.

HMTA, the char yield of cured NR8063, NR-4, NR-2 and NR-0 were 48.74, 48.84, 53.79 and 55.78% (Table S5), respectively. It is believed that DHDMs were difficult to participate in the curing reaction in comparison with that of high molecular weight components in NR. As a result, DHDMs were easy to volatile during thermal pyrolysis of cured NRs. There was another situation that DHDMs were involved in the curing reaction, but they were grafted at the edge of the crosslinked network becoming the terminal groups, which were also easy to volatile when heating. It can be drawn that removing DHDMs from NR can fundamentally improve the thermal stability of the cured resin. Thus the present study provided important value for industrial production and application of PRs.

4. Conclusion

After 100 years, PRs are still a prominent resin using in a variety of fields that is superior to most other polymeric resin systems. An overlooked problem was that DHDMs were commonly existed in industrial NRs. The contents and kinds of DHDMs in different types of industrial NRs were different. DHDM, acted as a plasticizer, not only significantly reduced the viscosity and thermal stability of NRs, but also decreased the crosslinking density, T_g and char yield of the cured NRs. In this work, the contents and kinds of DHDMs in NRs were accurately quantified by LC and GPC, and almost few DHDM was contained after extraction. The processibility and thermal stability of NRs were significantly improved after removing DHDMs, especially the weight loss below 300 °C. As the volatilization of DHDMs took place below 300 °C, the presence of DHDMs increased the unstable terminal single C—C bond contents in NRs, leading to an obvious decrease in thermal decomposition temperature and char yield of NRs and cured NRs. Therefore, removing DHDMs from NR can fundamentally improve the processibility and thermal stability of NRs, its application scope could be expended when this structure optimization method was combined with other modification methods.

In the present paper, a method to remove DHDMs from NR was established. It is beneficial to manufacturing commercial phenolic resin with optimized structure and performance, especially high char yield. In order to promote the wide industrial application of this technology, it is urgent to develop a new purification process to remove DHDMs, or propose a new NR synthetic route to avoid the formation of DHDMs.

Supporting Information

Supporting Information is available from the Elsevier Online Library or from the author.

Additional experimental data and discussion (PDF).

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymdegradstab.2019.108946.

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