The influence of molecular structure on the thermal properties and processability of nitrile-based resin molecules

Chen Mengdi¹,a, Liao Wei¹,b, Yin Changping¹,c, Xing Suli¹,d, Ju Su¹,e*, Sheng Liping²,f*

¹Department of Materials Science and Engineering, National University of Defense Technology, Changsha, Hunan, China
²Department of Polymer Chemistry and Physics, Hunan Normal University, Changsha, Hunan, China
*aemail: chenmengdi_nudt
*b*Corresponding author: e*email: suju-nudt@nudt.edu.cn;
*f*email: shenglp@hunnu.edu.cn

Abstract: With the increase in the speed of various aircraft and the demand for lightweight weapons and equipment, the demand for high-performance, high-temperature-resistant resin-based composite materials has become more urgent. The temperature resistance and molding process of composite materials are determined by the temperature resistance and manufacturability of the resin, so there is an urgent need to develop a resin that has both high temperature resistance and excellent process performance. The temperature resistance and processability of the resin are essentially determined by the molecular structure of the resin system. Therefore, in order to design a resin system with excellent heat resistance and processability, the relationship between molecular structure and performance must first be recognized. This paper collects a large amount of experimental data and preliminarily summarizes the influence of different molecular structures on the thermal performance and resin processability of resin polymers from the perspective of structure and performance. This provides a good experience and theoretical basis for the design of high-performance resin systems, providing references and ideas for related research.

1. Introduction
Resin-based composite materials are widely used in various fields because of their high specific strength, high specific modulus, and strong designability [1]. In particular, in the field of weapons and equipment, as the military’s load ratio and flight speed of missiles, fighters, and other aircraft are further improved, the advantages of fiber-reinforced resin matrix composites in lightweight and high strength have become more prominent, with high performance, high temperature resistance, and low strength. The demand for cost-resin-based composite materials in the field of weapons and equipment has greatly increased [2]. The high-performance resin system that is resistant to high temperature and can be formed in the liquid phase at low temperature is the key to the development of advanced resin-based composite materials. Composite materials prepared by liquid phase molding have the advantages of low cost, good performance, one-time molding, and large-size components. It is the molding process with the best comprehensive indicators at present and the preferred low-cost molding process for composite materials preparation. Low temperature liquid phase molding requires resin has
the characteristics of low melting point and low viscosity \[3\].

However, it is difficult for the various high-performance resins currently developed to have the two excellent qualities of high temperature resistance and liquid phase molding at the same time \[4\,5\]. This is because the requirements of the two properties on the molecular structure are contradictory \[6\], leading to long-term checks and balances between the two, which severely restricts the development of advanced composite materials. Therefore, how to start with the molecular structure of the resin system and find the relationship between the molecular structure and thermal properties and manufacturability will help design new molecules with excellent thermal properties and molding processes at the same time \[7\,8\]. This article summarizes the influence of the molecular structure of the resin on the thermal properties, melting point and viscosity of the resin from a large number of previous works, which is expected to provide some references for related research.

2. The influence of molecular structure on the thermal properties of resin polymers

The thermosetting resin system is usually a multi-component organic molecular mixture, which is cross-linked and polymerized under appropriate external conditions to form a polymer. Therefore, the thermal properties of the polymer are closely related to the initial structure of the organic molecules that make up the resin. By summarizing the literature data, we can obtain the following more subtle cognitions.

2.1 The influence of the main chain structure on the thermal properties of resin polymers

Compared with single bonds, double bonds have higher bond energy and are not easy to rotate. Therefore, the temperature resistance of phthalonitrile resins containing double bonds in the main chain is higher than that of single bonds. For example, after curing at 375°C/8h, the T50% of the molecular polymer in Figure 1 is 510°C\[9\], and the T50% of the molecular polymer in Figure 2 is 500°C\[9\], so the molecule 1, containing double bonds, has relatively high temperature resistance. In addition, by observing 1 and 2, we can find that these two molecules both contain three ether nitrile segments, and the heat resistance is above 500 °C, which indicates that the molecules containing ether nitrile segments in the main chain have better temperature resistance.

Comparing molecules 2 and 3\[10\], we can find that after the same curing conditions, the T50% of the cured product is identical. Compared with molecule 3, molecule 2 is equivalent to introducing a carbon-carbon single bond and an oxyphthalonitrile group at the same time. As a result, the T50% of the
two molecules is basically the same, that is, after curing at 375°C/8h, the T5% of the polymer is 500°C, indicating that the negative influence of the introduction of carbon-carbon single bonds on the thermal stability of the molecule and the positive influence of the introduction of oxophthalonitrile groups on the thermal stability of the molecule can cancel each other out.

The introduction of aryl ether segments in the main chain will increase the heat resistance. For example, when n=2, the polymer’s T5% is 501°C, when n=4, the T5% of the polymer is 509°C, so the thermal stability of the cured product is slightly improved. Compared with the molecule in Figure 4 whose T5% is 475°C[11,12], the introduction of the aryl ether segment in Figure 5 improves the thermal stability of the molecule to a greater extent.

When a benzene ring is introduced into the main chain, since the benzene ring is a rigid structure, the heat resistance of the polymer will be improved. For example, after curing at 375°C/8h, the T5% in Figure 4 is 475°C, and the T5% in Figure 3 is 500°C[11,12], which shows that the introduction of the benzene ring structure increases the thermal stability. In particular, molecule 7 introduces a benzene ring on the basis of molecule 6. After cured at 225°C/1h. The T5% of the polymer of molecule 7 is 345°C, and the T5% of the polymer of molecule 6 is 417°C, relative to molecule 6, the thermal stability of molecule 7 is reduced[13]. Although molecule 6 and molecule 7 both contain autocatalytic phenolic hydroxyl group, the relative molecular mass of molecule 6 is smaller and the steric hindrance is smaller. The catalytic effect of the phenolic hydroxyl group is more obvious, so the degree of polymerization of the cured product is higher, which results in higher thermal stability.

When introducing bisphenol A aryl ether nitrile segment into the main chain, the longer the segment, the lower the thermal stability[14]. As shown in Figure 8, the phthalonitrile resin containing the bisphenol A aryl ether nitrile segment is all cured after 375°C/8h. When n=2, the polymer T5% is 512°C. When n=4, The polymer T5% is 509.45°C, and when n=6, the polymer T5% is 507.31°C, indicating that the increase in the value of n will lead to a decrease in the thermal stability of the polymer, but the decrease is not too obvious. The reason is that as the molecular chain length increases, the relative concentration of terminal nitrile groups will decrease, so the content of triazine rings polymerized from nitrile groups in the polymer also decreases, that is, the proportion of groups with excellent thermal stability decrease, so the stability of the cured product will also be reduced.

The introduction of phenylethynyl groups into the main chain of phthalonitrile is beneficial to improve the heat resistance of the polymer. For example, for 3PNODPA (Figure 9), after curing at 350°C/3h, the T5% of the polymer is 474°C. After the phenylethynyl group be introduced into the main chain, when cured under the same conditions. The T5% of 3PN3PEODPA (Figure 10) increased to
532°C, showing that phthalonitrile capped with phenylacetylene has higher heat resistance [15].

The introduction of dimethylmethylene in the main chain will increase the flexibility of the molecule and promote the movement of the chain segment at high temperatures, thereby reducing the thermal stability of the molecule. For example, for BPh (Figure 3) and BAPh (Figure 11), after curing at 375°C/8h respectively, T5% is 500°C [16] and 480°C [17], that is to say, the introduction of dimethylbutyl in the main chain of BPh (Figure 3) reduces the thermal stability by about 20°C; similarly, for the molecules in Figures 12 and 13 [15], after curing at 225°C/1h, T5% is 354°C and 325°C, respectively. For 2PEN-BPh (Figure 14) and 2PEN-BAPh (Figure 15), after curing at 375°C/8h, the T5% is 556.2°C and 509.45°C respectively [14], which shows that the introduction of dimethylbutyl group in the main chain will reduce the thermal stability of the molecule. And 2PEN-BAPh is equivalent to the introduction of two dimethyl butyl groups in 2PEN-BPh, so the thermal stability is reduced by two times compared to when there is only one dimethyl butyl group, indicating that the the introduction of groups has a superimposing effect on the reduction of thermal stability.

When the flexible group dimethylmethylene and the rigid group benzene ring are introduced into the main chain at the same time, as the molecules in Figure 17 and 18, after curing at 425°C, the T5% is 545°C and 550°C, respectively [18]; molecule 18 is equivalent to introducing these two groups into molecule 17 at the same time, and the final thermal stability is increased; similarly, the phthalonitrile resin containing phosphoroxy groups in the main chain shown in Figure 16 (Figure 16a), after curing at 375°C/8h, the T5% of the cured polymer is 490°C, when a benzene ring and dimethylbutyl group are added to the main chain, the T5% of 16 b is 495°C, so the stability has been improved [19]. The latter two examples both show that the benzene ring has a more obvious effect on improving the thermal stability of molecular polymers.
When the carbonyl structure is introduced into the main chain, the thermal stability of the molecule can be greatly improved. For the molecules corresponding to Figures 29 and 30, after curing at 250°C/6h, the T₅₀% is 544°C and 423°C, respectively [18, 20], it can be seen that compared with molecules containing dimethylbutyl in the main chain, carbonyl groups can greatly improve the thermal stability of polymer molecules. It also further illustrates that the introduction of dimethylethyl structure can reduce thermal stability.

When the phthalonitrile resin molecule contains a benzimidazole structure in the main chain, the temperature resistance of the molecule is higher, and the thermal decomposition temperature of the prepolymer is generally greater than 500°C. For example, if molecule 19 and molecule 9 are mixed according to 3:7 and 5:5 and cured at 375°C, T₅₀% will be 502°C and 511°C, respectively [21], so it can be roughly inferred that the T₅₀% of molecule 19 containing imidazole structure is greater than 511°C. The reason is that the imidazole structure is a rigid group, which can improve the heat resistance of the molecule; in addition, because the imidazole structure contains strong acidic proton hydrogen, it can catalyze the curing and crosslinking of the cyano group in the molecule to form a rigid triazine ring.
and phthalonitrile ring. Therefore, the thermal stability of the molecule is improved.

![Figure 21](image1.png)

**Figure 21** Structure of molecule 19

### 2.2 The influence of the introduction of side chains on the thermal properties of resin polymers

Methyl is a flexible group, and the introduction of methyl into the side chain will promote the movement of the molecular chain at high temperatures, thus reducing the thermal stability of the polymer. The molecules corresponding to Figures 31 and 32 [20], after curing at 250°C/6h, T5% are 450°C and 414°C respectively. Molecule 32 is equivalent to introducing two methyl side chains in molecule 31, resulting in the thermal stability of polymer molecules is greatly reduced.

![Figure 22](image2.png)  
![Figure 23](image3.png)

**Figure 22** Structure of molecule 31  
**Figure 23** Structure of molecule 32

Compared with the methyl side chain, the phthalonitrile containing trifluoromethyl side chain has higher heat resistance. For example, after curing at 375°C, BFPh (Figure 24) loses 0.7% weight at 343°C [22], and BAPh (Figure 11) loses 4% [16, 17]. The reason is that the bond energy of the CF bond is much higher than that of the CH bond, so the final polymer formed is more stable, and compared to hydrogen atoms, fluorine atoms can prevent oxidation at high temperature, so it has stronger temperature resistance.

![Figure 24](image4.png)

**Figure 24** Structure of molecule 20

The introduction of allyl groups in the side chain will reduce the thermal performance of the polymerized phthalonitrile resin. For example, after curing at 375°C, the T5% of BAPh (Figure 11) is 500°C [16, 17], after introducing the side chain allyl group in BAPh (Figure 12), the T5% of the formed DBPA-Ph (Figure 25) polymer is 477.8°C [16]. The reason is that the allyl group is a flexible chain and the polymer has no side chain. The chain can move to a higher degree and so it has lower thermal performance.

![Figure 25](image5.png)

**Figure 25** Structure of molecule 21

Substituting a benzene ring for the alkyl group in the side chain of phthalonitrile can also improve
the thermal stability of the resin correspondingly. As shown in Figure 26 and Figure 27, the glass transition temperature of the monomer of molecule 33 is 12°C, and the glass transition temperature of 34 monomer is 27°C [22].

The above mainly compares the influence of the introduction of different main chain and side chain groups on the thermal properties of the cured polymer on the basis of high temperature resistant phthalonitrile and its derivatives. From the above comparison, it can be seen that the introduction of double bonds, benzene ring, phenylacetylene, carbonyl, and benzimidazole in the main chain can all improve thermal stability, but the introduction of more bisphenol A aryl ether nitrile groups will make thermal stability slightly decreased. Compared with methyl side chain and allyl side chain, trifluoromethyl and side chain-free polymers are more thermally stable.

3. The influence of molecular structure on resin manufacturability

3.1 The influence of molecular structure on the melting point of resin

The melting process of polymer, from the perspective of thermodynamics, is an equilibrium process, so it can be described by the following thermodynamic function relationship: \( \Delta G = \Delta H - T \Delta S \). When in balance, \( \Delta H = 0 \), there is: \( T_m = \frac{\Delta H}{\Delta S} \), any molecular structure that is conducive to increasing the interaction force between molecules or between segments will increase \( \Delta H \) during the melting process, which will increase the melting point; when increasing the resistance to rotation within the polymer chain and making the polymer chain more rigid, then in the melting process, the conformational change is smaller, that is, \( \Delta S \) is smaller, and the melting point is also increased. For example, generally introducing a cyclic structure on the main chain, conjugated double bonds or introducing large rigid substituents on the side chain can achieve the purpose of increasing the melting point.

3.1.1 The influence of main chain structure on molecular melting point

The introduction of a cyclic structure into the main chain can increase the rigidity of the molecule, so that the conformation of the molecular chain changes less before and after melting, that is, the change is smaller, so the melting point is increased. As shown in Figure 21, the benzimidazole structure is introduced into the main chain, and the melting point of the molecule is 220°C, which is higher.

In the same way, the introduction of a benzene ring into the main chain, because the benzene ring is a rigid structure, which will also reduce the flexibility of the molecule, thereby increasing the melting point of the molecule. For example, the melting point of BDB (Figure 4) is 185°C, while the melting point of BPh (Figure 3) is 233°C [11, 12].

The introduction of ethylene groups in the phthalonitrile backbone will lower the melting point of the molecule. For example, the melting point of 3PNODPA (Figure 1) is 75°C. Compared with the vinyl group in Figure 1, the melting point of the formed 3PN3PEODPA (Figure 2) is less than 75°C [9].

The introduction of dimethylmethylene structure in the main chain will increase the flexibility of the molecule, so that the conformation of the molecular chain changes greatly before and after melting, that is, the change is greater, so the melting point is lowered. For example, the introduction of dimethylmethylene into the main chain of BPh (Figure 3) changes to BAPH (Figure 11), and the melting point decreases from 233°C [11, 12] to 195°C [16]; 2PEN-BPh (Figure 14) The melting points of PEN-BAPH and 2PEN-BAPh (Figure 15) are 140-150°C and 60°C, respectively [14]. Both of these examples show that the introduction of dimethylmethylene in the main chain will lower the melting point of the molecule. And compared to BPh (Figure 3) and BAPH (Figure 11), 2PEN-BAPH (Figure
15) is equivalent to introducing two dimethylmethylene groups in 2PEN-BPh (Figure 14), so the melting point is also reduced more than 80 degrees, indicating that the introduction of the group has an additive effect on the melting point reduction.

3.1.2 The influence of side chain structure on molecular melting point

The introduction of allyl groups in the side chain will greatly reduce the melting point of the phthalonitrile resin. For example, the melting point of BAPh (Figure 11) is 194-200°C, while DBPA-Ph (Figure 25), which is formed by the introduction of side chain allyl in BAPh (Figure 11), has a melting point of 122°C\textsuperscript{[16]}.

The introduction of a cyano group in the side chain will increase the melting point of the molecule accordingly. For example, for the molecule in Figure 28, the melting point is 226°C, while for the molecule in Figure 29 \textsuperscript{[23]}, the melting point is 236°C, compared to that in Figure 28, the melting point increased by 10°C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure28.png}
\caption{Structure of molecule 22}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure29.png}
\caption{Structure of molecule 23}
\end{figure}

3.1.3 The influence of other factors on molecular melting point

Generally speaking, the greater the relative molecular mass, the greater the intermolecular force, which increases during the melting process, and the higher the melting point. Therefore, molecules with a smaller relative molecular mass usually have a lower melting point. As shown in Figures 7 and 25 \textsuperscript{[24]}, the relative molecular masses of the two molecules are relatively small, and the melting points are generally low, 153.35°C\textsuperscript{[13]} and 134°C, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure30.png}
\caption{Structure of molecule 25}
\end{figure}

3.2 The influence of molecular structure on resin viscosity

3.2.1 The influence of main chain structure on resin viscosity

Compared with a single bond, the introduction of a double bond in the main chain will increase the viscosity of the monomer to a greater extent. For example, the viscosity of the molecule in Figure 1 is 58.8 Pa.s at 175°C, while the viscosity of the molecule in Figure 2 is 2.2 Pa.s at the same temperature \textsuperscript{[9]}.

The introduction of a cyano group into the side chain will increase the viscosity of the molecule correspondingly \textsuperscript{[23, 25]}. For example, for Figure 28, when the temperature is greater than 230°C, the viscosity of the molecule is less than 0.8 Pa.s, while for the molecule in Figure 29, the viscosity is less than 0.8 Pa.s only when it reaches about 245°C.

When the main chain contains a carbonyl group and a sulfoxide structure, the viscosity of the
molecule is relatively large, and the viscosity of the molecule containing the sulfoxide structure is smaller. The viscosity of the molecule corresponding to Figure 31 (n=1) \cite{25} is 15 Pa.s at 150°C, while the viscosity of the molecule in Figure 32 (n<1) \cite{26,27} is 255 Pa.s at 150°C. When the temperature is between 160-340°C, the viscosity of molecule 27 is less than 0.8 Pa.s.

When benzene ring and dimethylmethylenone are introduced into the main chain molecule at the same time, the viscosity of the molecule will be reduced. For example, when the temperature is between 160-340°C, the viscosity of molecule 27 is less than 0.8 Pa.s, and the lowest viscosity of molecule 28 is 6.2 Pa.s \cite{22} at a temperature of 212°C.

The introduction of aromatic ether segments into the main chain can reduce the melting temperature of the molecules to a greater extent. For example, when the viscosity of BDB (Figure 4) is 0.01-0.1 Pa.s, it needs to reach a temperature of 180°C. For n-PN (Figure 5), after the aromatic ether segment is introduced, when the viscosity is 0.01-0.1 Pa.s, the temperature is between 150-175°C, but when the aromatic ether segment is gradually increased, as the segment length increases, the viscosity will increase, but the increase is not too large. For example, when n=2, the viscosity of 2-PN at 160°C is 0.08 Pa.s, and when n=4, the viscosity of 4-PN at the same temperature increases by about 0.01 Pa.s relative to 2-PN \cite{11,12}.

Relatively more data can be collected and compared on the influence of small molecular structure on melting point. Here we mainly compare the introduction of phenyl, ethyl, allyl, nitrile, etc. on the basis of phthalonitrile and its derivatives. The effect on the melting point of the molecule. When it comes to the influence of small molecular structure on its melt viscosity, experimental data is relatively small, and there is no more systematic study. Here we roughly compare the effects of ethylene, vinyl, nitrile, sulfoxide, carbonyl, dimethylmethylenone, and aromatic ether segments on melt viscosity.

4. Conclusions
The analysis found that the introduction of rigid groups in the main chain, such as double bonds, benzene ring, phenylacetylene, carbonyl, benzimidazole, etc., can improve the thermal stability of the polymer \cite{28}, and the introduction of side chains will correspondingly reduce the polymerization. On the contrary, the introduction of a cyclic structure on the main chain, conjugated double bonds or the introduction of large rigid substituents on the side chain will increase the melting point and viscosity of the molecule \cite{28-30}. It can be seen that the thermal stability and manufacturability of the molecule are a pair of contradictions. In order to introduce certain groups to improve the thermal stability of the resin polymer, it will inevitably lead to the deterioration of the manufacturability of the resin. At present, the research method of high-performance resin matrix molecules is still based on experimental attempts, through experimental synthesis and performance testing to obtain molecules with target properties, and the lack of theoretical guidance \cite{31-33} will inevitably cause a waste of time and financial
resources. The data provided in this article is conducive to rational molecular design based on the relationship between molecular structure and performance, so as to quickly obtain a resin system with excellent temperature resistance and processability at the same time, this article provides a good basis for the research of high-performance resin-based composite materials.

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