

Synthesis and Characterization of Styrene, Maleic Anhydride and N-phenyl Maleimide Terpolymer

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Keywords: Terpolymer; characterization; thermal resistance; DSC/TG test

Abstract. A terpolymer resin (NSMA) was synthesized with styrene, maleic anhydride and N-phenyl maleimide. The structure and composition was characterized with FT-IR and ^{13}C -NMR. The thermal resistance of NSMA was determined through integrated thermal analysis. The results indicated that, when the molar ratio of N-PMI, St and MA was 1:3:1, the T_g , $T_{wt10\%}$, $T_{wt20\%}$, $T_{wt50\%}$, and T_{max} of NSMA was 227°C, 394°C, 409°C, 431°C and 434°C, respectively, much higher than those of styrene/maleic anhydride copolymer. Furthermore, the thermal resistance of NSMA increased with the content of N-phenyl maleimide. The results showed that NSMA had a favorable application prospect in the thermal resistance resin.

Introduction

With the excellent mechanical properties, dielectric properties, thermal stability and outstanding bonding ability, epoxy resin has been widely applied as coating, insulation materials, etc, in the electronic, electrical, mechanical manufacturing, aerospace and other fields, especially in the E-insulating material. However, with the development of printed circuit board (PCB), the demand on the thermal resistance of insulation material becomes severe^[1, 2], which the traditional epoxy resin could not meet. In recent years, scientists have modified the epoxy resin system with polyphenylene oxide (PPO), and have greatly improved the heat-resistance of the system^[3]. However, PPO is a thermoplastic resin, which needs thermosetting modification in the application. With the high cost and complex process in the modification, the application of PPO has been limited in the high-performance printed circuit boards^[4]. Styrene/maleic anhydride copolymer and styrene/maleimide copolymer also have favorable thermal resistance property^[5, 6], but still could not meet the demands of PCB. Therefore, it is significant to develop a new thermosetting resin which can be utilized in the high-performance PCB.

It is known that N-phenyl maleimide (N-PMI) has high thermal resistance^[7]. The molecule formula is shown in Fig.1.

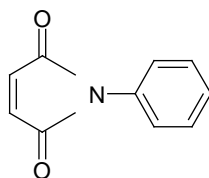


Figure 1 The molecular formula of N-PMI

There is a five-member ring in the N-PMI molecule. When it is embedded in a polymer chain, the internal rotation resistance of the chain would be increased, so does the thermal resistance of polymer^[8]. Moreover, N-PMI has the properties of non-toxicity, favorable compatibility^[9]. Thus, as a new heat-resistant co-monomer, N-PMI has attracted more and more attention.

In this study, N-PMI is introduced into the styrene and maleic anhydride copolymer system, to improve the thermal resistance of the system. The structure and composition of the product, a new N-PMI/styrene/maleic anhydride polymer (NSMA), is characterized by nuclear magnetic resonance,

infrared spectroscopy and elemental analysis. Further, the integrated thermal property is measured by DSC/TG. This work could explore the potential application of NSMA in the PCB.

Experimental

Materials

Maleic anhydride (MA), analytical grade, was obtained from Guangzhou Jinhuada Chemical Co., Ltd, China; styrene (St) and triethylamine, chemically pure, were obtained from Guangzhou Jinhuada Chemical Co., Ltd, China; benzoyl peroxide (BPO), analytical grade, was obtained from Guangzhou Reagent Factory, China; N-phenyl maleimide (N-PMI), chemically pure, were obtained from Guangzhou Reagent Factory, China.

Synthesis of NSMA

Solution polymerization method was adopted in this experiment. A mixed solvent of toluene/cyclohexanone (with a molar ratio of 1:1) was added into a 4-neck flask (fitted with a blender, funnel and thermomer), and then was heated to 90°C. A certain amount of reactant monomers (consisted of MA, St and N-PMI) were dropped into the solvent slowly, together with BPO (as the initiator). The dropping process was finished in 4-5 h, and then the reaction system was kept for 2h at 90°C. After the reaction was terminated, the liquid was deposited with large number of methanol (or ethanol) under quick mixing, so as white floc was precipitated. The floc was re-crystallized at least three times, and then dried at 50°C. The final result was NSMA. The copolymerization formula was as follows:

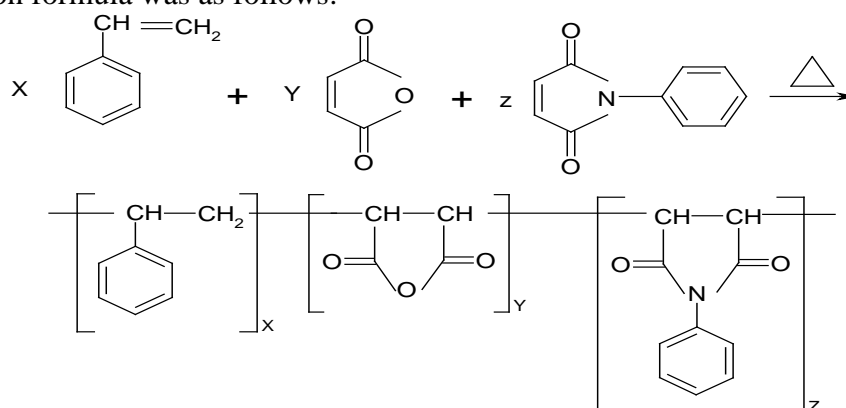


Figure 2 Scheme of copolymerization for NSMA

Infrared spectroscopy

The sample was compressed as a tablet with KBr, the test was carried under a Nicolet 5700 fourier transform infrared spectrometer (from Thermo Nicolet CO., US).

¹³C-NMR spectrum

Refined polymer sample was dissolved with acetone first. The ¹³C-NMR test of the sample was conducted with a picoSpin nuclear magnetic resonance spectrometer (from Thermo Fisher Scientific CO., US).

Integrated thermal analysis

A TGA/DSC1 integrated thermal analyzer (from Mettler-Toledo CO., Switzerland) was adopted to measure the DSC/TG curves of the polymer and the initial thermal decomposition temperature. The experimental conditions are as follows, protection atmosphere: high-purity N₂; ventilation rate: 20mL/min; heating rate: 10°C/min; reference: α-Al₂O₃.

Results and discussion

Infrared spectroscopy of NSMA

In the infrared spectra of NSMA (synthesized at a molar ratio of 1:3:1 (n(N-PMI):n(St):n(MA))), 1525cm^{-1} and 1625cm^{-1} is the vibration absorption of benzene skeleton; 1805cm^{-1} and 1737cm^{-1} is the absorption of C=O in MA unit and N-PMI unit; 1210cm^{-1} and 1409cm^{-1} is the adsorption of the pentagon of MA unit and N-PMI unit^[10]. In the spectra, there is no vibration absorption of C=C bond. From the above, it can be deduced that N-PMI has been introduced into the polymer.

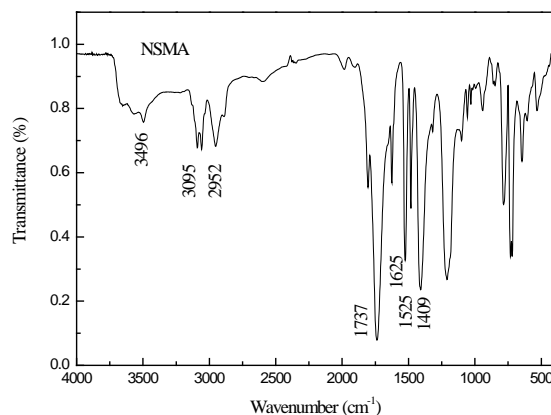


Figure 3 FT-IR spectrum of NSMA

^{13}C -NMR of NSMA

In the ^{13}C NMR spectrum of NSMA, the chemical shift of $\delta=179.224$ is the characteristic absorption of carbonyl in MA; $\delta=129.596$ is the characteristic absorption of the quaternary carbon in the benzene ring, and $\delta=127.658$ is that of the tertiary carbon atom. From the spectrum, it can be further confirmed that the sample is the copolymer of styrene, MA and N-PMI.

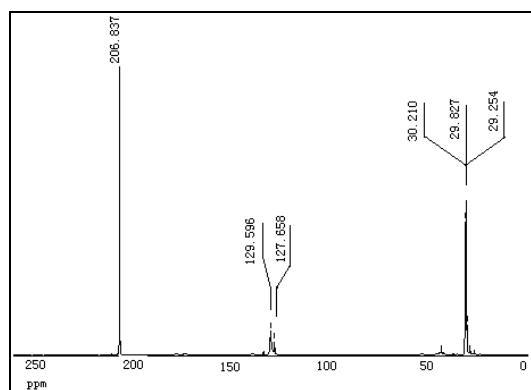


Figure 4 ^{13}C NMR spectrum of NSMA

The thermal resistance of NSMA

DSC test was conducted on NSMA; the results were shown as Fig.5. The control was SMA (synthesized at a molar ratio of 3:1 (n(St): n(MA))).

From the DSC curve, the T_g of NSMA is 227°C , higher than that of SMA by 106°C , indicating that the introduction of N-PMI increases the thermal resistance of the polymer obviously. The main reason is that the N-PMI molecule contains a five-member ring, with a 1, 2-double substituted ethenyl in the structure, which has a higher steric resistance. When N-PMI is introduced into the molecular chain of NSMA, the rotation of the molecule is restricted, and the internal rotation resistance of the chain is increased, resulting in the reduction of the flexibility of the molecule, and the increasing of the stiffness^[11]. Therefore, the thermal resistance of the polymer is increased.

It can be also seen that, there is only one plat in the DSC curve of NSMA, presenting that this material has only one glass transition temperature, which further indicates that NSMA is a homogeneous copolymer synthesized with N-PMI, St and MA, rather than a mixture.

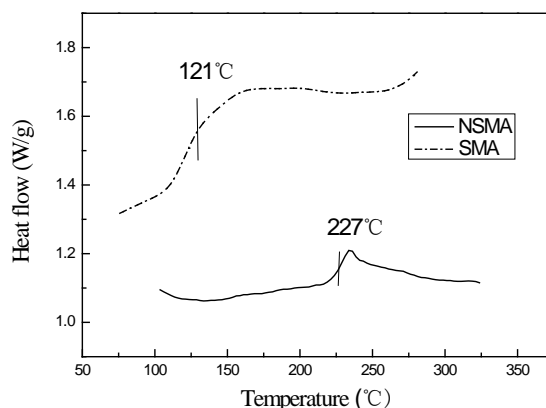


Figure 5 DSC test of NSMA

Fig.6 is the TG curve of NSMA and SMA. Temperature when material loses 10 wt%, 20 wt% and 50 wt% of its mass (marked as $T_{wt10\%}$, $T_{wt20\%}$ and $T_{wt50\%}$, respectively) and the temperature at the maximum weight-loss rate (T_{max}) are other important parameters indicating the thermal properties of materials. The results were listed in Table 1.

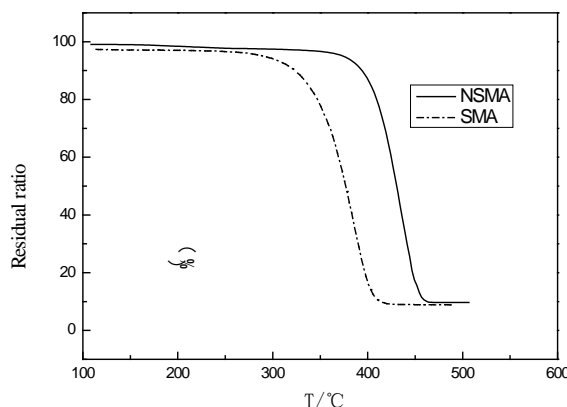


Figure 6 The residual ratio of NSMA as a function of temperature

From Table 1, the parameters of NSMA are all higher than those of SMA, especially for $T_{wt10\%}$, which is 71°C higher than that of SMA. When the material reaches the maximum weight-loss rate, the thermal decomposition temperature of NSMA is also 47°C higher than that of SMA. The reason is that the introduction of N-PMI increases the internal rotation resistance of the polymer molecule, resulting in the thermal decomposition curve of NSMA shifting to the direction of high temperature [12].

Table 1 $T_{wt10\%}$, $T_{wt20\%}$, $T_{wt50\%}$ and T_{max} of NSMA

Sample	$T_{wt.10\%}/^{\circ}\text{C}$	$T_{wt.20\%}/^{\circ}\text{C}$	$T_{wt.50\%}/^{\circ}\text{C}$	$T_{max}/^{\circ}\text{C}$
NSMA	394	409	431	434
SMA	323	347	375	387

Effect of N-PMI content on the thermal resistance of NSMA

Fig.7 showed the TG curves of NSMA with different N-PMI contents. From Fig.7, when the molar content of N-PMI is 11.1%, 20.0 % and 33.3%, the temperature at the maximum decomposition rate is 370°C, 387°C and 420°C, respectively. It also can be concluded that the

thermal stability of NSMA improves with the increasing content of N-PMI.

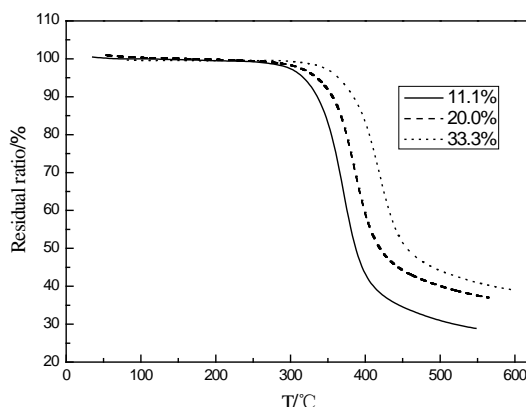


Figure 7 Effect of N-PMI content on the thermal resistance of NSMA

As for NSMA, the main factor of affecting the thermal properties is N-PMI, with a five-member ring in the molecular. The higher content of N-PMI, the larger the internal rotation resistance^[13], so the thermal stability of NSMA is higher.

Conclusions

1) A terpolymer(NSMA) was synthesized with solution polymerization method. FT-IR and ¹³C-NMR was applied to characterize the structure and composition. The results confirmed that NSMA is a homogeneous polymer.

2) The integrated thermal properties of NSMA were measured through DSC and TG test. The results indicated that when the molar ratio of N-PMI, St and MA was 1:3:1, the T_g , $T_{wt10\%}$, $T_{wt20\%}$, $T_{wt50\%}$, and T_{max} was 227°C, 394°C, 409°C, 431°C and 434°C, respectively, much higher than those of SMA. Furthermore, the thermal stability of NSMA increases with the content of N-PMI. As a result, the introduction of N-PMI enhances the thermal resistance of the system obviously. Thus NSMA has a favorable application prospect in the thermal resistance resin.

Acknowledgement

This research was financially supported by Hainan Natural Science Fund (No.20155202).

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