Mechanical, Heat-resistant, Crystallographic and Dynamical Mechanical Properties of Nylon 6/ P(N-phenylmaleimide-alt-styrene) Blends

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Abstract: In this work, nylon 6/ P(N-phenylmaleimide-alt-styrene) blends were prepared by melt blending, and the mechanical, heat-resistant, crystallographic and dynamical mechanical properties of nylon 6/ P(N-phenylmaleimide-alt-styrene) blends with different contents were investigated and analyzed. The results showed that the mechanical properties decreased with increasing PNS, while the heat deflection temperature (HDT), relative crystallinity (X_n), and storage modulus (G') increased with increasing PNS. The results of differential Scanning Calorimetry (DSC) proved the PNS played the positive role of nucleating PA6. And the results of dynamic mechanical analysis (DMA) proved the PNS could improve the rigidity of PA6/PNS blends. From the SEM, these PNS domains were between 0.2 and 4 μm in diameter. The experimental results indicated that the addition of PNS improved the rigidity of PA6/PNS blends, and then improved the heat-resistant property.

Keywords: Heat-resistant; Nylon 6; P(N-phenylmaleimide-alt-styrene); Blends;

1. Introduction

Nylon 6 (PA6) is a type of typical semi-crystalline polymer material[1-3] with wide applications in aerospace, electrical equipment, and automobile industry due to its properties, such as high toughness, high rate of crystallization, and high performance. However, PA6 has a relatively low heat resistance, compared with other high performance engineering plastics, such as Polycarbonate (PC), polyphenyl ether (PPO) and polyphenylene sulfide (PPS), which limits PA6's use in high-heat resistant applications such as automotive engines, fuel systems and electrical equipment. As a result, more and more researchers are interested in the research on the heat resistance of PA6. Lalit Guglani and and his co-works[4] studied the heat resistance temperature of PA66/TiO₂ composite and found that the heat-resistant temperature of PA66 was increased by 5℃ by the addition of TiO₂ of 6%. M. Kodal and his co-works[5] studied the heat-resistant temperature of PA6/Talc/Wollastonite composite and found that the heat-resistant temperature of PA6 was increased by 24℃ by the addition of 20Talc/20Wollastonite. Mária Porubskáand his co-works[6] studied the effect of electron beam irradiation on heat-resistant properties of virgin and glass fiber-reinforced polyamide 6 and found that the heat-resistant temperature of PA6 was increased by 9℃ by the effect of electron beam irradiation. Wei-Ming Peng and his co-works[7] studied the heat-resistant properties of PA6T/6/30%GF and found that the heat-resistant temperature was 293℃, but difficulty in processing. To sum up in conclusion, TiO₂, Talc, wollastonite and electron beam irradiation could improve the heat resistance of PA6. But the heat resistance of PA6 was not much improved.

In addition, N-phenyl maleimide (NPMI) copolymer as the commonly used polymer heat-resistant agent has been a hot topic of polymer synthesis. In order to improve the heat resistance and compatibility of the polymer materials, A variety of NMI monomers and their copolymer are designed   and synthesized. Jianting Dong and his co-works[8,9] have synthesized N-phenyl

maleimide(NPMI)-styrene(St)-maleic anhydride (MAH) (NSM) copolymer, and found that the Vicat softening point, tensile strength, flexural strength, flexural modulus, and Rockwell hardness of the ABS/ NSM blends were all significantly enhanced with increasing NSM content. M. Yuksel and his co-works[10] found that the glass transition temperature and thermal stabilities of the copolymers were increased by increasing the N-substituted maleimide (N-cyclohexylmaleimide) content. Last but not the least, Shantilal Oswal and his co-works[11] have synthesized CPMI/ MMA copolymer and CPMI homopolymer, and found CPMI enhanced the initial decomposition temperature of the copolymers. This is because the incorporated five member plannar cyclic structure in the chain of copolymer enhances the thermal stability of copolymer.4 The above literature shows that N-phenyl maleimide and its copolymers have played a positive role in improving the thermal stability and thermal stability of polymers. However, the heat resistance of nylon 6 *via* NPMI and their copolymers has to our knowledge not been reported. Enlightened by the above publications, we, therefore, synthesized the N-phenyl maleimide and its copolymers with styrene, in order that its copolymer could well improve the heat resistance of nylon 6.

In this paper, Nylon 6/ P(N-phenylmaleimide-alt -styrene) (PNS) blends are prepared by the melt-impregnation process. The static and dynamic mechanical properties, heat-resistant properties, crystallographic properties, and morphologies of blends are investigated in detail. The aim of this work is to evaluate the influence and mechanism of PNS on the heat resistance of nylon 6 to investigate the feasibility to improve the heat resistance of nylon 6/ PNS blends.

2. Materials and Methods

2.1. Materials

Nylon 6 (PA6) was purchased from Yueyang petrochemical co. LTD. The P(N-phenylmaleimide-alt -styrene) (PNS) was synthesized according to our research. It could be seen from supplementary materials.

2.2. Preparation of the Samples

PA6 and its blends were prepared by mixing PA6 and PNS in a two-screw extruder (TSE–40A, L/D = 40, D = 40 mm, Coperion Keya machinery, Co., Ltd., Nanjing China) at 200–240 ℃). PA6 and its blends were dried for 24 hours at 80 ℃ to remove water. Then PA6 and its blends were injection moulded (type CJ80M3V,Chen De Plastics Machinery Co., Ltd., Chengde, China) at 240 ℃ into various specimens for testing and characterization.

2.3. Measurements and Characterization

2.3.1. Mechanical Property Test

The tensile and bending strengths of samples were carried out on a tensile tester (type WDW-10C, Shanghai Hualong Testing Instrument Co., Ltd., Shanghai, China) with a speed of 100 mm/min (GB/T 1040.1-2008). Notched Izod impact strength was measured using a pendulum impact testing machine (type ZBC-4B, Xinsansi Measurement Technology Co., Ltd., Shenzhen, China). The radius of the notch used in the specimens was 2 mm (GB 1043-79). All of the tests were performed at 25 ± 2 ℃. The results were the average values of at least five specimens.

2.3.2. Heat Deflection Temperature (HDT)

Heat deflection temperature (HDT) measurements were performed on a Thermal Deformation Temperature Tester (USA. MTS ZWK1000). The measurements were carried out according to GB/T1634.1-2004, with pressure of 0.45 MPa and temperature rate of 120 ℃ h^{-1}.

2.3.3. Differential Scanning Calorimetry (DSC)

The DSC thermograms were carried out under nitrogen using a TA instrument Q10 for measuring non-isothermal crystallization and melting behaviours of the blends. Thermograms were recorded at a heating or cooling rate of 5 ℃/min in the second cycle from 40 ℃ to 260 ℃. The percent crystallinity was determined by dividing the heat of fusion value by the heat of fusion of 100% crystalline PA6 per the equation:

$$X_c = \frac{\Delta H_m}{(1-x)\Delta H_m^0}$$

where ΔH_m is crystallization enthalpy of the samples (J/g), ΔH_m^0 is the enthalpy value of the melting of a 100% crystalline form of PA6, which is 230 J/g[12]and x is the weight fraction of the PNS.

2.3.4. Morphology Observation

Scanning electron microscopy (SEM) images were obtained on a KYKY-2800B (Beijing Branch in the Bureau of Technology Development Co., Ltd.) to investigate the impact fracture of the samples, which were etched by tetrahydrofuran for 24 hours. SEM graphs of the blends were recorded after gold coating surface treatment, with an accelerating voltage of 10 kV.

2.3.5. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) measurements were performed on a Q800 DMA (TA Instruments, USA). The measurements were carried out at 1 Hz under a heating rate of 2 ℃ min^{-1}. The temperature range was from 25 ℃ to 120 ℃. and the high temperature measurements were carried out in a stream of dry N$_2$.

3. Results and Discussion

3.1. Mechanical Properties

The variation of the mechanical properties of PA6/PNS blends with different contents are displayed in Figure 1. From Figure 1, the tensile strength, bending modulus and impact toughness of PA6/ PNS blends, decrease with increasing PNS. The tensile strength of PA6/PNS blends (10%, 15%, and 20%) is decreased by 3.5%, 15.2% and 15.2%, compared with that of pure PA6 specimens. The bending modulus of PA6/PNS blends (5%, 10%, and 20%) is decreased by 4.4%, 5.3% and 19.6%, compared with that of pure PA6 specimens. The impact toughness of PA6/PNS blends (5%, 10%, 15% and 20%) is decreased by 8.4%, 15.5% 19.7% and 33.8%, compared with that of pure PA6 specimens. These results indicate that the mechanical properties decrease slightly with a small amount of PNS, but decrease obviously over 15% of PNS. It has been reported that heat-resistant copolymer of N-phenyl-maleimide (NPMI)–styrene (St)–maleic anhydride (MAH) could reinforce the mechanical properties of ABS[9]. Compared with those composites, the performance of PA6/PNS blends shows a distinct difference in the mechanical properties. Combining the following analysis with the electron microscope, due to its poor compatibilitywith PA matrix, phase separation during blending results in poor mechanical properties[8].

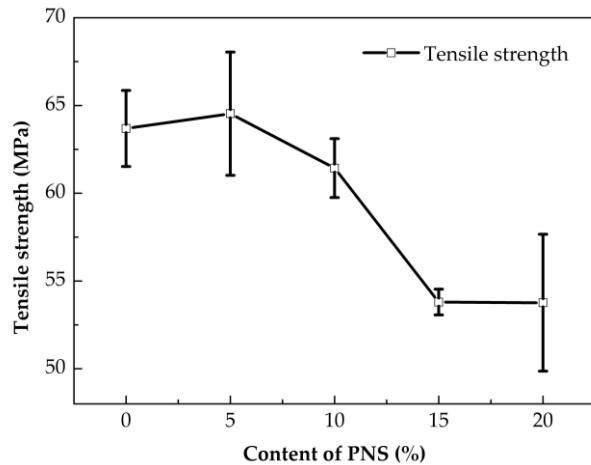
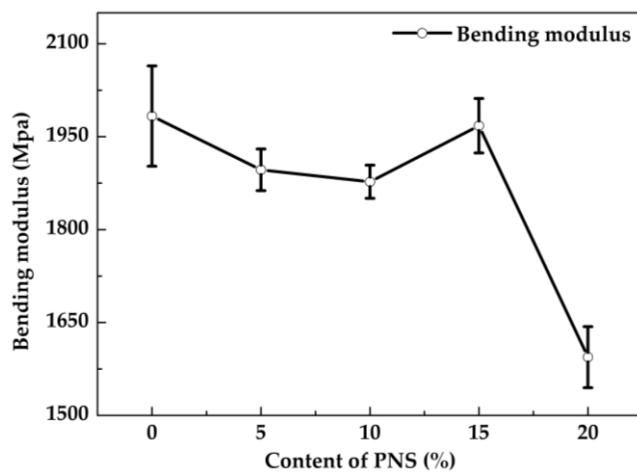
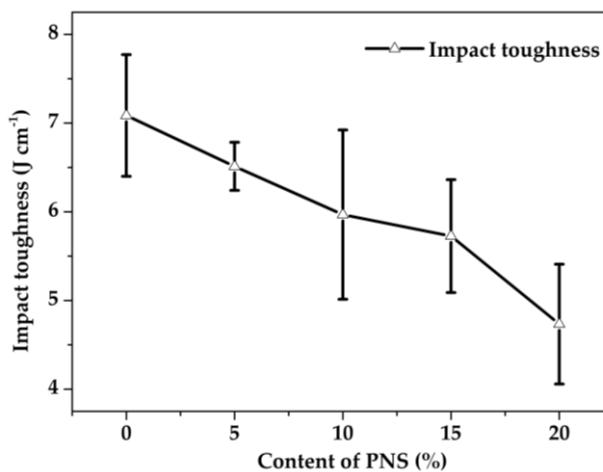



Figure 1. Mechanical properties of PA6/PNS blends with different contents: (a) tensile strength; (b) Bending modulus; (c) Impact toughness

3.2. Heat-resistant Properties

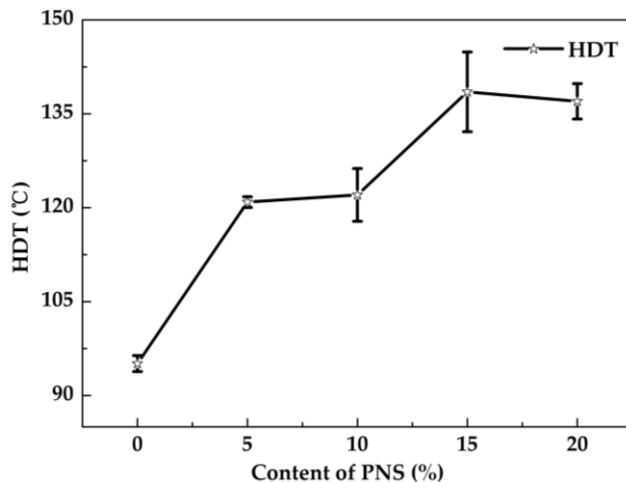



Figure 2 Heat deflection temperature of of PA6/PNS blends with different contents

Heat deflection temperature (HDT) is a widely employed parameter for quality control and material development in industry. It could be taken as the material's ultimate use point[13]. The measurement of HDT is shown Figure 2. The HDT of PA6/ PNS blends increase obviously with increasing PNS. The HDT of PA6/PNS blends (5%, 10% and 20%) is increased by 27.2%, 28.4% and 44.1%, compared with that of pure PA6 specimens. These results indicate that the HDT of PA6 was increased obviously by PNS. It has been reported that copolymer of N-phenyl-maleimide (NPMI)-styrene (St)-maleic anhydride (MAH)-alpha methyl styrene could reinforce the HDT of ABS[14]. Compared with those composites, the performance of PA6/PNS blends shows no difference in the heat-resistant properties. Many researchers have reported an NPMI-St copolymer with alternative chain structure with a T_g as high as 230.0 ℃ [15–17]. The polymer chain contains a five-membered planar ring and a strong polar carbonyl group; these hinder the rotation of the backbone chain and result in greater structural stiffness and higher heat-resistant Properties[9]. In order to study the heat resistant mechanism, in following, crystallization properties, morphology observation and dynamic mechanical properties were characterized.

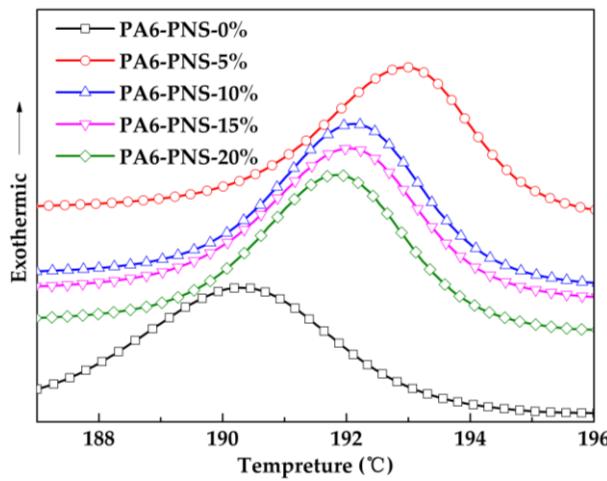
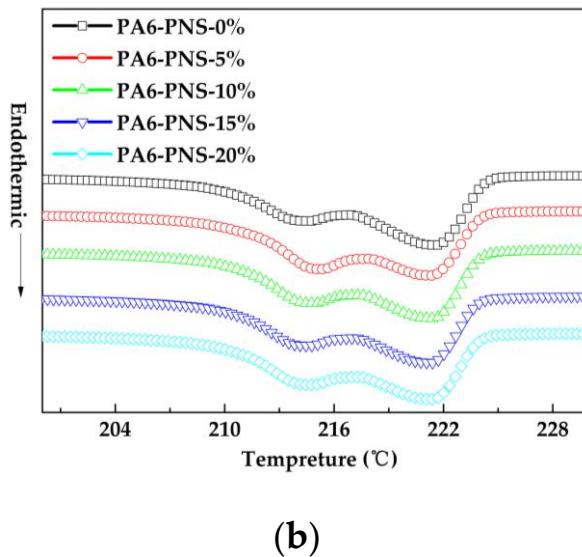
3.3. Crystallization Properties

(a)

(b)

Figure 3 DSC curves of PA6/PNS blends with different contents: (a) crystallization; (b) melting.

Table 1. DSC results of PA6/PNS blends with different contents

Samples	X_n(%)	T_0(°C)	T_p（°C）	T_0- T_p（°C）
0%PNS	23.05	195.68	190.32	5.36
5% PNS	23.00	197.53	192.94	4.59
10% PNS	23.88	196.76	192.15	4.61
15% PNS	26.19	196.19	191.82	4.37
20% PNS	29.15	196.44	192.04	4.4

Figure 3 (a), it is observed that the peaks change in the crystallization curves with different contents of PNS. Figure 3 (b) shows melting curves, which is used to calculate relative crystallinity (X_n.). It can be seen from Figure 3 (a) that plain PA6 has a single peak at about 190.3 ℃, whereas PA6/PNS blends are at about 192 ℃ or above. The specific onset crystallization temperature (T_0) and crystallization peak temperature (T_c) are shown in Table 1. X_n increase obviously with increasing PNS and T_0-T_c decrease slightly with increasing PNS. Those demonstrate that PNS play the positive role of nucleating PA6. As is known to all, crystallization can improve heat resistance of polymer. Therefore, PNS as the heterogeneous nucleating agent promote nylon 6 crystal, which is one of the reasons why PNS can be as heat-resistant to modify nylon 6.

3.4. Morphology Observation

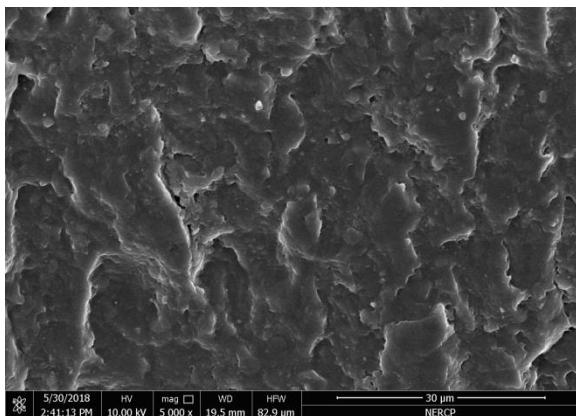
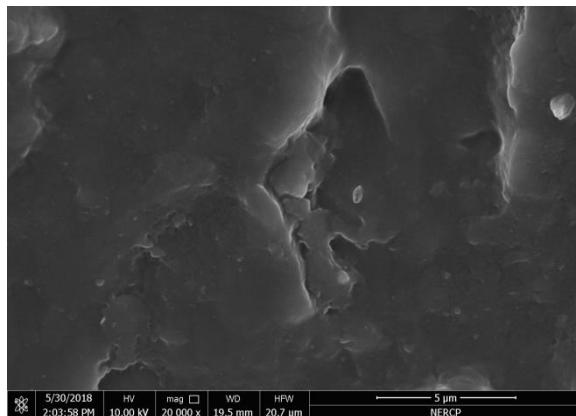
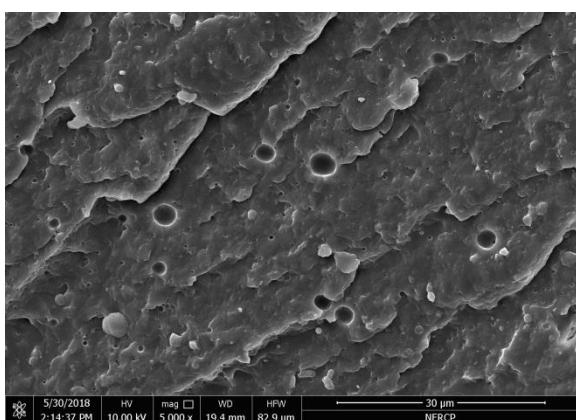
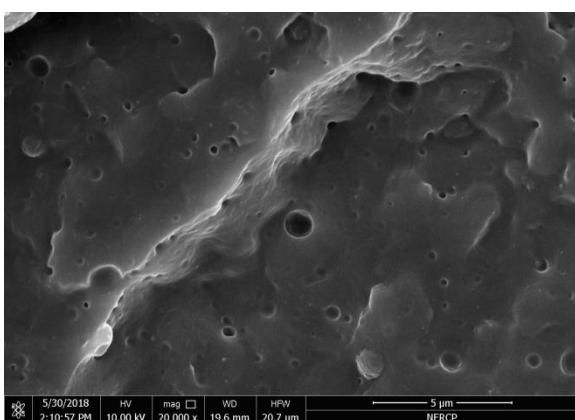
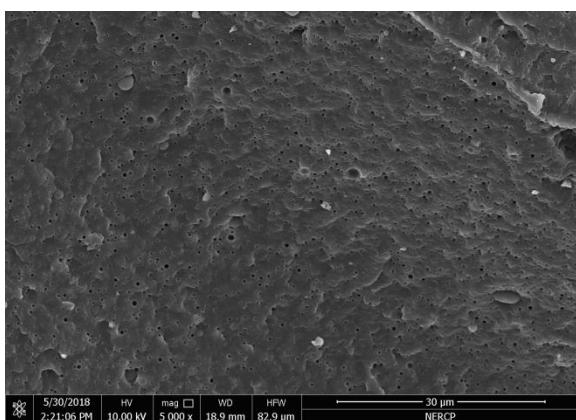
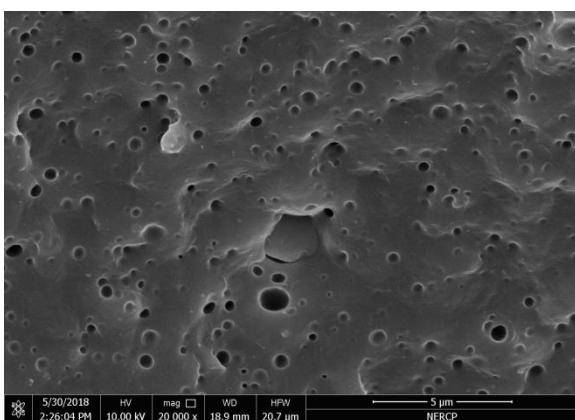
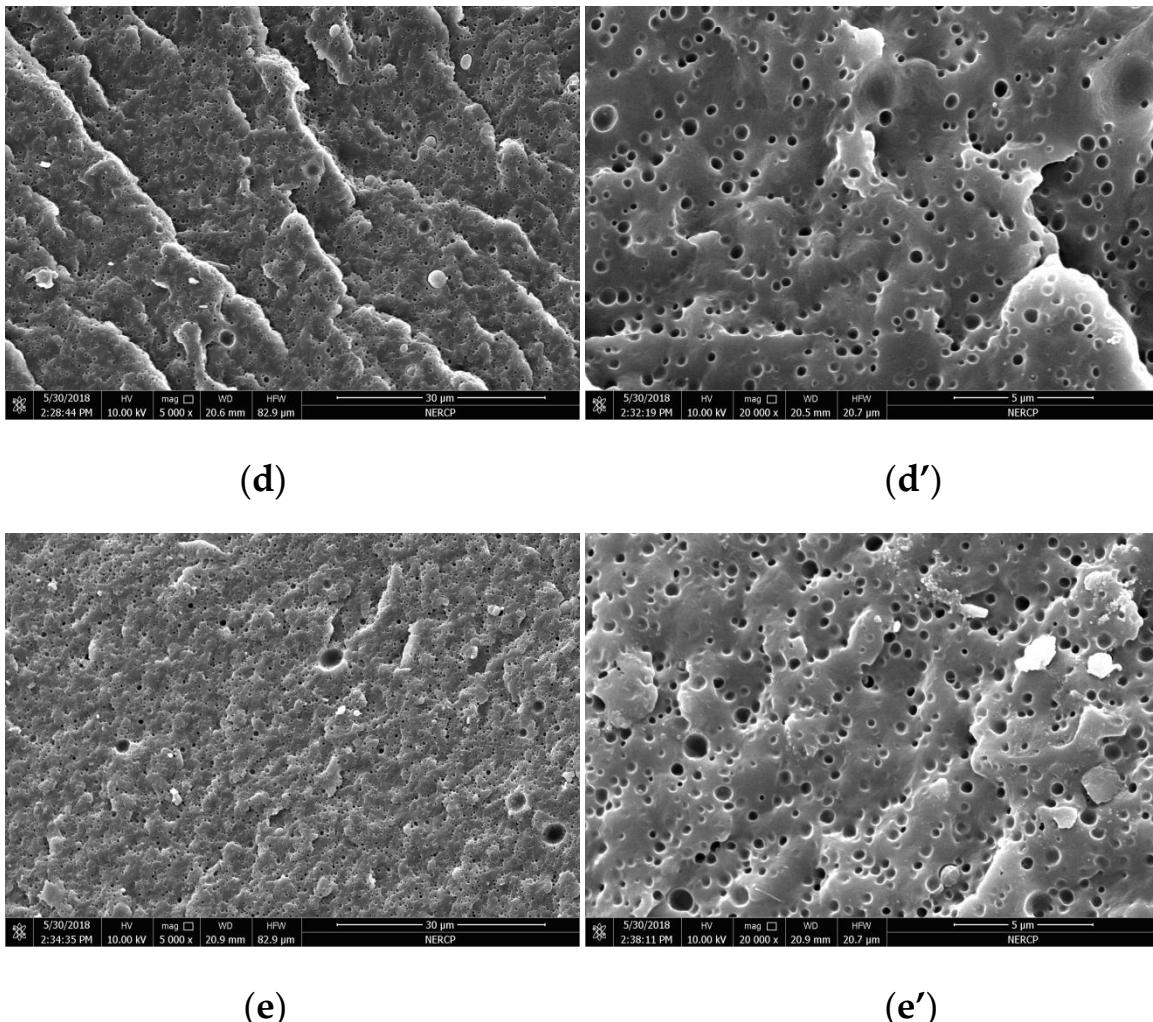



Figure 4 Morphology (5000 × and 20000 ×) of PA6/PNS blends with different contents: (a and a')
PNS 0%; (b and b') PNS 5%;(c and c') PNS 10%;(d and d') PNS 15%;(e and e') PNS 20%;.

The morphology of the etched cut surface of the PA6/PNS binary blends are shown in Figure 4. THF was used to dissolve the PNS fraction of the blend revealing the PA6 structure. In this blend PNS forms spherical domains uniformly dispersed in the PA6 matrix and the two-phase interface is clear. This phenomenon is consistent with our previous research[18]. These PNS domains are between 0.2 and 4 μm in diameter. This is due to lower viscosity of PA6 as compared to the PNS[19]. PNS spherical domains are dispersed in PA6, resulting in stress concentration. This may also explain the decline in mechanical performance.

3.5. Dynamic Mechanical Properties

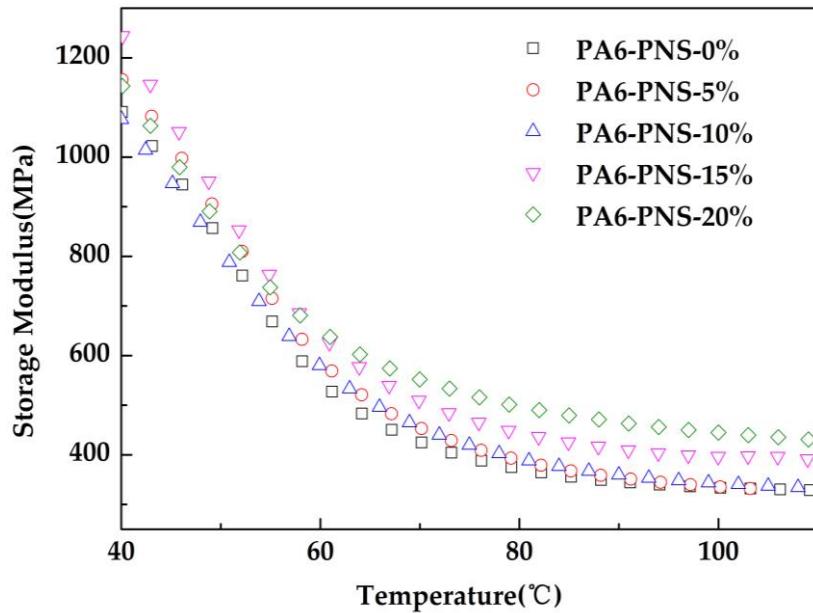



Figure 5. The DMA spectra of PA6/PNS blends with different contents.

DMA data for composites can provide the information about the glass transition temperatures of blends to give a better observation of the phase structure and interphase mixing of the blends[20,21]. Plots of the storage modulus (G') as a function of temperature for PA6/PNS blends with the frequency of 5 Hz are displayed in Figure 5 . In Figure 5, the magnitude of the storage modulus of PA6 and PA6/PNS blends decrease approximately linearly and then become constant as a function of temperature. But in the constant stage, the storage modulus increase with increasing PNS. This proves the PNS could improve the rigidity of PA6/PNS blends.

5. Conclusions

The mechanical, heat-resistant, crystallographic, dynamical mechanical properties and SEM of nylon 6/ P(N-phenylmaleimide-alt -styrene) blends are investigated in this work. The mechanical property decreases with increasing PNS, while the heat deflection temperature (HDT), relative crystallinity (X_n), and storage modulus (G') increase with increasing PNS. From the SEM, these PNS domains are between 0.2 and 4 μm in diameter. The experimental results indicate that the addition of PNS improve the rigidity of PA6/PNS blends, and then improve the heat-resistant property.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: ^{1}H and ^{13}C NMR spectra of NPMI in CDCl₃, Figure S2: ^{1}H and ^{13}C NMR spectra of P(NPMI-alt-St) in DMSO, Figure S3: FT-IR spectra of the synthesized NPMI and P(NPMI-alt-St).

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Conflicts of Interest: The authors declare no conflict of interest.

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