

Effect of Styrene on the Properties of Transparent Flame Retardant Unsaturated Phosphate Copolymer

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Abstract

The effect of styrene on unsaturated phosphate ester polymers was investigated. Copolymerization was carried out by adding different proportions of styrene when the unsaturated phosphate was polymerized to obtain an unsaturated phosphate-styrene copolymer. The structure and crosslink density of the copolymer was determined by fourier transform infrared (FTIR) spectra and gel fraction (G) testing. The heat resistance and flame retardancy of the polymer were tested by thermogravimetric (TGA) analysis, limiting oxygen index (LOI) and micro-combustion calorimeter (MCC). The infrared test proved that the styrene was successfully introduced into the polymer system. The gelation test results showed that the introduction of the rigid benzene ring increased the crosslink density of the copolymer. The tensile strength increased from 17.84 MPa to 34.63 MPa, and the impact strength remained stable within a certain range. At the same time, the solid ultraviolet absorption test results showed that the light transmittance of the materials was higher than 90%. The TG and DTG spectra showed that the heat resistance of the polymer was improved, but the residual carbon ratio was reduced from 30.47% to 25.54%. The LOI value decreased from 29.0% to 26.1%, and the UL-94 vertical burn rating was all V-0.

Keywords

Flame Retardant, Phosphate Ester, Strength, Styrene

1. Introduction

The transparent polymer mainly refers to a polymer material having a light

transmittance (wavelength between 400 nm and 800 nm) of not less than 80% in the visible light range. Due to its good transparency, such material is widely used in interior decoration, food packaging, instrument casing packaging, biomedical, window glass and toy manufacturing, etc. [1] [2] [3] [4]. A wide range of applications has certain requirements on the performance of polymer materials. Since most of the polymers are composed of carbon and hydrogen, they are easily burned and may release toxic gases [5]. Therefore, flame retardancy and heat resistance are important indicators of polymer properties.

Flame retardants are mainly divided into four categories, halogen flame retardants, silicon flame retardants, nitrogen flame retardants and phosphorus flame retardants. Among the commonly used flame retardants or flame retardant materials, halogen flame retardants are the most used additives and have been developed for many years, but they are easy to release toxic gases when burned and decomposed, which seriously violate the principle of environmental protection [6] [7]. Therefore, in recent years, environmentally friendly flame retardants are regarded as the focus of development by the researchers. Silicon, nitrogen and phosphorus flame retardants are rapidly developing due to their environmental friendliness. Silicon-based flame retardant system is a new type of halogen-free, low-smoke, low-toxic, anti-droplet environment-friendly flame retardant material [8] [9]. It can not only impart excellent flame retardancy to the material, but also improve the mechanical properties and heat resistance of the material [10] [11]. However, due to the semi-crystalline structure of the silicon system, the transparency of the material is greatly reduced. Nitrogen-based flame retardant has low smoke, low toxicity and environmental friendliness [12], but its flame retardant effect is not very excellent, so it is necessary to combine with a phosphorus-based or silicon based flame retardant to form a synergistic effect, and the synergistic system can have more excellent flame retardant effect [13] [14]. Phosphorus flame retardants have been rapidly developing in the last three or four decades due to their properties of low smoke, low toxicity, corrosion resistance and environmental friendliness, and are becoming the current mainstream flame retardant system [15] [16]. Although the flame retardant effect of the phosphorus-based flame retardants is good, the lower mechanical properties have become a limitation of their development. Maintaining or even improving their mechanical properties while improving flame retardancy has become a major challenge in flame retardant research.

Polymer-enhanced methods include nanomaterial filling [17] [18], interpenetrating polymer networks [19] [20] [21] and copolymerization [22] [23] [24]. Among them, copolymerization is a method that is now more common in applications. Liu [25] *et al.* have achieved certain results in the phosphorus-based flame retardant system, and prepared an unsaturated phosphate ester with excellent flame retardant properties and transparency. However, the mechanical property of this transparent polymer material is not good enough. Styrene has

high activity in the molecule itself due to its C=C structure, and bulk polymerization is easy to occur. The presence of the benzene ring structure makes the polymer molecular chain rigid and can increase the strength of the polymer to some extent. This experimental design is to form unsaturated phosphate-styrene copolymer by copolymerization of styrene into unsaturated phosphate system, and to discuss the related properties.

2. Experimental Preparation

2.1. Experimental Material

Triethyl phosphate (TEP. Product of Sichuan Cologne Chemical Co., Ltd. Analytical grade), Ethylene glycol (EG. Product of Sichuan Cologne Chemical Co., Ltd. Analytical grade), α -Methylacrylic acid (MAA. Product of Sichuan Cologne Chemical Co., Ltd. Analytical grade), Styrene (St. Product of Sichuan Cologne Chemical Co., Ltd. Analytical grade), p-Toluenesulfonic acid (TsOH. Product of Sichuan Cologne Chemical Co., Ltd. Analytical grade), Azobisisobutyronitrile (AIBN. Product of Sichuan Cologne Chemical Co., Ltd. Analytical grade). Styrene needed to be purified by vacuum distillation before use. Others were used without any additional purification.

2.2. Preparation of Unsaturated Phosphate-Styrene Copolymer

The synthesis of trihydroxyethyl phosphate ester (THPE) and tri (2-methacrylateethyl) phosphate ester (UPE) was completed by the method of Liu *et al.* [1]. Pure UPE polymer (PUPE) was prepared by bulk polymerization, and the method is as follow. First, 90 g of UPE was weighed into a 250 mL Erlenmeyer flask with a magnetic stirrer, and then the Erlenmeyer flask was placed in an oil bath whose temperature was set to 65°C. AIBN was added to the Erlenmeyer flask when the oil bath temperature was up to 65°C and the AIBN's mass was 0.5% of the UPE. After that, the reaction system was kept at 65°C for 2 hours. The temperature of the oil bath was then lowered to 60°C, and small molecules and bubbles in the liquid were removed by a vacuum pump. Then the prepolymer was poured into a homemade glass mold, and the glass mold was put into an oven whose temperature was setted to 50°C, once the polymerization is complete, set the oven temperature up to 80°C, for 2 hours. Then let the oven down to room temperature naturally, and we can get the polymer. The resulting polymer is cut into suitable splines for transparency test, mechanical properties test and flame retardant test.

To study the effect of styrene on polymers, we added styrene in different amounts (10 wt%, 15 wt%, 20 wt%, 25 wt%) of pure UPE and named Poly(UPE-co-St). The preparation method of Poly(UPE-co-St) is basically consistent with PUPE. When the reaction temperature reached 65°C, add St with a burette. The other steps are the same as the preparation of PUPE.

2.3. Characterization.

Fourier transform infrared (FTIR) spectra were recorded with a NICOLET6700 (Waters Corporation) at $4000 - 400 \text{ cm}^{-1}$. Thermogravimetric analysis (TGA) was carried out by using a TGAQ500 (Waters Corporation) from 25°C to 600°C at a linear heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. The weight of each sample was about 5 mg. Dynamic mechanical analysis (DMA) of sample was conducted on a TA Q800 equipment (U.S.A.) at a fixed frequency of 1 Hz from -20°C to 200°C at a linear heating of $5^\circ\text{C}/\text{min}$ under nitrogen. Transmittances of PUPE and poly(UPE-co-St) copolymers (3 mm thick) were measured by using a solid ultraviolet absorption spectrometer with Solidspec-3700. Limiting oxygen index (LOI) measurement was carried out at room temperature on a JF-3 LOI meter according to standard ASTM D2863. And the sample dimensions were $100 \times 6.5 \times 3 \text{ mm}^3$. Vertical burning (UL-94) tests were performed on a CZF-2-type instrument according to the testing procedure GB/T 2408, and the sample dimensions were $130 \times 13 \times 3 \text{ mm}^3$. The scanning electron microscope (SEM) tests were performed with a TM-1000 to examine the morphology of the char residues after LOI test and the surface of char residues was sputter-coated with a gold conductive layer.

3. Results and Discussion

3.1. Synthesis of Poly(UPE-co-St) Copolymers

Figure 1 shows the FTIR spectrum of UPE, PUPE, and copolymer UPE + St 20%. Since the poly(UPE-co-St) series has a similar structure, FTIR characterization is represented by UPE + St 20% to illustrate the entire copolymer series. The main characteristic absorption peak of UPE is C-O-C, -CH₃, C=C and C=O at 1299 cm^{-1} , 2981 cm^{-1} , 1634 cm^{-1} and 1718 cm^{-1} respectively, all of which are attributed to the acrylate groups present in the molecular chain. However, no C=C characteristic absorption peak was found in the spectrum of PUPE and UPE + St 20%. This phenomenon indicates that bulk polymerization occurs between the UPE monomer itself or with St, and making C=C form an active

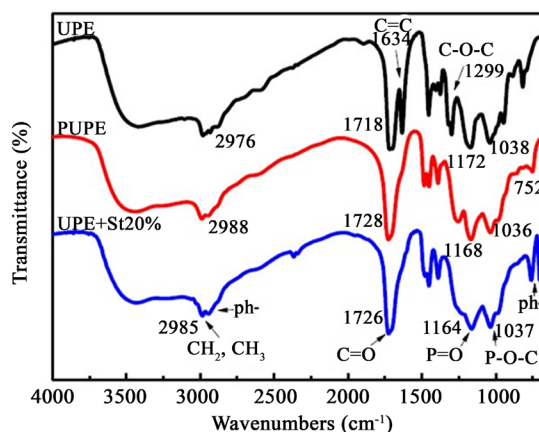


Figure 1. The FTIR spectrum of UPE, PUPE, and UPE + St 20%.

group under the action of initiator to carry out molecular chain recombination. Finally, polymer macromolecule is formed by chain reaction. As can be seen in the PUPE and UPE + St 20% spectra, the peak shape of UPE + St 20% varies between 1490 cm^{-1} and 1470 cm^{-1} . The $-\text{CH}_3$ bending vibration of PUPE at 1484 cm^{-1} was transformed into the vibration of the benzene ring skeleton at 1477 cm^{-1} , and the out-of-plane bending vibration of the monofunctional benzene ring appeared between 700 cm^{-1} and 765 cm^{-1} . It means that the benzene ring structure was successfully introduced into the polymer PUPE.

The crosslinked network structure of the copolymer poly(UPE-co-St) is shown in **Figure 2**. And **Figure 3** shows the gel change curve of the poly(UPE-co-St) series. Depending on the insolubility of the crosslinked portion of the copolymer in an organic solvent, this test selected the THF test poly(UPE-co-St) gel degree. As can be seen from **Figure 3**, with the St content increasing, the gel fraction of the polymer increases, indicating an increase in the degree of cross-linking of the polymer. The proportion of pure PUPE in the undissolved part of THF was 79.9%, and the undissolved part of poly(UPE-co-St) increased significantly after adding St. In detail, as the St content increased from 0 wt% to 25 wt%, the gel fraction increased sharply from 79.9% to 85.9%. The results show that the chain transfer occurs when the benzene ring is introduced into the polymer PUPE by bulk polymerization, which forms a more excellent cross-linking structure, indicating that the participation of the rigid chain of the

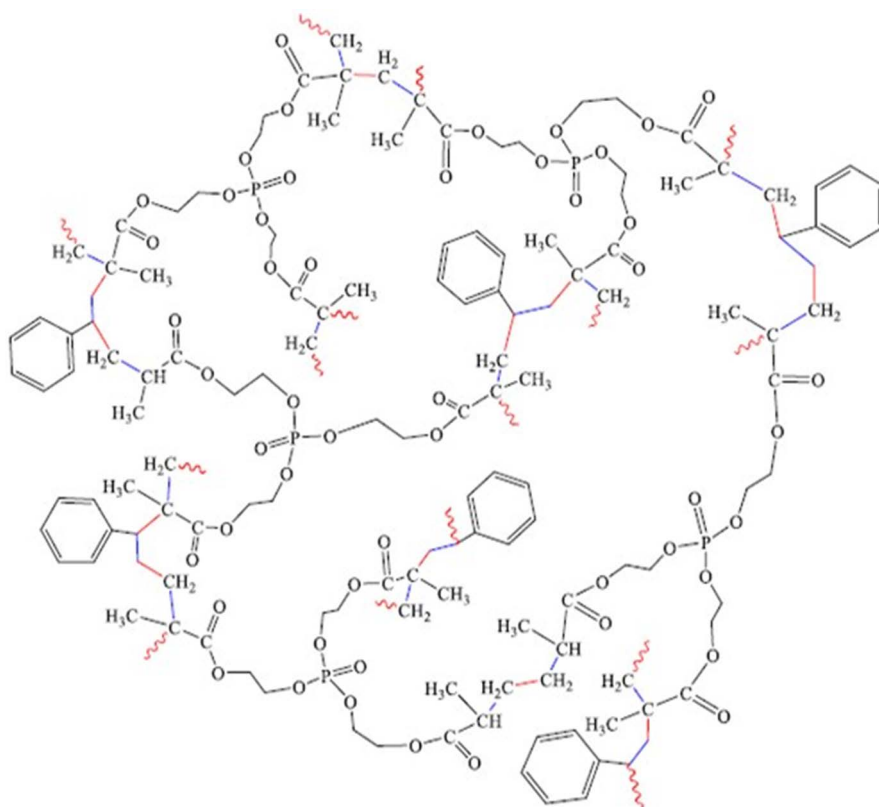


Figure 2. Cross-linking network structure of poly(UPE-co-St) copolymers.

benzene ring can increase the crosslinking density of the PUPE.

3.2. Thermal Stability of Poly(UPE-co-St) Copolymers

Figure 4 shows the TGA (a) and DTG (b) spectra of UPE and poly(UPE-co-St) in nitrogen, with a temperature change from 25°C to 600°C. The corresponding data is shown in **Table 1**. It can be seen from **Table 1** that the addition of styrene increases the initial decomposition temperature ($T_{0.1}$) of PUPE. This proves that the addition of St can improve the thermal stability of the polymer. With the

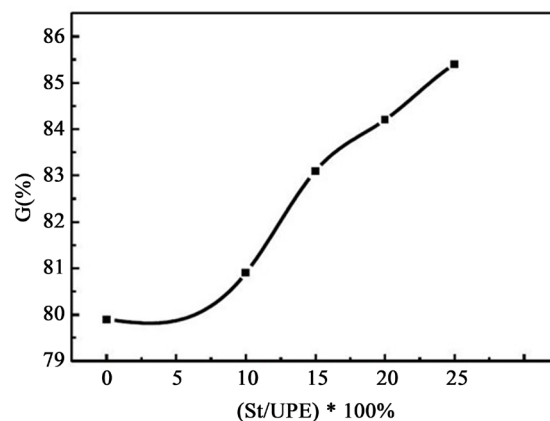


Figure 3. The gel fraction of poly(UPE-co-St) copolymers.

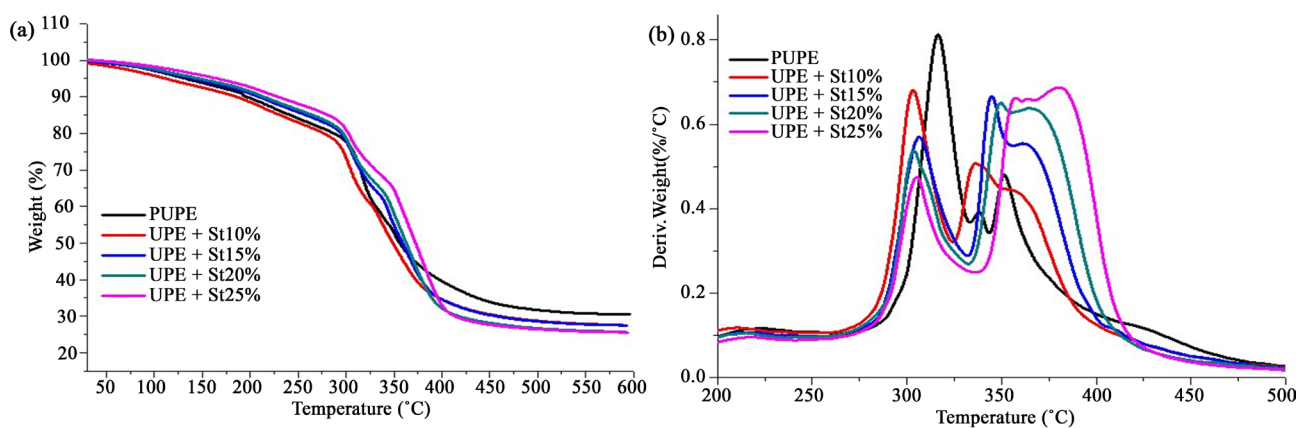


Figure 4. TGA (a) and DTG (b) curves of poly(UPE-co-St).

Table 1. TGA and DTG data of poly(UPE-co-St) copolymers.

sample	$T_{0.1}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$			Chr/wt% (600°C)
		Stage 1	Stage 2	Stage 3	
PUPE	204.31	220.87	316.84	351.47	30.47
PUPE + St 10%	206.11	218.67	310.60	358.60	27.59
PUPE + St 15%	211.83	218.57	308.94	364.42	27.47
PUPE + St 20%	218.16	218.33	307.26	368.51	25.74
PUPE + St 25%	230.10	218.26	306.47	381.27	25.54

increase of temperature, the TGA curve appears intersection at 350°C - 400°C, which means that the decomposition rate is significantly higher than PUPE after adding St. With continuous increase in temperature, the quality of the copolymer is no longer reduced, and the residual carbon ratio of the copolymer exceeds 25.54 wt% at 600°C, and the residual carbon ratio of PUPE even reached 30.47 wt%. The result shows that the addition of St can improve the thermal stability of the copolymer, but reduce the residual carbon ratio.

From the analysis of the DTG (b) spectra, it can be seen that the poly(UPE-co-St) decomposition is divided into three stages, and the corresponding three-stage temperature table is shown in **Table 1**. The first stage occurs at 170°C to 250°C. At this point, reaction is between the residual water molecules in the copolymer network and the unreacted monomer small molecules. The second stage occurs at 285°C to 335°C. This is due to the fracture decomposition of the acrylic-based side chain in the copolymer network and the formation of the carbon layer. The third stage occurs at 340°C to 420°C and it is caused by the cleavage of the benzene ring during the decomposition of the copolymer and the formation of an unstable carbon layer [2] [3]. And it can be seen from **Figure 4** that PUPE and UPE + St reach the maximum thermal weight loss rate in the second stage, while other copolymers reach the maximum heat loss rate in the third stage. The cross-linking density of PUPE and UPE + St 10% copolymers is low, and the molecular chain movement of the materials is intense when heated, which accelerates the decomposition rate in the second stage. However, the cross-linking density of other samples is so large that the decomposition rate reaches the maximum value in the third stage, which indicates that the introduction of the benzene ring slows down the decomposition rate of the polymer at lower temperatures and improves the thermal stability of the material. The above results show that with the introduction of St, the thermal stability of the polymer can be improved, but with the St content increasing, the char formation rate decreases, which affects the flame retardant effect of the material. It is worth noting that when the St content is increased to 25%, the carbon residue rate still exceeds 25 wt%. Therefore, with the introduction of St, poly(UPE-co-St) has good thermal stability.

Figure 5 shows the DMA spectrum of poly(UPE-co-St) and PUPE. Here, the dynamic mechanical properties and glass transition temperature T_g of the copolymer are characterized by the storage modulus E' and the loss factor $\tan \delta$. **Figure 5(a)** shows the logarithmic value ($\lg E'$) of the storage modulus as a function of temperature. As can be seen from this figure, the storage modulus of each sample hardly changed at low temperature after the addition of St, but after 50°C, the storage modulus of the copolymer increased with the increase of St content. The introduction of the benzene ring enhances the ability of the molecular chain to store energy, which proves that as the St content increases, the mobility of the segment and the free volume of the molecule is reduced. **Figure 5(b)** shows the curve of $\tan \delta$ with temperature. There is a wide peak at 60°C ~

140 °C, the highest point of the peak represents the respective T_g . It can be clearly observed from the figure that with the increase of St content, the T_g of the copolymer gradually increases. The T_g of copolymers are 95.4 °C, 97.5 °C, 99.2 °C, 100.8 °C, and 101.7 °C, respectively. This is because the introduction of the benzene ring leads to an increase in the crosslink density of the copolymer, a decrease in the chain motion of the molecule, and an increase in the internal frictional resistance. The above results prove that the introduction of the benzene ring can increase the crosslink density of the copolymer and improve the T_g .

3.3. Transparency and Mechanical Property of Poly(UPE-co-St) Copolymers

Figure 6 depicts the transmittance of the poly(UPE-co-St) series as measured by the Solidspec-3700 solid-state UV absorption spectrometer as a function of wavelength.

The graph shows the transmittance of poly(UPE-co-St) samples at visible

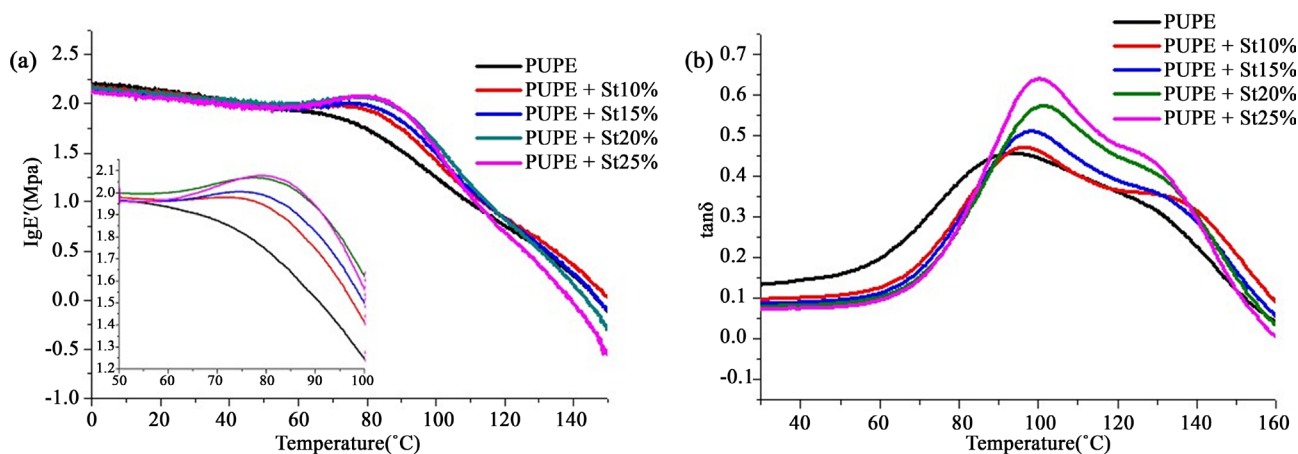


Figure 5. DMA of poly(UPE-co-St) copolymers under nitrogen.

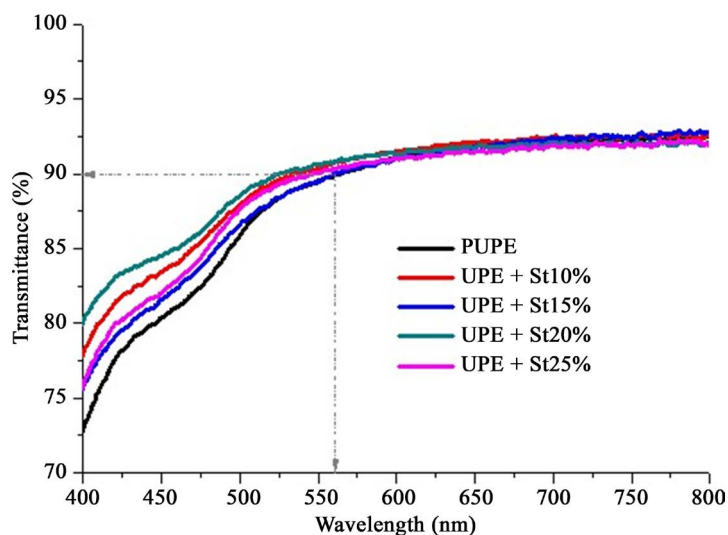


Figure 6. Transparency test curves of poly(UPE-co-St) copolymers.

wavelengths (400 nm to 800 nm). At a wavelength of 561 nm, the transmittance of each sample is mostly higher than 90%. When the wavelength is 700 nm, the transmittances of the samples are 92.3%, 92.5%, 92.4%, 92.1%, and 91.8%, respectively. We can see that after the introduction of St, the transparency of the copolymer is slightly increased and then decreased compared with pure PUPE. This is because the introduction of the benzene ring changes the helical structure of the polymer chain. It can be seen from the DMA spectrum that each sample has only one $\tan \delta$ peak. These analysis results indicate that poly(UPE-co-St) is a homopolymer having a random helical structure and is excellent in transparency.

Figure 7 shows the tensile strength σ_t and impact strength σ_k of the copolymer poly(UPE-co-St). It can be seen from the figure that with the increase of St, the tensile strength increases from 17.84 MPa of pure PUPE to 34.63 MPa of UPE + St 25%, and the change basically rises linearly, while the impact strength does not change much. This is because the presence of the benzene ring causes a decrease in the free volume between the molecular chains, and the steric hindrance increases, which makes the molecular chain of the copolymer difficult to move. This result is basically consistent with the change in the degree of crosslinking of poly(UPE-co-St) and the change in DMA curve.

3.4. Flame Retardancy of Poly(UPE-co-MMA) Copolymers

The flame retardancy of poly(UPE-co-St) series was characterized by the LOI test and the UL-94 vertical burn rating test. **Table 2** shows the LOI value of the copolymer and the UL-94 burning rating test. As can be seen from **Table 2**, the

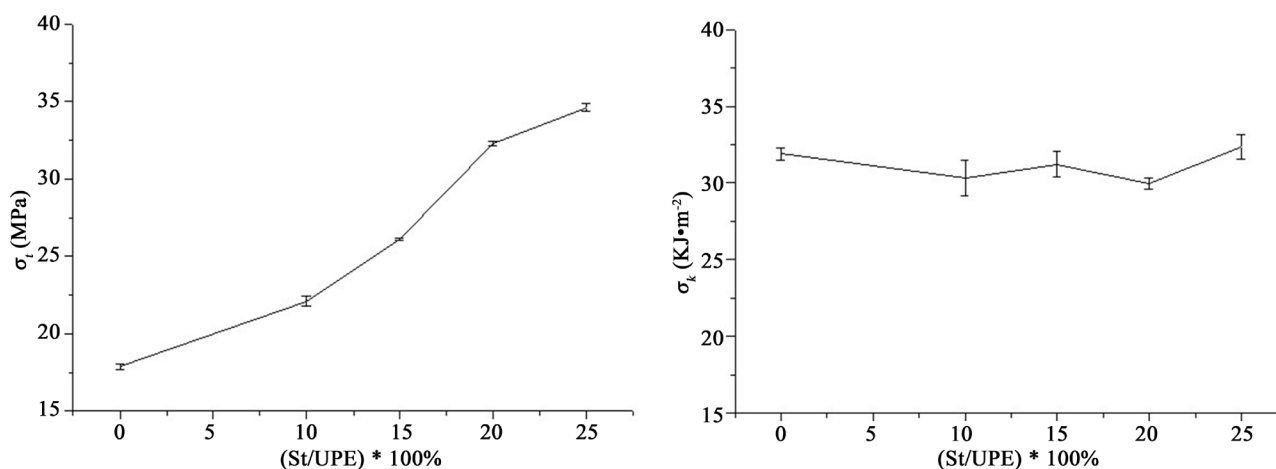


Figure 7. Tensile strength σ_t and impact strength σ_k curves of poly(UPE-co-St).

Table 2. Flame retardancy data of poly(UPE-co-St) copolymers.

Sample	PUPE	PUPE + St 10%	PUPE + St 15%	PUPE + St 20%	PUPE + St 25%
LOI/%	29.00	28.50	27.90	26.70	26.10
UL-94	V-0	V-0	V-0	V-0	V-0

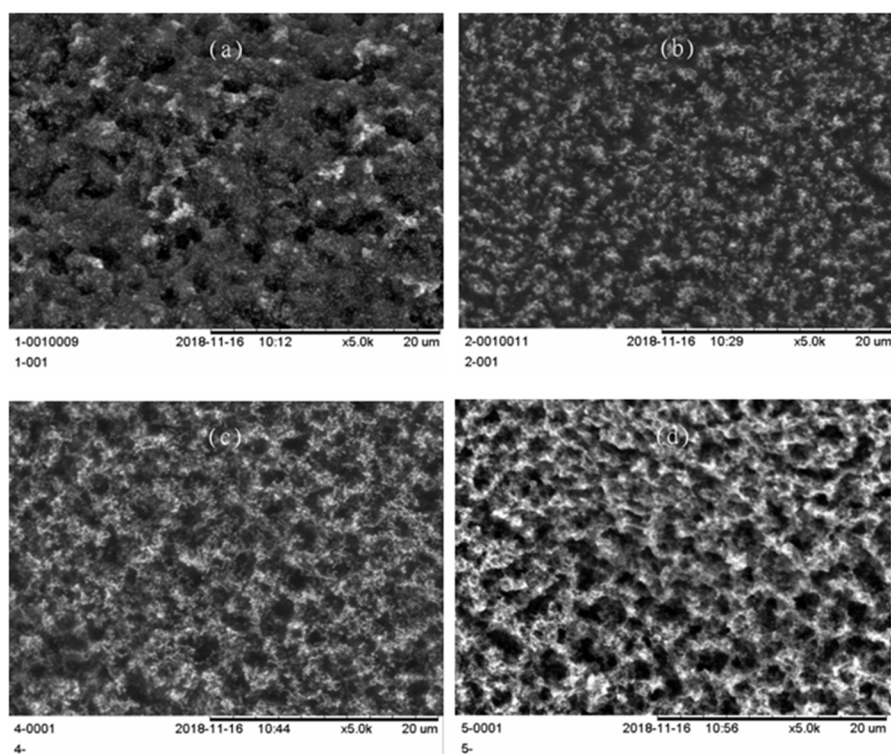


Figure 8. SEM image of the outer char residue of poly(UPE-co-St): (a) PUPE; (b) UPE + St 10%; (c) UPE + St 20%; (d) UPE + St 25%.

LOI value of the copolymer decreased from 29.0 to 26.1 with the increase of St, but the UL-94 vertical burn rating still reached V-0. This is because the stability of the carbon layer is destroyed due to the addition of the benzene ring, resulting in a large proportion of unstable carbon layers in the late combustion stage. The decomposition rate in the third stage is maximized (as described in 3.2), which exacerbates the combustion of the matrix and reduces the flame retardancy of the polymer. **Figure 8** shows samples in the poly(UPEco-St) series (a) PUPE, (b) UPE + St 10%, (c) UPE + St 20%, (d) UPE + St 25% carbon layer surface after LOI test SEM image, and the magnification is 5.0 K times. By comparison, it is found that the surface of UPE is relatively smooth, but with the increase of St content, the pores on the surface of the carbon layer gradually increase and become larger, the protection ability to the substrate is deteriorated, and the flame retardant performance is lowered. However, due to the presence of phosphorus, UPE + St 25% still have a certain flame retardant effect. The results show that the introduction of benzene ring will reduce the flame retardancy of the polymer.

4. Conclusion

In summary, the copolymers were prepared by copolymerization of unsaturated phosphates and different ratios of styrene, and the structural characterization and properties were carried out. The test results showed that the addition of styrene improved the crosslink density of the polymer and improved the T_g , the

transparency was basically stable, the mechanical properties of the copolymer are significantly improved, the tensile strength was significantly improved from 17.84 PMA to 34.63 PM, and impact properties were basically stable. The LOI showed a downward trend, decreased from 29.0% to 26.1%, but the vertical burning level reached V-0. From the thermal performance test of poly(UPE-co-St), it was found that the introduction of St is beneficial to improve the thermal stability of the copolymer; however, the carbon residue rate at 600°C decreased with the increase of St content, which was attributed to the presence of the benzene ring made the pyrolysis reaction of the third stage rapid and thorough, and reduced the stability of the carbon layer. The introduction of benzene ring improved the cross-linking degree of PUPE and the Tg. At the same time, with the increase of St content, the transparency of poly(UPE-co-St) decreased slightly, the impact strength changed little, and the tensile strength increased. The introduction of benzene ring changed the helical structure of the polymer chain and helped to increase the strength of the polymer. With the increase of St content, the LOI value of poly(UPEco-St) decreased to 26.1%, indicating that the introduction of benzene ring destroyed the stability of the carbon layer and aggravated the burning of the matrix, reduces the flame retardancy of the polymer, but the UL-94 grade remains at V-0 level.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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