



Silicone rubber composites fabricated using KH550-modified poplar leaves graphene

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Abstract. Silicone rubber (SR) composites were fabricated using poplar leaves graphene (PG). PG was synthesized from poplar leaves and modified-poplar leaves graphene (MPG) was obtained by treating graphene with a silane coupling agent γ -aminopropyltriethoxysilane (KH550). The biosynthesized PG and MPG were characterized by using organic elemental analysis, X-ray photoelectron spectroscopy, atomic force microscopy and scanning electron microscopy (SEM). The PG-modified SR composites were studied by using their mechanical properties, Fourier transform infrared spectroscopy, SEM and thermogravimetric analysis. The results showed that the PG synthesized by poplar leaves had high-carbon content and purity. The MPG was more evenly dispersed into SR than the PG, the mechanical properties of the MPG/SR composites were better than those of the PG/SR when the MPG content was 0.1 phr (parts per hundred rubber), the tensile strength and elongation at break were increased by 36.2 and 19.4% respectively and the wear resistance was increased by 57.1%. The thermal stability of the MPG/SR was higher than that of the PG/SR and SR. This important discovery could not only solve the problem of the origin of graphene, but also broaden the application of SR composites.

Keywords. Green synthesis; SR; graphene; mechanical properties; thermal stability.

1. Introduction

Silicone rubber (SR) is a kind of special synthetic rubber with the largest yield and is most widely used in organic silicon products [1]. Owing to its high elasticity [2], thermal stability [3,4], optical transparency, durability and chemical inertness, SR has been applied in national defence industry [5], medical and health care, industrial and agricultural production and people's daily life [6], and has become an important and indispensable new polymer material for national economy [7,8]. Among most applications, the high performance of SR mainly relies on the addition of functional fillers [9]. Therefore, it is important to choose appropriate fillers to cater to the specific application requirements of SR. Graphene, with its large specific surface area, tensile strength, elastic modulus, electron mobility and excellent conductivity [10], has become one of the hotspots in the research of new materials all over the world [11,12]. Pradhan and Srivastava [13] prepared the graphene–mwcnts mixture by solution mixing, and modified-SR by solution intercalation using the graphene–mwcnts hybrid. Valentini *et al* [14] prepared damaged repaired graphene/SR composites by the method of liquid phase mixing; the composite material did not only show that with an increase of temperature, the resistance lowered quickly, but could also repair itself and sealed auto parts, etc., thereby satisfying many strict requirements of the material. However, graphene is expensive and graphite is currently used as a raw material to prepare graphene [15]. However, a

large number of poplar grows in northern China and their leaves fall in autumn. The carbon content of poplar leaves is 57.16% and so the resource rich poplar leaves were chosen as raw materials to prepare graphene. However, it is a bottleneck problem that graphene is difficult to uniformly disperse into SR [16]. To improve the compatibility between graphene and SR, the silane coupling agent KH550 was used to treat graphene.

Poplar leaves graphene (PG) was prepared by the oxidation–reduction method of poplar leaves in a novel, green and eco-friendly manner, and the SR properties were improved with KH550-modified poplar leaves graphene (MPG), thereby broadening the application of SR composites.

2. Experimental

Poplar leaves were collected from a local Qiqihar in northern China. The KH550 ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$) silane coupling agent was received from Tianjin Shengli Trade Co., Ltd., China. SR was purchased from Dongjue Organic Silicon Group Co., Ltd., China. Silica was supplied from Qingdao Weite Silica Co., Ltd., China. All aqueous solutions were prepared using deionized water.

The collected poplar leaves were washed thoroughly with deionized water to remove visible impurities and dried. About 10 g of dried poplar leaves were ground to powder and then poplar leaf powder was carbonized in a tube furnace at 800°C

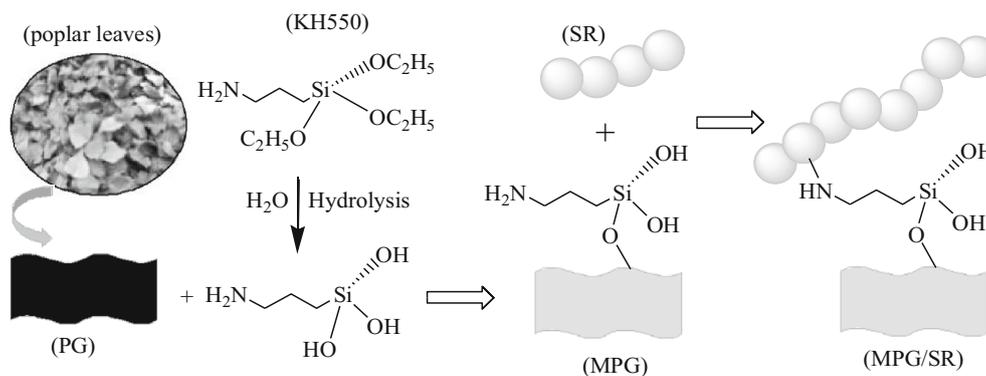


Figure 1. Fabrication process of the MPG/SR composites.

for 1 h under nitrogen. After this, the carbonized sample was activated to prepare acticarbon with phosphate treatment, and the acticarbon was continuously treated with concentrated sulphuric acid, potassium permanganate and hydrazine hydrate, washed and dried to obtain PG, and then the PG was placed into a beaker containing deionized water with ultrasonic processing for 2 h. The silane coupling agent KH550 was placed in a beaker containing ethanol with ultrasonic treatment for 20 min, and then KH550 was added to the PG, stirred fully until uniformly mixed, and finally dried to obtain MPG powder.

The SR was mixed on a XK-160 two-roll mill (Tianjin Electrical Machinery Plant, China) with the nip gap of about 1 mm, at 45°C for 10 min, and various other ingredients (DCP 3 phr, accelerant M 2 phr, antioxidant D 1.5 phr, silica 10 phr, stearic acid 2 phr and ZnO 3 phr) were added, and then 0.1 phr of MPG was added and mixed well for 30 min. Finally, the mixture was cured in the form of films (1 mm thick) in an electrically heated hydraulic press (XLB-D350 × 350, Shanghai First Rubber Machinery Co., Ltd., China) at 170°C under a pressure of 1.2 MPa for 10 min, and post cured at 170°C under 1 atm for 2 h. The preparation of the MPG/SR composites is shown in figure 1. Heat-aged test samples were obtained by placing the samples in an aging box (401B, Jiangdu True Power Machinery Co., Ltd., China) at 200°C under 1 atm of air for 2 h (used for testing their tensile strength and elongation at break after heat aging).

3. Experimental techniques

X-ray diffraction (XRD) patterns were used to determine the crystal structure of PG, and were recorded with a SmartLab XRD meter (Rigaku Corporation, Japan) under a voltage of 45 kV and a current of 200 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB-250XI XPS (Thermo Co., Ltd., USA) with an aluminium (mono) K α source. The aluminium K α source was operated at 15 kV and 10 mA. All core level spectra were

referenced to the C 1s neutral carbon peak at 284.8 eV. The organic element analysis test was carried out on a PE2400 analyser (Perkin Elmer USA), the temperatures of the combustion and the reduction tubes are 925 and 640°C, respectively. The mechanical properties of the PG/SR-based composites were measured according to ISO 37 specifications, on a universal testing instrument (model CSS-2200, Zhongji Application Technical Institute, China) under ambient conditions (at 25 ± 2°C) at a crosshead speed of 100 mm min⁻¹. The effect of heat aging on the mechanical properties of the samples was evaluated according to ISO 188. Abrasion tests were conducted according to ISO 4649:2002 on a roller abrasion tester (High-speed Rail Testing Instrument Co., Ltd.), 2.5 N farmar load. At least five specimens of each sample type were tested and the errors in the measurement of their mechanical properties were within 10%. Scanning electron microscopy (SEM) analysis of the cryo-fractured surfaces of the composites and elemental analysis of PG were carried out in an S-4300 SEM (Hitachi Co., Japan). The composites were fractured in liquid nitrogen and the fractured samples were gold coated in prior before SEM analysis.

The morphologies of the composites were observed by using a transmission electron microscope (TEM, H-7650, Hitachi Co., Japan), the accelerating voltage of which is 100 kV. An atomic force microscope (AFM, MultiMode 8, Bruker Instruments Inc., Germany) in tapping mode was used at a scan rate of 0.7–1 Hz. The thermal stability of the samples was measured through thermogravimetric analysis (TG, STA449F3 Jupiter, Netzsch Co. Ltd., Germany) under a nitrogen atmosphere at a heating rate of 5°C min⁻¹ from 20 to 600°C. The samples were prepared with dimension of 5 × 5 × 1 mm³. Fourier transform infrared spectroscopy (FTIR, model Spectrum One, Perkin Elmer Co. Ltd., USA) of SR, PG/SR and MPG/SR was carried out from 500 to 4000 cm⁻¹ with 256 scans at 2 cm⁻¹ resolution at room temperature. The samples were prepared by grinding 1–2 and 200 mg KBr together (both be dried), placed in the mould and pressed into slices with a hydraulic press under 5–10 MPa.

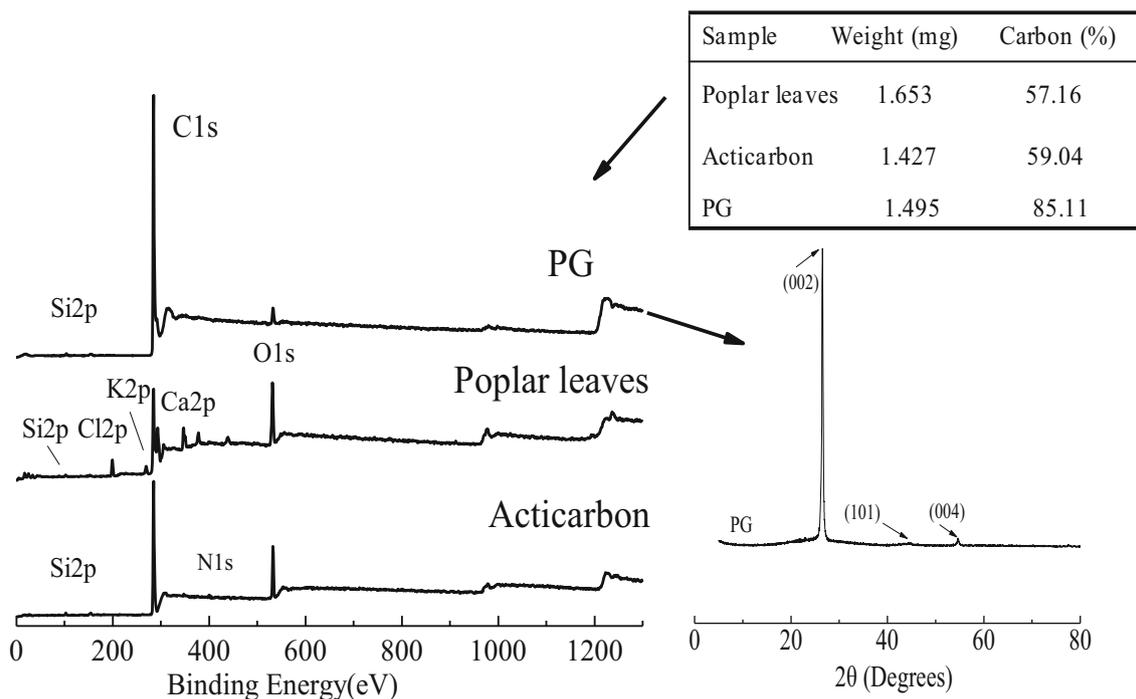


Figure 2. Carbon content, XPS spectra and XRD pattern of poplar leaves, acticarbon and PG.

4. Results and discussion

Graphene was fabricated by using poplar leaves and the carbon content of PG is shown in figure 2. The carbon contents of poplar leaves, acticarbon and PG were 57.16, 59.04 and 85.11%, respectively. This indicates that graphene can be fabricated from poplar leaves. In order to determine the element types of the three materials, XPS analysis was performed on the materials. Peaks of Si 2p, C 1s, O 1s, K 2p, Cl 2p and Ca 2p were observed on the poplar leaves curve, indicating the existence of Si, C, O, K, Cl and Ca elements in the poplar leaves. Peaks of Si 2p, C 1s, O 1s and N 1s were observed in the activated carbon, indicating the existence of Si, C, O and N elements in the acticarbon, and the mixed elements in poplar leaves disappeared after the acticarbon was made, and the carbon content had not changed much. The PG prepared by the redox method also had the peaks of Si 2p, C 1s and O 1s, illustrating that there were only C, Si and O elements on the surface of PG, and the content of carbon element was increased to 27.95% (from 85.11 to 57.16%), making the PG fabrication from the poplar leaves successful. At the same time, the XRD patterns of PG showed the diffraction peaks at 26.43, 44.70 and 54.54°, they were the typical peaks of the orthorhombic phase of graphene, which were assigned to the (002), (101) and (004) of graphene, respectively. This demonstrates that the regularity and crystallinity of graphene were greatly improved during the oxidation–reduction process, and the purity of PG was high.

The surface morphology of graphene was observed by AFM as shown in figure 3. There were some rounded

protrusions on the surface of the PG sample (figure 3a), and there were irregular and thick protrusions on the surface of the MPG (figure 3b). This suggests that some material was adsorbed on the surface of the PG, presumably KH550.

In order to prove adhesive KH550 on the PG surface, energy-dispersive X-ray spectroscopy (EDS) analysis was conducted as shown in figure 4. Figure 4a shows unmodified PG, and figure 4b shows MPG. It is obvious from the EDS patterns that the PG contains only C element, and the MPG contains C, Si and O elements. This proves that the silane coupling agent KH550 had been successfully attached onto the PG surface to fabricate MPG.

Table 1 shows the effects of PG and MPG on the mechanical properties of SR. With the addition of the PG and MPG, the tensile strength and elongation at break of the composites increased first and then decreased. This indicates that the two kinds of graphene had an improved effect on the SR. When 0.1 phr PG was added, the tensile strength and elongation at break of the PG/SR composites showed the best value, this suggests that the PG was dispersed evenly into the SR, and the mechanical properties were improved. When the content of PG was more than 0.1 phr, the decrease of the tensile strength and elongation at break were due to the aggregation of PG, resulting in an uneven dispersion in the SR, and the worse compatibility between PG and SR. The Shore A hardness of the PG/SR composites increased with the increasing amount of PG, and the Shore A hardness of the composites gradually increased, it seemed that the more the PG content was, the more cross-linking points between rubber and PG were, and the harder the material. In addition, the tensile strength and the

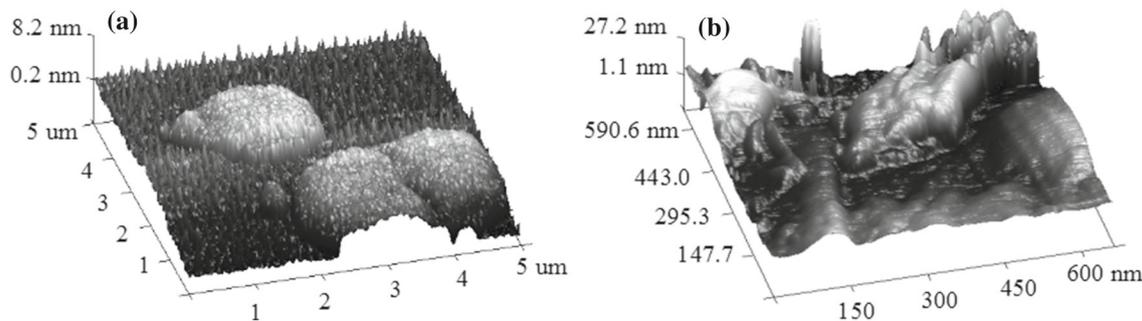


Figure 3. AFM images of: (a) PG and (b) MPG.

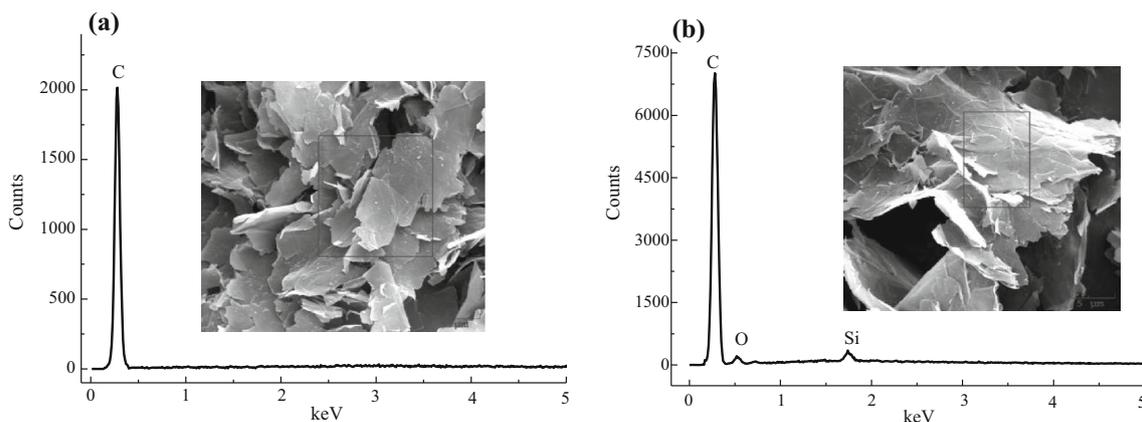


Figure 4. Microstructures of: (a) PG and (b) MPG in SEM images with EDS analyses.

Table 1. Mechanical properties of PG/SR, MPG/SR and commercial graphene/SR (before and after heat aging).

| Sample | Tensile strength (MPa) | Elongation at break (%) | Shore A hardness | Wear (cm ³ km ⁻¹) |
|-------------------------------|------------------------|-------------------------|------------------|--|
| | Before/after | Before/after | Before/after | Before/after |
| <i>PG/SR</i> | | | | |
| 0.05 | 5.3/3.7 | 122/96 | 51/53 | 0.31/0.36 |
| 0.075 | 6.2/4.9 | 168/126 | 53/54 | 0.26/0.3 |
| 0.1 | 6.9/5.6 | 201/172 | 54/56 | 0.14/0.21 |
| 0.125 | 5.8/4.5 | 161/103 | 56/58 | 0.21/0.32 |
| 0.15 | 4.4/2.9 | 124/89 | 57/59 | 0.34/0.35 |
| <i>MPG/SR</i> | | | | |
| 0.05 | 6.4/3.8 | 146/93 | 52/55 | 0.24/0.25 |
| 0.075 | 7.3/4.9 | 198/109 | 57/59 | 0.17/0.19 |
| 0.1 | 9.4/7.6 | 240/172 | 62/64 | 0.06/0.12 |
| 0.125 | 8.2/6.8 | 212/152 | 65/65 | 0.11/0.14 |
| 0.15 | 5.7/6.1 | 118/148 | 66/67 | 0.2/0.22 |
| <i>Commercial graphene/SR</i> | | | | |
| 0.05 | 4.9/3.9 | 138/107 | 49/51 | 0.33/0.37 |
| 0.075 | 5.7/4.3 | 157/123 | 52/53 | 0.27/0.34 |
| 0.1 | 6.7/4.8 | 174/148 | 55/58 | 0.19/0.24 |
| 0.125 | 7.8/5.9 | 191/167 | 58/57 | 0.13/0.24 |
| 0.15 | 5.4/3.7 | 149/108 | 61/62 | 0.32/0.34 |

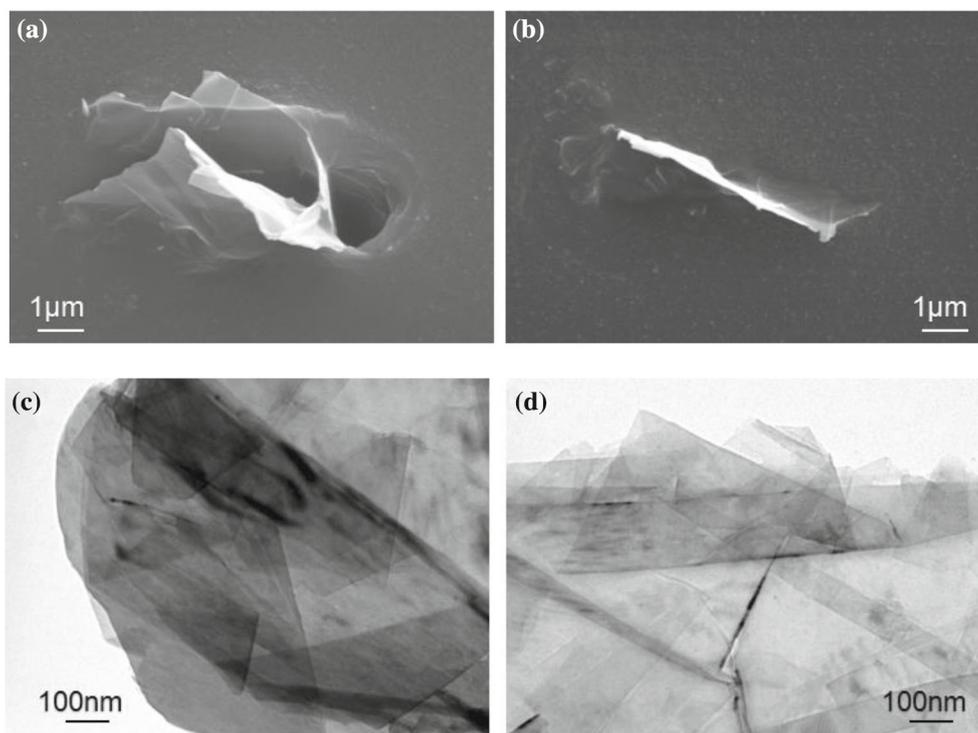


Figure 5. SEM and TEM images of: (a, c) PG/SR and (b, d) MPG/SR.

elongation at break after heat aging were basically the same as those before heat aging, but the Shore A hardness was higher than that before the aging due to heat embrittlement of the rubber. Similarly, it can be explained that the wear of the composites decreased first and then increased with the addition of PG.

It can also be seen that the tensile strength and elongation at break of the MPG/SR composites increased first and then decreased at 0.1 phr of MPG after the addition of MPG. Compared to the PG/SR composite with 0.1 phr of PG, the tensile strength and the elongation at break of the MPG/SR composite increased by 36.2 and 19.4%, respectively, this shows that the effect of MPG reinforced SR was much better than that of PG. It was considered that PG was easily agglomerated and had poor compatibility with SR. Therefore, the coupling agent KH550 was used as the interface phase between PG and SR, and the surface of the PG was treated to disperse evenly in the SR matrix. The trend of Shore A hardness of the MPG/SR composites increased first and then tended to be constant, and the wear decreased and then increased, and the best mechanical properties appeared at 0.1 phr of PG or MPG. Compared with PG/SR composites, the hardness was increased by 20.4%, and the wear resistance was increased by 57.1%. In addition, compared with the addition of commercial graphene, the mechanical properties were the same as those of SR with PG.

Figure 5 shows the dispersion of PG and MPG in SR, the PG/SR composites had some holes and large gaps as shown in figure 5a, this indicates that the binding force between PG

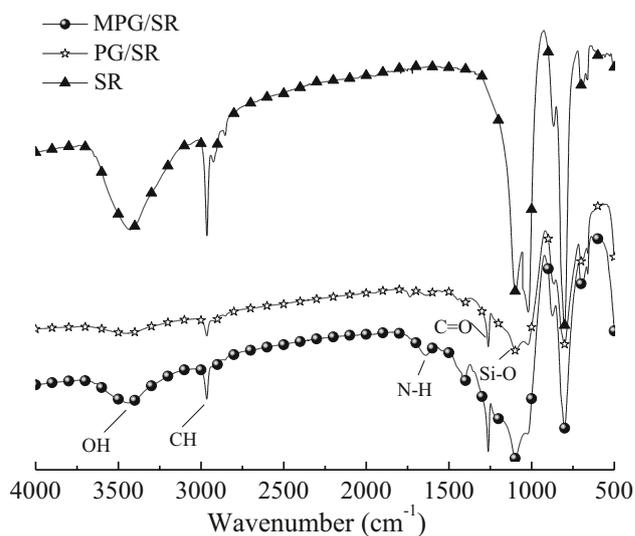


Figure 6. FTIR of SR, PG/SR and MPG/SR.

and SR was weak. And the fractured surface of the MPG/SR composites had no stratification and was closely connected with SR as shown in figure 5b, this suggests that the binding force between the MPG and the SR was significantly enhanced. By comparing figure 5c and d, it can also be noted that the MPG was uniformly dispersed into the SR, and so the compatibility between KH550 modified-PG and SR was better than that between PG and SR.

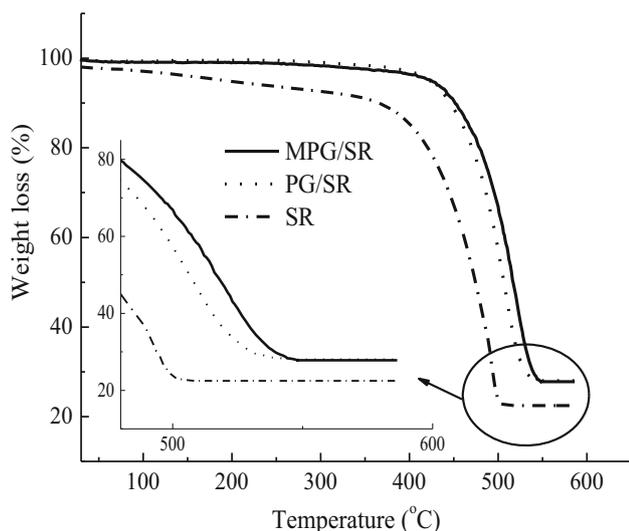


Figure 7. TG curves of SR, PG/SR and MPG/SR.

In figure 6, the absorption peaks of OH (3430 cm^{-1}), CH (2956 cm^{-1}), C=O (1257 cm^{-1}) and Si-O (1100 cm^{-1}) are seen in the IR spectra of the PG/SR composites, which seemed to be the characteristic peaks of the SR and silica. A new absorption peak of NH bonds at 1631 cm^{-1} appeared in the MPG/SR curve; it was believed that KH550 reacted with the composites and generated the NH group, which promoted the crosslinking between the PG and SR. So KH550 has a good cross-linking function.

In order to understand the thermal stability of the MPG/SR composites, the TG of the composites was tested as shown in figure 7. Firstly, the weight loss of the MPG/SR, PG/SR and SR slowly occurred above 300°C due to the evaporation of water and decomposition of some impurities after heating, then the weight loss rate of SR dropped rapidly above 450°C , and the weight loss rate of MPG/SR was slower than those of PG/SR and SR above 500°C , indicating that the thermal stability of MPG/SR was good.

5. Conclusion

The synthesized PG had been successfully fabricated using poplar leaves; the content and purity of the obtained carbon element of PG were high, and the silane coupling agent KH550 was attached onto the PG surface to prepare MPG.

The MPG could be better dispersed into the SR than PG. When the content of MPG was 0.1 phr, the mechanical properties of the MPG/SR composites were the best. Compared to the PG/SR composites, the tensile strength and elongation at break increased by 36.2 and 19.4%, respectively, and the wear resistance increased by 57.1%. The thermal stability of the MPG/SR was higher than that of the PG/SR and SR. This important discovery could not only solve the problem of the origin of graphene, but also broaden the application of SR composites, and the design concept of combining PG with SR would possibly lead to new revolution in material engineering, aerospace and medical fields.

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References

- [1] Lev Y, Faye A and Volokh K Y 2018 *Exp. Mech.* **58** 847
- [2] Aminuzzaman M, Ying L P, Goh W S and Watanabe A 2018 *Bull. Mater. Sci.* **41** 50
- [3] Zhang B, Li R, Luo J M, Chen Y, Zou H W and Liang M 2018 *Polym. Bull.* **75** 2105
- [4] Wu W L and Chen Z 2017 *Results Phys.* **7** 2445
- [5] Bleszynski M and Kumosa M 2017 *Polym. Degrad. Stab.* **146** 61
- [6] Abraiz K, Muhammad I and Muhammad A 2017 *Sci. Eng. Compos. Mater.* **24** 679
- [7] Kumar V, Lee J Y and Lee D J 2017 *Polym. Int.* **66** 450
- [8] Gajewski J B, Głogowski M J and Hałuszka N 2017 *Electrostat. J.* **88** 214
- [9] Awad S A and Khalaf E M 2018 *Bull. Mater. Sci.* **41** 67
- [10] Kumar R and Bhargava P 2017 *Bull. Mater. Sci.* **40** 1197
- [11] Gang D 2017 *J. Thermoplast. Compos.* **31** 1219
- [12] Savadkoobi M, Dorrani D and Solati E 2018 *Mater. Sci. Semicond. Process.* **75** 75
- [13] Pradhan B and Srivastava S K 2014 *Polym. Int.* **63** 1219
- [14] Valentini L, Bittolo Bon S and Pugno N M 2016 *Compos. Sci. Technol.* **134** 125
- [15] Kim H and Lee S 2017 *Fibers Polym.* **18** 1304
- [16] Kasar A K and Menezes P L 2018 *Int. J. Adv. Manuf. Technol.* **97** 3999