Research Article

Xinmou Kuang*, Minru Su, Liang Wang, Hao Li, Xiaolan Shen, Mengyun Yu and Yiran Wu

Study on properties of recycled mixed polyester/nylon/spandex modified by hydrogenated petroleum resin

https://doi.org/10.1515/secm-2022-0225
received February 13, 2023; accepted September 08, 2023

Abstract: In order to improve the utilization value of recycled materials, the study considers recycled materials such as polyester/nylon/spandex as raw materials. Using polyester/polyamide/spandex as raw materials, the recycled polyester/polyamide/spandex mixed materials were first pretreated to obtain the pretreated mixed materials. Then, the pretreated mixed materials were evenly mixed with hydrogenated petroleum resin. The composite materials were prepared through extrusion and injection molding. By comparing the mechanical properties, the effects of different hydrogenated petroleum resins and their additives on the tensile strength, bending strength, impact strength, elongation at break, and bending modulus of the composites were investigated. And the microstructure of the fracture surface was characterized by scanning electron microscopy. The results showed that: (a) when the addition amount of hydrogenated C5 petroleum resin was 4.5%, the maximum impact strength and fracture elongation were 18.03 kJ/m^2 and 15.92%, respectively. (b) The maximum tensile strength, bending strength, and bending modulus could reach 22.9, 38.72, and 2217.9 MPa, when the addition amount of hydrogenated C9 petroleum resin was 4.5, 29.5, and 39.5%, respectively.

Keywords: recycled polyester/nylon/spandex, hydrogenated C9 petroleum resin, hydrogenated C5 petroleum resin, pellet

*** Corresponding author: Xinmou Kuang**, Zhejiang Collaborative Innovation Center for High Value Utilization of byproducts from Ethylene Project, Ningbo Polytechnic, Ningbo, China; College of Chemical Engineering, Ningbo Polytechnic, Ningbo, China,
e-mail: kuangxinmou@163.com
Minru Su: Zhenhai District Technical School, Ningbo, China
Liang Wang: School of Materials Science and Engineering, Xi'an Polytechnic University, Xi'an, China
Hao Li, **Xiaolan Shen**, **Mengyun Yu**, **Yiran Wu:** Zhejiang Collaborative Innovation Center for High Value Utilization of byproducts from Ethylene Project, Ningbo Polytechnic, Ningbo, China; College of Chemical Engineering, Ningbo Polytechnic, Ningbo, China

1 Introduction

Polyester has the advantages of high strength and high modulus in mechanical properties [1,2]. As a general material, polyamide/spandex are similar to polyester. In recent years, the use and recycling of polyamide/spandex have been increasing. Polyester/nylon/spandex recycling usually comes in the form of a mixture; therefore, it is of great practical significance to study the recycling of mixed materials such as polyester/polyamide/spandex. On the issue of recycling polyester materials, need to add some additives to solve the compatibility problem between polyester and other materials. For example, by adding compatibilizer [3,4], the compatibility between polyester and high density polyethylene [5] and polypropylene (PP) [6–8] could be solved, which provides ideas for the comprehensive utilization of polyester/polyamide/spandex mixed materials.

In previous studies, our research group studied the process of mixed polyester/polyamide/spandex to modify PP by adding different compatibles [9] and using different pretreatment processes [10]. In the process of research, it is also found that the "bonding" between polyester/nylon/spandex and the modified matrix material was not obvious due to the differences in compatibility and bonding of the mixture material of polyester/nylon/spandex. Therefore, the microstructure of the fracture surface of the composite material was defective, and the mechanical properties were also affected to some extent. Hydrogenated petroleum resin has good advantages in compatibility, viscosity enhancement, and thermal stability [11]. Similarly, hydrogenated petroleum resins were widely used in the coatings, paints, adhesives, rubber, and other fields. It plays a significant role in improving the microstructure and mechanical properties of materials [12,13].

In this study, hydrogenated C9 petroleum resin and hydrogenated C5 petroleum resin were used to modify polyester/nylon/spandex mixtures to prepare composite materials with better mechanical properties, and the mechanical properties and fracture surface microstructure of

the prepared composite materials were characterized. They found that with the change in the amount of hydrogenated C5 petroleum resin and hydrogenated C9 petroleum resin, the mechanical properties of the composite material such as tensile strength, bending strength, impact strength, fracture elongation, and bending modulus also changed, and the optimal mechanical properties of the composite material were obtained. The research results of this article can provide theoretical basis and data support for the recycling of polyester/nylon/spandex materials.

2 Experimental method

2.1 Main experimental materials

Starting materials such as maleic anhydride grafted polypropylene (PP-g-MAH) and hydroglyceryl methacrylate grafted with ethylene-octene copolymer (POE-g-GMA) were purchased from Ningbo Nengzhiguang New Material Technology Co., Ltd. Hydrogenated C5 petroleum resin (Model: H5-1000, Softening point: 101.3°C, Gardner color number: #0–1) and hydrogenated C9 petroleum resin (Model: HM-1000, Softening point: 100.7°C, Gardner color number: #0–1) were purchased from Zhejiang Henghe Petrochemical Co., Ltd. Polyester/nylon/spandex and other short fiber materials were provided by market sorting and recycling companies (tensile strength: 15.17 MPa, bending strength: 24.34 MPa, impact strength: 10.275 kJ/m^2, fracture elongation: 3.72%, and bending modulus: 1427.84 MPa). All other reagents and solvents were of reagent grade and used without further purification.

2.2 Pretreatment of experimental materials

The polyester/nylon/polyurethane were evenly mixed according to the molar ratio of 1:1:1, and the pellet pretreatment method was carried out according to literature [10]. Similarly, the pretreated material was placed in an oven at 120°C for 4 h, and cooled for later use. The hydrogenated C5 petroleum resin, hydrogenated C9 petroleum resin, compatibilizer, and other materials were put into the oven at 100°C for 4 h, then removed and cooled for later use. The pretreatment materials, hydrogenated C5 petroleum resin, hydrogenated C9 petroleum resin, compatibilizer, antioxidant, and other materials were mixed according to Tables 1 and 2.

2.3 Sample preparation

The materials in Tables 1 and 2 were extruded and pelleted by twin screw extruder (WLG10A, Shanghai Xinshuo Precision Machinery Co. Ltd), respectively. The extrusion conditions of the extruder were set as follows: the temperature of the upper cavity plate was 200°C, the temperature of the lower cavity plate was 200°C, the working time was 16.5 s, and the screw speed was 74 rpm. The pellet was injected by the injection molding machine. The injection molding conditions were set as follows: the mold temperature was 43°C, the cylinder temperature was 200°C, and the pressure holding time was 6 s. The detailed schematic diagrams for sample preparation can be seen from Figure 1.

2.4 Performance test

Tensile performance test: according to GB/T 10400.1-2018 standard test, using type II spline (CMT6104, Shenzhen New Think Material Testing Co., Ltd), test speed was 5 mm/min. Bending performance test: according to GB/T 9341-2000 standard test, the test speed was 5 mm/min. Notched impact strength performance test: according to GB/T 1843-2008 standard test, the impact energy was 2.75 J. Using V-shaped splines in pendulum testing experiments, pendulum speed was 9 m/s. Scanning electron microscopy (SEM) analysis: the plastic profile sample was taken and fixed on the conductive tape, and treated with gold spraying. The appearance of the cutting surface was observed. And the accelerated voltage

Table 1: Material composition in the modification experiment of hydrogenated carbon 9 petroleum resin (%)

Number	Pretreatment material	Antioxidant 225	PP-g-MAH	POE-g-GMA	Hydrogenated C9 petroleum resin
1	54	0.5	4	2	39.5
2	64	0.5	4	2	29.5
3	74	0.5	4	2	19.5
4	84	0.5	4	2	9.5
5	89	0.5	4	2	4.5

Table 2: Material composition in the modification experiment of hydrogenated carbon 5 petroleum resin (%)

Number	Pretreatment material	Antioxidant 225	PP-g-MAH	POE-g-GMA	Hydrogenated C5 petroleum resin
6	54	0.5	4	2	39.5
7	64	0.5	4	2	29.5
8	74	0.5	4	2	19.5
9	84	0.5	4	2	9.5
10	89	0.5	4	2	4.5

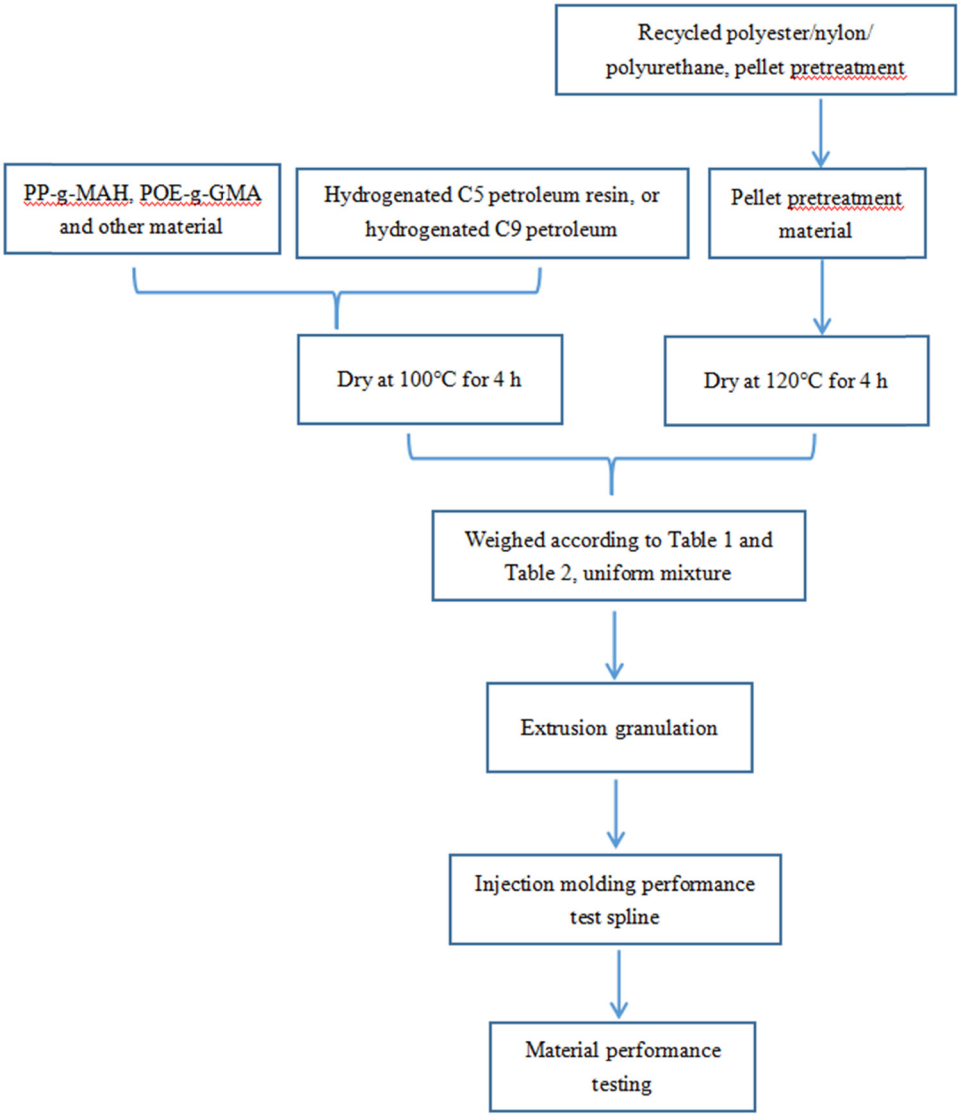

Figure 1: Schematic diagrams for sample preparation.

was 20 kV. Cold field emission scanning electron microscope (SEM): Quanta-600FEG, FEI Company, the Netherlands.

3 Results and discussion

3.1 Influence of petroleum resin content on mechanical properties of composites

3.1.1 Tensile strength

As can be seen from Figure 2, with the increase in hydrogenated C5 petroleum resin and hydrogenated C9 petroleum resin, the tensile strength of the composite showed a law of obvious decrease. When the additive content of petroleum resin was less it may be because of the high strength of chemical fiber material acting as skeleton [14]. The bonding property of petroleum resin strengthens the skeleton action of chemical fiber material, so the tensile strength of the composite material was larger. First, as the additive content of petroleum resin increased, petroleum resin has obvious dilution effect on the whole composite system [15]. On the other hand, the composition of the high-strength chemical fiber material decreases, while the matrix viscosity gradually increases, the regularity of the chemical fiber material decreases, and the skeleton cannot be evenly dispersed, so the tensile strength of the composite material decreases significantly.

When the content of petroleum resin was 4.5%, the mechanical properties of the composites prepared by hydrogenated C9 petroleum resin were slightly stronger than

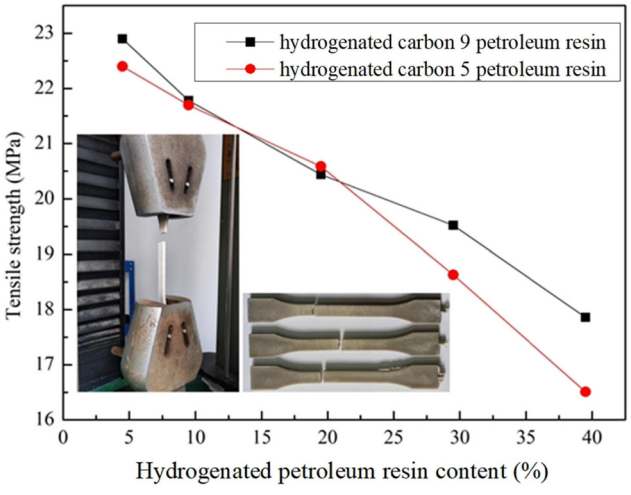

Figure 2: Effect of hydrogenated petroleum resin content on tensile strength.

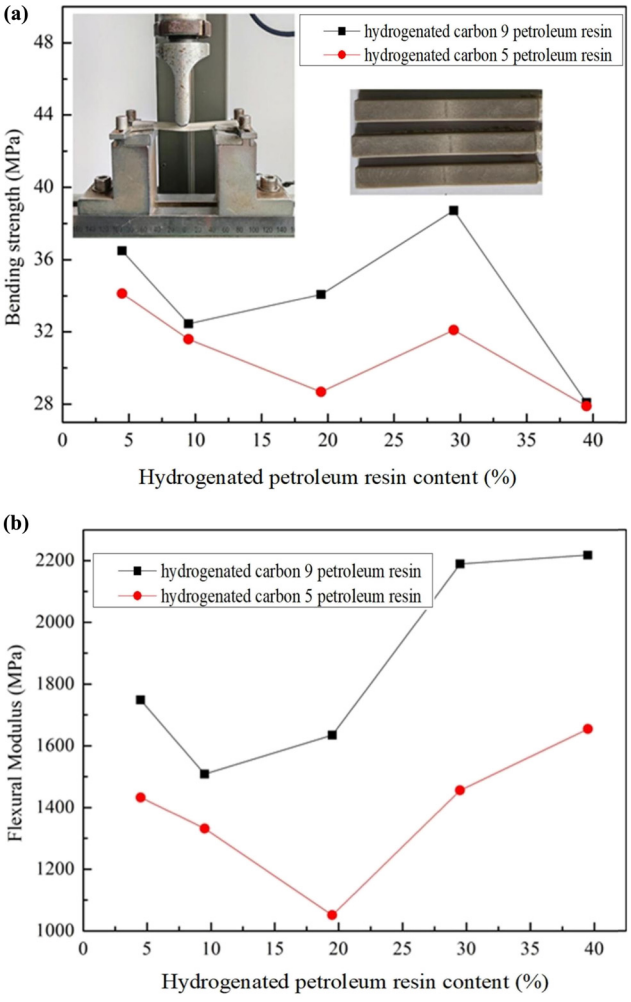

Figure 3: (a) Effect of hydrogenated petroleum resin content on bending strength and (b) effect of hydrogenated petroleum resin content on bending modulus.

those prepared by hydrogenated C5 petroleum resin. This may be due to the fact that hydrogenated C5 petroleum resin mainly has aliphatic hydrocarbon structure, and hydrogenated C9 petroleum resin molecule contains benzene ring and other structures. So, hydrogenated C9 petroleum resin has better compatibility with chemical fiber materials under the action of compatibilant, resulting in better mechanical properties of tensile strength.

3.1.2 Bending strength and bending modulus

As can be seen from Figure 3(a), with the increase in petroleum resin content, the bending strength of composite materials decreased first and then increased. When the content of hydrogenated C9 petroleum resin was 29.5%, the bending strength of the composite reached the maximum.

When the content of hydrogenated C5 petroleum resin was 4.5%, the bending strength of the composite reached the maximum. The bending strength of the composites prepared by hydrogenated C9 petroleum resin was stronger than that of the composites prepared by hydrogenated C5 petroleum resin.

When the amount of hydrogenated petroleum resin was 4.5%, the chemical fiber material has a high strength to act as a skeleton [14], which was strengthened by the adhesive property of hydrogenated petroleum resin. With the increase in hydrogenated petroleum resin content, this skeleton effect was weakened, so the mechanical properties of bending strength showed a decreasing trend. When the amount of hydrogenated petroleum resin was between 9.5 and 29.5%, the bending strength of the composite was significantly improved. When the amount of hydrogenated petroleum resin was 29.5%, the bending strength reaches its maximum. Hydrogenated petroleum resin may have the most obvious effect on the stiffness enhancement of the composite skeleton [15].

When the content of hydrogenated petroleum resin continued to increase, the mechanical properties of hydrogenated petroleum resin materials had more obvious influence on the mechanical properties of composite materials because the skeleton effect of chemical fiber materials continues to weaken. With the increase in hydrogenated petroleum resin, hydrogenated petroleum resin made materials become brittle [16]. Therefore, material properties were significantly reduced. On the other hand, with the increase in hydrogenated petroleum resin components, due to the bonding effect of hydrogenated petroleum resin, the molecular structure regularity of chemical fiber materials decreased, and the framework of chemical fiber materials could not be evenly dispersed. These two factors lead to a significant decrease in the mechanical properties of the composite bending strength.

It can also be seen from Figure 3(a) that hydrogenated C9 petroleum resin is superior to hydrogenated C5 petroleum resin in terms of mechanical properties of composite bending strength. It may be that the molecular structure polarity of hydrogenated C9 petroleum resin was greater than that of hydrogenated C5 petroleum resin and it had better compatibility with chemical fiber materials.

As can be seen from Figure 3(b), with the increase in hydrogenated petroleum resin content, the bending modulus of the composite decreased first and then increased significantly. The maximum bending modulus of hydrogenated C9 petroleum resin composite was 2217.9 MPa, the maximum bending modulus of hydrogenated C5 petroleum resin composite was 1654.2 MPa, and the maximum bending modulus of reference product was 1427.84 MPa.

When the hydrogenated petroleum resin content was low, the chemical fiber material skeleton effect had a large effect on the composite material. Therefore, the bending modulus of composite materials decreased gradually. With the increase in hydrogenated petroleum resin content, the hydrogenated petroleum resin had the strength of the frame, and the performance of the composite material was gradually improved.

The bending modulus and mechanical properties of the composites prepared by hydrogenated C9 petroleum resin were obviously better than those of hydrogenated C5 petroleum resin. This was due to the structural differences between the two hydrogenated petroleum resins. Because the molecular structure of hydrogenated C5 petroleum resin was less polar, it had poor compatibility with the framework of chemical fiber materials. Hydrogenated C9 petroleum resin molecules contained rigid groups such as benzene ring and other structures, the material rigidity was strong, and hydrogenated C9 petroleum resin molecules had greater polarity and better compatibility with chemical fiber materials.

3.1.3 Impact strength

It can be seen from Figure 4 that the impact strength of the composite prepared by hydrogenated C5 petroleum resin decreased first and then increased. The impact strength reached the maximum (18.03 kJ/m^2) when the addition amount of hydrogenated C5 petroleum resin was 4.5%. The impact strength of the composites prepared by hydrogenated C9 petroleum resin increased first and then

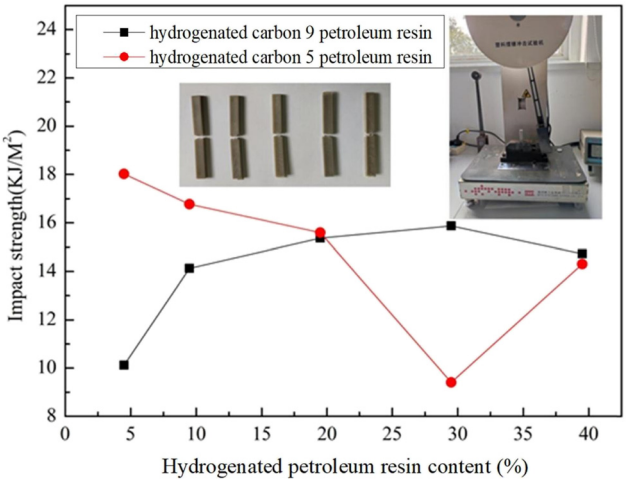

Figure 4: Effect of hydrogenated petroleum resin content on impact strength.

decreased. When the addition of hydrogenated C9 petroleum resin was 29.5%, the impact strength reached the maximum (15.878 kJ/m^2).

For the composite prepared by hydrogenated C5 petroleum resin, when the hydrogenated C5 petroleum resin increased from 4.5 to 29.5%, it may act as a skeleton due to the high strength of chemical fiber materials [14]. With the increase in hydrogenated C5 petroleum resin content, the effect of this framework was weakened, so the mechanical properties of impact strength showed a decreasing trend. While the content of hydrogenated C5 petroleum resin continues to increase, which may be due to the stiffening effect of hydrogenated petroleum resin [15], the mechanical properties of hydrogenated C5 petroleum resin material itself play a major role.

However, the impact strength of the composite prepared by hydrogenated C9 petroleum resin increased significantly when the addition amount was 4.5–29.5%. On the one hand, the hydrogenated C9 petroleum resin molecule had greater polarity and better compatibility with chemical fiber materials. On the other hand, the hydrogenated C9 petroleum resin molecule contained benzene ring and other rigid groups. When the addition amount was greater than 29.5%, the impact strength of the composite had a downward trend, which was due to the bonding effect of hydrogenated C9 petroleum resin, which reduced the regularity of the chemical fiber material and made it unable to disperse evenly.

3.1.4 Elongation at break

As can be seen from Figure 5, the fracture elongation of hydrogenated C5 petroleum resin composite decreased with the increase in hydrogenated petroleum resin content, and the maximum fracture elongation was 15.92%. The fracture elongation of hydrogenated C9 petroleum resin composite increased weakly and then decreased sharply, and then increased slowly, and the maximum fracture elongation was 14.59%. First, it was possible that the elongation of composite materials was mainly determined by chemical fiber materials. With the increase in hydrogenated petroleum resin, the hydrogenated petroleum resin made the materials brittle [16] and had an obvious dilution effect on the entire composite system [17]. Second, due to the bonding effect of hydrogenated petroleum resin, the regularity of chemical fiber materials was reduced and could not be evenly dispersed. Therefore, it had great influence on fracture elongation of composites.

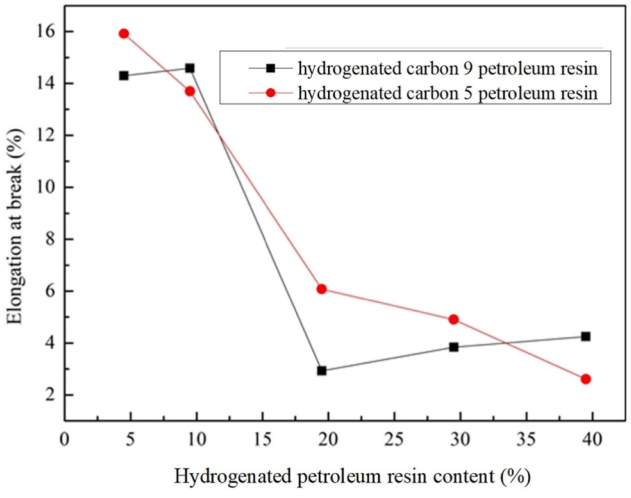

Figure 5: Effect of hydrogenated petroleum resin content on elongation at break.

3.2 Microstructure of fracture surface of composite material

Figure 6(a) and (b) shows the scanning electron micrograph of fracture surface of composite material experiment No. 2 in Table 1 and experiment No. 7 in Table 2. The addition amount of hydrogenated petroleum resin, chemical fiber aggregate, PP-g-MAH, POE-g-GMA, and antioxidant were 29.5, 64, 4, 2, and 0.5%, respectively. As can be seen from Figure 6(a), most of the fiber materials could be evenly dispersed with hydrogenated C5 petroleum resin, and there were “small pits” on the fracture surface. This was where some of the fibers were pulled out of the matrix. As can be seen from Figure 6(b), most of the fiber materials could be evenly dispersed with hydrogenated C9 petroleum resin. Similarly, there were “small pits” on the fracture surface.

By comparing Figure 6(a) and (b), it can be seen that by using hydrogenated C5 petroleum resin, the fracture surface “small pit” was relatively obvious, and many fibers were pulled out from the matrix of composite materials. By using hydrogenated C9 petroleum resin, the bond between fiber and composite matrix was more firm, and the force was obviously strengthened. This verifies that hydrogenated C9 petroleum resin had better compatibility with chemical fiber materials because of its larger molecular polarity.

In the fracture surface structure, it was also found that the chemical fiber material was relatively less, and the matrix material seemed to be mainly petroleum resin. The main reason may be that with the increase in the content of petroleum resin, stickiness increased, so that chemical fiber materials bond in hydrogenated petroleum resin, resulting in uneven dispersion of chemical fiber

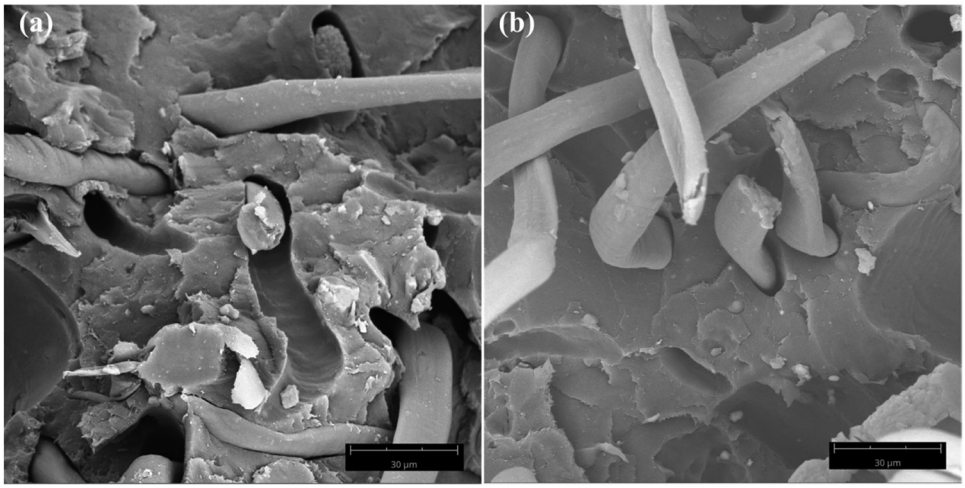

Figure 6: (a) SEM of fracture surface of hydrogenated C5 petroleum resin composite and (b) SEM of fracture surface of hydrogenated C9 petroleum resin composite.

materials and hydrogenated petroleum resin. During the experiment, it was also found that the content of hydrogenated petroleum resin was greater than 39.5%, the viscosity of hydrogenated petroleum resin and chemical fiber material melt body was large, and the operation of extrusion and injection molding was more and more difficult. Therefore, in the process of using hydrogenated petroleum resin to modify chemical fiber materials, it was necessary to consider the mechanical property index and processing difficulty, and select the appropriate addition ratio, which can also provide reference for the optimization of the process of using hydrogenated petroleum resin to modify other materials.

4 Results and prospects

The aim of this study was to improve the utilization value of recycled materials such as polyester/nylon/spandex. Polyester/polyamide/spandex composite were prepared by hydrogenated petroleum resin blending modified polyester/polyamide/spandex by hydrogenated C5 petroleum resin and hydrogenated C9 petroleum resin. It was found that the mechanical properties of the composite prepared by hydrogenated C5 petroleum resin are better in impact strength and fracture elongation. The mechanical properties of the composites prepared by hydrogenated C9 petroleum resin were better in tensile strength, bending strength, and bending modulus. The results showed that the maximum impact strength and fracture elongation were 18.03 kJ/m^2 and 15.92%, respectively, when the addition amount of hydrogenated C5 petroleum resin was 4.5%. The maximum tensile strength of hydrogenated C9 petroleum resin was 22.9 MPa when the addition amount was 4.5%, the maximum bending strength was 38.72 MPa when the addition amount is 29.5%, and the maximum bending modulus was 2217.9 MPa when the addition amount is 39.5%. In the future, when hydrogenated C5 petroleum resin and hydrogenated C9 petroleum resin are used to modify other chemical fiber materials to prepare composite materials, the appropriate addition ratio can be selected according to the comprehensive consideration of the mechanical property index and the difficulty of the processing process, and even further, other engineering plastics can be modified by blending hydrogenated C5 petroleum resin or hydrogenated C9 petroleum resin and chemical fiber materials.

Acknowledgements: This work was supported by the following funds or institutions: Ningbo Polytechnic's 2022 project: Study on Modification of PE with Petroleum Resin Coated Polyester, Nylon, and Spandex (Program No: NZ22004); Key Research and Development Program of Shaanxi (Program No. 2023-YBNY-245); Science and Technology Guidance Project from China Textile Industry Association (Program No. 2022042); The Science and Technology Plan of Beilin District (Grant No. GX2302); and Zhang Farao Academician workstation of Ningbo.

Conflict of interest: The authors state no conflict of interest.

References

[1] Shi SY, Wang LN, Zhao K, Song HF, Wang YF. Structure and mechanical property of recycled PET fiber/PP Composite. Acta Mater Compos Sin. 2017;34(7):1511–6 (Chinese).

[2] Parvinzadeh M, Ebrahimi I. Atmospheric airplasma treatment of polyester fiber to improve the performance of nanoemulsion silicone. Appl Surf Sci. 2011;257:4062–8.
[3] Kalfoglou NK, Skafidas DS, Kallitsls JK, Lambert JC, Van der Stappen L. Comparison of compatibilizer effectiveness for PET/HDPE blends. Polymer. 1995;36(23):4453–62.
[4] Zhang Y. Super toughness in recycled poly(ethylene terephthalate)/polyethylene compatibilized blend. Shanghai: East China University of Science and Technology; 2011.
[5] He MS, Wang ZK, Cao XW, Sun XM, Lu XZ. The properties and morphology of PET/PE allots. Plastics. 2016;45(6):13–6 (Chinese).
[6] Qi YH, Sun J, Ma YH, Dong JH, Luo Z, Wei LQ. Effect of compatilizers contents on foaming and mechanical properties of PET/IPP blend. Plastics. 2016;45(2):69–72 (Chinese).
[7] Qiu LQ, Liu HZ, Zhao SY, Liu RL. Preparation and characterization of crystallization and thermal property of poly(ethylene terephthalate) and poly(lactic acid) blends promoted by compatilizer. Polym Mater Sci Eng. 2018;34(3):73–80 (Chinese).
[8] Wang CG, Huang T, Yan JF, Liu SQ, Tang HQ. Effect of PET fiber on crystallization behavior and mechanical properties of PP. China Synth Resin Plastic. 2018;35(4):70–4 (Chinese).
[9] Kuang XM, Su MR, Li H, Shen XL, Yuan ZY, Yan XD, et al. Effects of pretreatment process on mechanical properties of recycled polyester/nylon/spandex mixed fiber modified polypropylene. Eng Plast Appl. 2020;48(9):78–82 (Chinese).
[10] Kuang XM, Su MR, Li H, Yuan ZY, Yang WQ. Study on property of polypropylene modified by polyester/nylon/spandex fiber with compatibilizer. N Chem Mater. 2021;49(9):98–101, 106 (Chinese).
[11] Liu X, Liu WB, Ma ZJ, Zhang Q. Hydrogenated C5 petroleum resin to qualitative research. Contemporary Chem Ind. 2014;43(1):15–6, 20 (Chinese).
[12] Colombo RP, Ibarra JG, Bidondo LF, Bidondo LF, Silvani VA, Bompadre MJ, et al. Arbuscular mycorrhizal fungal association in genetically modified drought-tolerant corn. J Env Qual. 2016;46(1):227–31.
[13] Porfirio S, Silva MD, Cabrita MJ, Azadi P. Reviewing current knowledge on olive adventitious root formation. Sci Hortic-Amsterdam. 2016;198:207–26.
[14] Tang XL, Tan HS, Tan H, Wang YG. Long aramid fiber reinforced impact polypropylene copolymer composites. Eng Plast Appl. 2013;41(2):5–9 (Chinese).
[15] Mu YJ, Chai HM. Application of stiffening agent to polypropylene. Plast Sci Technol. 2005;33(2):11–4, 19 (Chinese).
[16] Cimmino S, Silvestre C, Vecchia GD. Morphology and properties of isotactic polypropylene modified with hydrocarbon resin MBG273. I. Binary blends. J Appl Polym Sci. 2010;92(6):3454–65.
[17] Liang WJ, Ge JF, Chen SD, Zheng WL, Lin JL, Sheng YH, et al. Compatibility and mechanical properties of SEBS-g-MAH/hydrogenated C5 petroleum resin blends. J ZhongKai Univ Agric Technol. 2015;28(1):31–4 (Chinese).