

Maleic Anhydride-Modified Polyolefins as Compatibilizer for Lignin-Reinforced Polypropylene Composites

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Lignin is an attractive renewable reinforcing agent for polyolefins, which is also an excellent free-radical scavenger and promising low-cost antioxidant for polymers, however, exhibiting poor compatibility with non-polar polymers. In this work, modified polyolefins containing maleic anhydride group like polybond (PB) were used as compatibilizer and incorporated into polypropylene (PP) with lignin to improve the blending ability of the polar filler in the non-polar matrix. The composite containing individual lignin possesses a much smaller elongation at break than neat PP, whereas owing to the significantly improved dispersion by compatibilizer, the incorporation of compatibilizer into PP/lignin blends gives rise to remarkably increased elongation at break. Besides, lignin greatly slows down the UV-induced degradation of PP and dramatically enhances anti-oxidant effect of PP composites in the existence of compatibilizer, in which the elongation at break of PP/PB/2%lignin retains 77% of its original value when it reduces by 92% for neat PP after 240 h of UV irradiation. POLYM. COMPOS., 40:2594–2601, 2019. © 2018 Society of Plastics Engineers

INTRODUCTION

Lignin is a natural macromolecular material, which accounts for nearly 30% of the organic carbon on earth, second only to cellulose [1,2]. It, with cellulose, forms the chief part of woody plant tissues [3]. As a by-product from paper production industry, causing pollution to environment, lignin is readily available at low cost, with a reported annual world production volume of about 50 million tons. In contrast to lignin's abundance in nature, humans have scarcely made full use of lignin [4,5]. Currently lignin is

mainly burned as fuels, which gives it very low value. Since lignin is one of the few renewable sources of aromatic macromolecules and possesses rich phenolic and aliphatic hydroxyl groups, enormous efforts have been devoted to the development of value-added applications for lignin [5–8]. For example, lignin has been used as a macromonomer to synthesize thermosetting polymers, such as epoxy resins [9], and polyurethane [10,11]. Lignin is also widely used as a precursor to prepare carbon-based materials, such as carbon fiber, carbon nanotubes (CNTs), carbon aerogel, and activated carbons [12–15]. Besides, it can also be incorporated into thermoplastic polymers as reinforcing or toughening agents [16–19].

As widely reported, the addition of lignin into polymers can modify mechanical and other physical properties of the polymers [20–22]. For example, thermal stability of epoxy/lignin composites could be enhanced by the incorporation of lignin [23,24]. In comparison with inorganic fillers, the advantages of lignin as fillers in polymers mainly lie in its light weight, low cost, and renewable nature [5,25]. In addition, owing to its abundant phenolic groups, lignin is also a free-radical scavenger, and can be used as a natural antioxidant. It has been employed as low-cost sustainable stabilizers in thermoplastics, like polyolefins, to improve the oxidative, thermal, and light stability of the polymers [26–29]. However, lignin contains a large number of polar groups. It has, therefore, poor compatibility with non-polar polymers as polyethylene and polypropylene (PP), causing very poor dispersion of lignin in these polymers [30–33]. As a result, the great potential of lignin as efficient free-radical scavenger and reinforcing/toughening agents in non-polar polymer systems so far has not been adequately demonstrated.

In this connection, classically important factors such as phenol content and intrinsic reactivity of the lignin molecules are less important than physical factors that can facilitate their dispersion in polymers. For instance, when modified lignin was employed to replace pristine lignin, the dispersion of lignin in non-polar polymers is typically not improved significantly and hence the enhancement in material performances can hardly be achieved [27,34]. To address this issue, recently greater efforts have been devoted to improve the dispersion of lignin in polymer

Additional Supporting Information may be found in the online version of this article.

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matrices via physical means [30–33]. And in our former work, freeze-drying manipulation was successfully developed to improve compatibility of polar lignin and non-polar PP, which significantly enhance the mechanical and thermal properties of PP, and improve the anti-oxidant properties of lignin in PP composites, however, which is limited only to the water-soluble lignin [35]. In particular, there is also a high demand for improving the dispersion of this fascinating low-cost multifunctional sustainable filler in high-volume non-polar polymers commonly used for outdoor applications.

In our work, polar group modified polyolefins were introduced into the PP/lignin composites that, with the aim, to improve the compatibility of polar fillers and non-polar polymer matrices and thereby enhance tensile mechanical and UV-resistant properties of the obtained composites. Herein, impressively, for the first time the improved dispersion of lignin in PP achieved by compatibilizing agent not only enhances reinforcement effect of the lignin in PP, but also drastically enhances their UV-oxidant stabilities.

EXPERIMENTAL

Materials

PP (Cosmoplene H101E, melt flow index = 3.5 g/10 min, density = 0.9 g/cm³) and were supplied by Polyolefin Company (Singapore) Pte. Ltd. Polybond-3200 (PB, melting point = 157°C, density = 0.91 g/cm³, maleic anhydride level = 1.0 wt%) is homo-PP modified by maleic anhydride, which was supplied by Chemtura Corporation. PP-graft-maleic anhydride (PP-MA, M_n = 3900, M_w = 9100, melting point = 156°C, density = 0.934 g/cm³), alkali lignin with low sulfonate content and all other chemicals were purchased from Sigma-Aldrich Chemicals Incorporation (USA) and used without further purification.

Preparation of PP/PB/Lignin or PP/PP-MA/Lignin Composites

The PP and 10 wt% of PB or PP-MA were mixed first by using Hakke mixer for 5 min at 180°C, and a certain amount of lignin were added into the PP/PB blends for another 15 min. Prior to compounding, PP pellets and other raw materials were all dried in a vacuum oven at 50°C for 24 h to remove moisture.

Characterization

The dispersion state of lignin in PP and the morphologies of the lignin samples were examined using an Olympus BX53 polarizing optical microscope (POM) at a magnification of 1 × 100, as well as a field emission scanning electron microscope (SEM, JEOL JSM 6340F) after coating the samples with gold. Thermo-gravimetric analysis (TGA) was conducted using a TA Q500 TGA at a heating

rate of 10°C/min from room temperature to 700°C in N₂ condition. Degradation temperature (T_d) is defined as the temperature at 50 wt% weight loss. Fourier transform infrared spectroscopic (FTIR) measurements were performed using a Perkin-Elmer Instruments Spectrum GX FTIR spectrometer at room temperature from 500 to 4,000 cm⁻¹, with each sample scanned 16 times at a resolution of 4 cm⁻¹. The tensile properties were measured using an Instron 5567 machine according to ISO standard 527 at a crosshead speed of 10 mm/min using dumbbell-shaped specimens (ISO 527-2-Typer 5A, 500 N load cell), which were prepared using Thermo Hakke microinjector (Germany) at 210°C with a pressure of 800 bar. More than five specimens were tested for each set of variation.

UV Stability Tests. The dumbbell-shaped test specimens of lignin-reinforced PP composites were placed in an Atlas Suntest XXL+ UV lamp chamber, which had a layer of reflective aluminium foil inside to ensure that all the specimens would have an even exposure to UV. The UV irradiation was conducted at 35°C for 240 h with light intensity of 50 W/m².

RESULTS AND DISCUSSION

Blending and Dispersion of Lignin in PP

To improve the compatibility of lignin and PP, chemically modified polyolefins containing maleic anhydride group as PB were incorporated into PP matrix with lignin by melt mixing, which were confirmed by FTIR analysis, it was conducted and the results are shown in Fig. 1a. It can be seen that for PP/PB compared with neat PP, an intense band at ~1,640 cm⁻¹ appears, which is attributed to stretching vibration of carbonyl (C=O) in maleic anhydride group. And for PP/PB/lignin composites, peak at ~1,718 cm⁻¹ can be attributed to stretching vibration of carboxyl (C=O) in lignin, whose intensity increases with lignin content.

Besides, the PP/PB/lignin composites exhibits much higher thermal degradation temperature (T_d) than neat PP, whereas, it is worth noting that the increase of lignin content from 2 to 4 wt% causes even a slight fall of the T_d . Since the T_d of PP/PB blend is much higher than that of neat PP and PP/PB/lignin composites shown in Fig. 1b, the enhanced T_d of PP/PB/lignin compared with neat PP is mainly due to the effect of PB. In other words, lignin acts as a role of lowering T_d of the polymer, and it is probably due to the oxygen-containing groups of lignin that accelerate the thermal degradation in N₂ atmosphere. On the other hand, PP-MA with lower molecular weight was also applied as compatibilizer by replacement of PB, exhibiting a lower T_d of PP/PP-MA blend than neat PP, and the PP/PP-MA/lignin composites therefore have further lower T_d than neat PP, which is shown in Supporting Information Fig. S1.

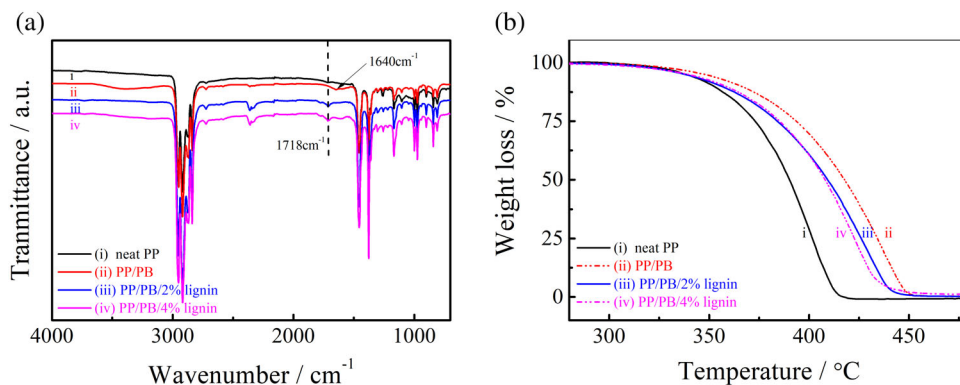


FIG. 1. FTIR spectra (a) and TGA curves (b) of neat PP (i), PP/PB blend (ii), PP/PB/lignin composites with 2 wt% lignin (iii) and 4 wt% lignin (iv). [Color figure can be viewed at wileyonlinelibrary.com]

As known, the performance of polymer composites strongly depends on the dispersion state of the fillers in the polymer matrices. For instance, a better dispersion may result in enhanced interactions between the polymers and fillers [36], and the mechanical properties of the composites may thereby be improved owing to the more effective stress transfer from the matrices to fillers. To investigate

the effect of polar group containing compatibilizer on the dispersion state of lignin in PP, PB was introduced into PP matrix as well as lignin incorporation via melt compounding. Besides, PP/lignin composite without the application of compatibilizer and neat PP are also prepared under the same conditions for comparison. The POM images in Fig. 2b show that the sizes and shapes of the lignin

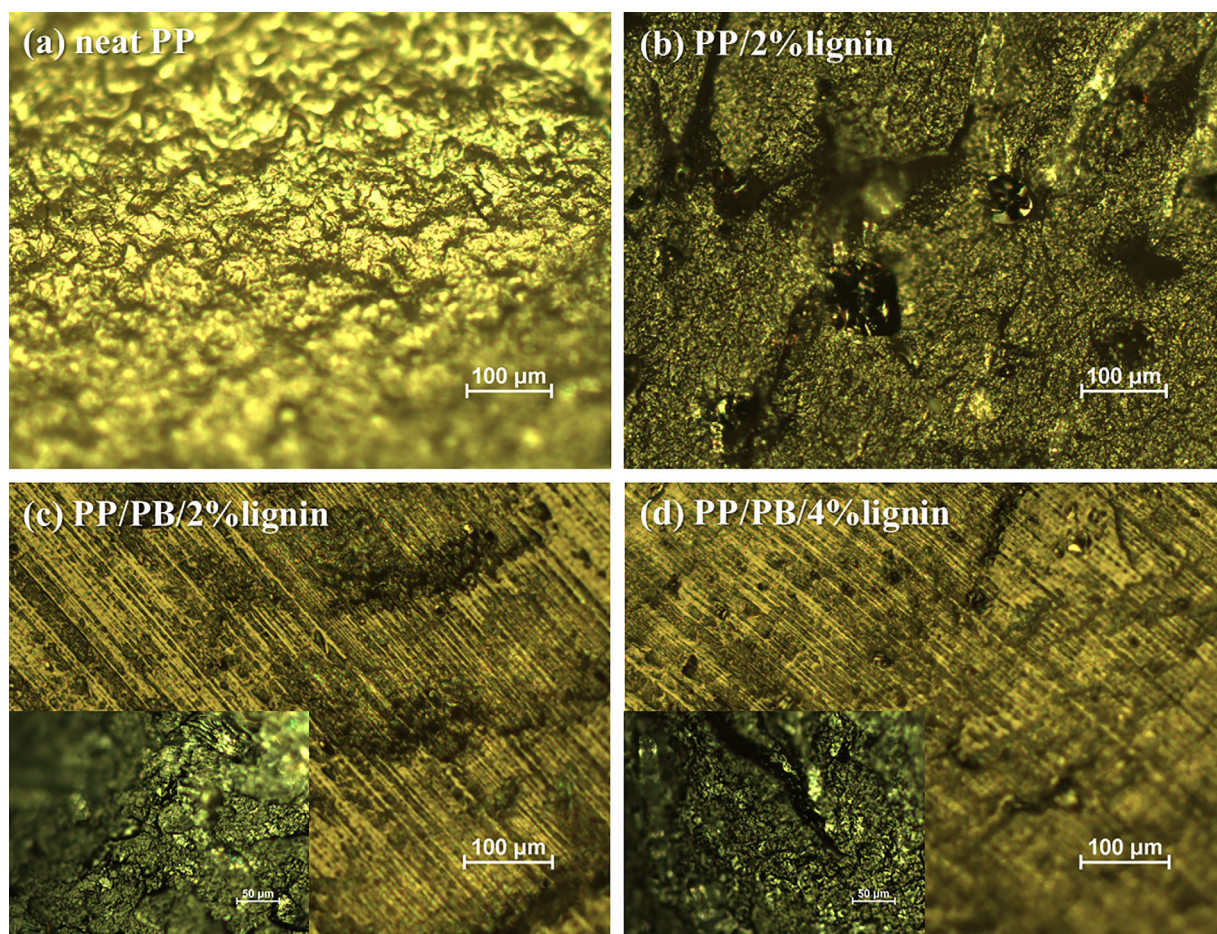


FIG. 2. POM ($\times 100$) of neat PP (a), PP/lignin composite with 2 wt% lignin (b), PP/PB/lignin composite with 2 wt% lignin (c), PP/PB/lignin composite with 4 wt% lignin (d). [Color figure can be viewed at wileyonlinelibrary.com]

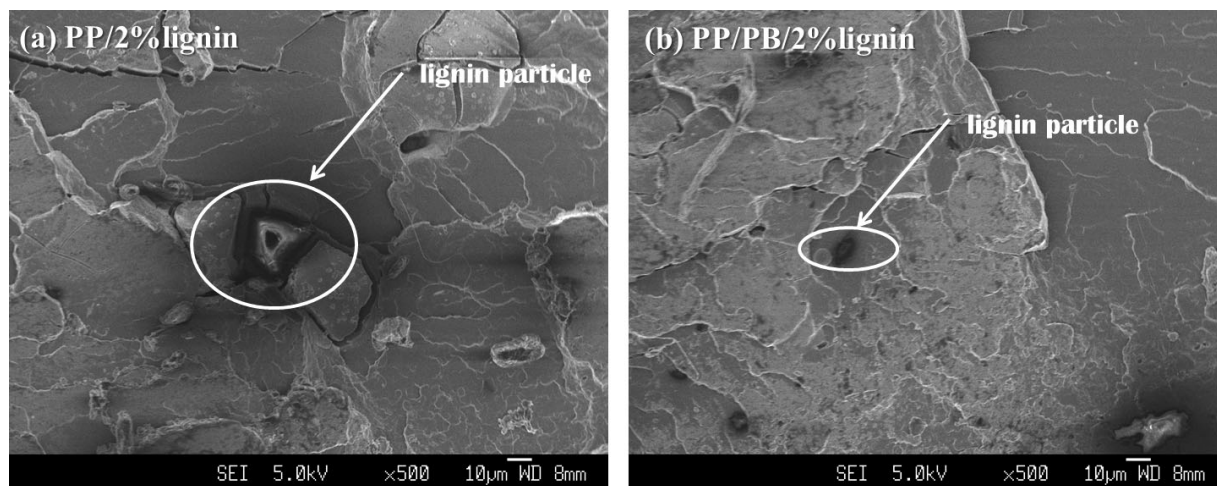


FIG. 3. SEM images showing the fractured surfaces of PP/lignin (a) and PP/PB/lignin composites (b) both containing 2 wt% lignin.

particles (the dark regions) are almost not changed after the melt compounding that is, they are still spherical or irregular large sizes shaped particles. In contrast, particle size of lignin in the PP matrix after introducing PB is much smaller, where many short fine dark particles are observed for the blends of lignin, PB and PP (Fig. 2c and d). The polar maleic anhydride group containing PP has a good compatibility with the polar lignin, which therefore significantly decreases the size of lignin particle in the PP matrix and facilitates their dispersion in the PP matrix. The relatively excellent dispersion of the lignin in PP/PB matrix is confirmed by SEM images given in Fig. 3. Thus, in existence of compatibilizer, the lignin can be dispersed more uniformly and exhibits much smaller shape compared with that in the individual PP matrix.

Tensile Mechanical Properties of Lignin-Blended PP Composites

As lignin consists of rigid aromatic macromolecules, it is recognized as an abundant and low-cost reinforcing agent in relatively flexible polymers. To investigate the reinforcement effect of lignin under the action of compatibilizer, a series of PP and lignin composites were prepared for tensile tests. Typical tensile stress–strain curves of PP/lignin composite samples are presented in Fig. 4 for easy comparison with that of neat PP. The compositions and preparation conditions for the composite samples are also summarized in Table 1. For example, PP/2%lignin refers to the composite containing only 2 wt% of individual lignin, while PP/PB/2%lignin represents the composite containing 2 wt% of lignin, and 10 wt% of compatibilizer PB is also included. The tensile properties of the composites are also listed together with those of neat PP in this table.

From Fig. 5 and Table 1, it is clear that the addition of individual lignin into PP increases its tensile modulus and yield stress, whereas at the same time, it lowers the yield

strain and elongation at break of the composites. By the further addition of compatibilizing agent PB can further enhances their modulus, as modulus of PP/PB/lignin is higher than neat PP and PP/PB blend. In other word, lignin containing PP/PB composites exhibits much higher modulus than their counterpart with the same amount of lignin but no compatibilizer. And the modulus also increases with the lignin content that is, reinforcing effect becomes more prominent influenced by PB. The enhanced tensile modulus may be attributed to the aromatic and rigid structure of lignin, and obvious improved compatibility of polar lignin and non-polar PP by PB leads to further enhanced filler–matrix interactions and certainly the reinforcement of modulus [36].

Similarly, it is easy to understand that as a rigid filler, lignin also induces a significant decrease in yield strain, it was also demonstrated by that the exiting compatibilizer further decreases the yield strain for PP/PB/2%lignin, exhibiting lower strain (0.142) than that of PP/2%lignin

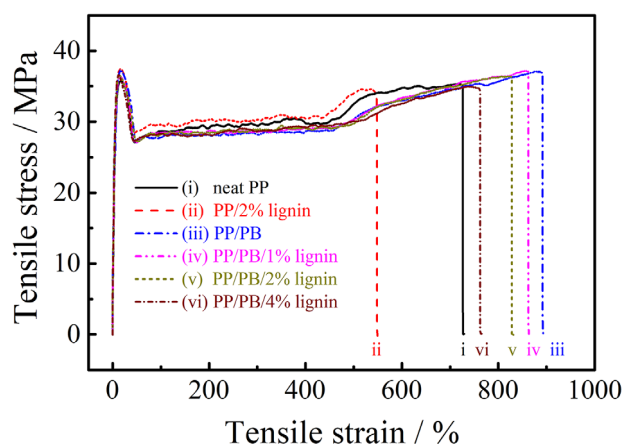


FIG. 4. Tensile stress–strain curves of neat PP (i), PP/lignin composites with 2 wt % lignin (ii), PP/PB blend (iii), PP/PB/lignin composites containing 1 wt% (iv), 2 wt % lignin (v), and 4 wt% lignin (vi). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1. Mechanical properties of neat PP and lignin blended PP composites tested with tensile speed of 10 mm/min.

Sample	PB content (wt%) ¹	Lignin content (wt%) ²	Young's modulus (MPa)	Yield stress (MPa)	Yield strain (mm/mm)	Elongation at break (%)
neat PP	0	0	611 ± 32	35.6 ± 0.2	0.168 ± 0.004	700 ± 73
PP/2%lignin	0	2	649 ± 31	37.4 ± 0.9	0.150 ± 0.012	545 ± 91
PP/PB	10	0	641 ± 8	36.9 ± 0.6	0.165 ± 0.007	826 ± 68
PP/PB/1% lignin	10	1	645 ± 16	36.4 ± 0.5	0.151 ± 0.005	855 ± 42
PP/PB/2% lignin	10	2	674 ± 18	36.8 ± 0.6	0.142 ± 0.003	771 ± 46
PP/PB/4% lignin	10	4	675 ± 15	36.3 ± 0.3	0.122 ± 0.003	763 ± 15

¹ PB content in the PP/PB blends;

² Lignin content in the lignin blended PP composites.

(0.150), whereas at the same time, PP/PB blend shows little change of the yield strain compared with neat PP. Furthermore, as the extent of lignin increases, yield strain dramatically decreases, which is depending upon the improvement of the dispersion state of lignin filler in the PP matrix as well as its rigid structure.

Unlike the changes in modulus and yield stress, the change in elongation at break brought by the addition of

PB and lignin is more impressive, as shown in Fig. 5 and Table 1. The composite containing 2 wt% lignin without PB (PP/2%lignin) possesses a much smaller elongation at break (545%) than neat PP. On the contrary, the introducing of compatibilizer as PB into PP significantly increases their elongation at break (826%), and the further incorporation of small amount of lignin can further give rise to the increased elongation at break. In particular, PP/PB/1%

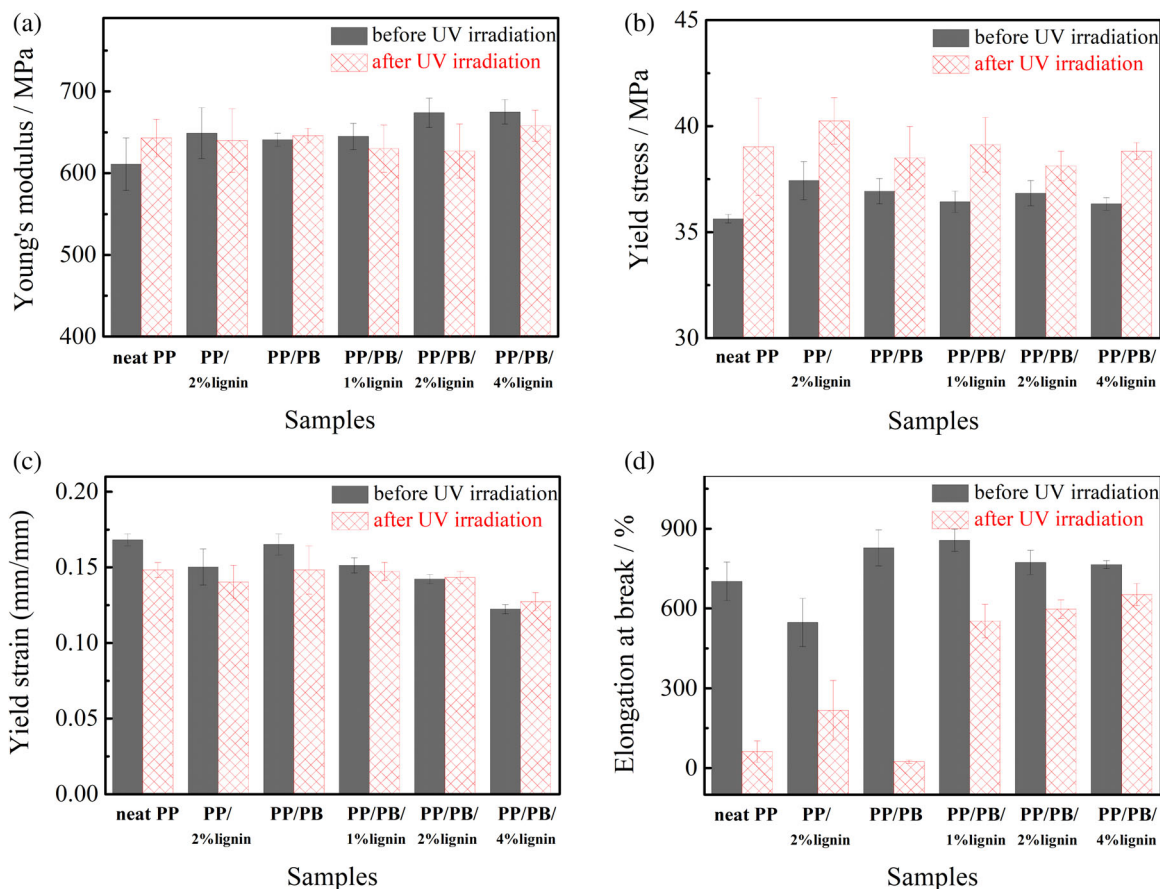


FIG. 5. Tensile mechanical properties of lignin containing PP composites before and after UV irradiation. (a) Young's modulus, (b) yield stress, (c) yield strain, and (d) elongation at break of neat PP, PP/lignin composites with only 2 wt% lignin, PP/PB/lignin composites containing 1 wt%, 2 wt% lignin, and 4 wt% lignin. [Color figure can be viewed at wileyonlinelibrary.com]

lignin has the longest elongation at break, 855%, which increases by nearly 22% of neat PP (700%) and 56% of PP/2%lignin (545%). Obviously, the drastically increased elongation at break given by the PB and lignin is likely due to the enhanced interaction between polar lignin filler and non-polar PP matrix under the improved dispersion and compatibility induced by compatibilizer [35]. For composites without PB, the much large lignin particles with smaller interaction area between PP results in very limited interfacial adhesion, and hence the elongation at break drops drastically, that is, the direct addition of individual lignin makes the composite much more brittle. The remarkable increase of the elongation at break also implies that a small amount of lignin with cooperative action of compatibilizer may act as an effective toughening agent to improve the toughness of the composites. On the other hand, the increased addition of the lignin results in the reduction of the elongation at break, as 2 and 4% lignin containing PP/PB/lignin composites respectively exhibit only 771 and 763% of the elongation at break. And the further addition of the filler results in further drop of the elongation at break, as PP/PB/6%lignin shows only 658% of the elongation (data not shown). It is presumably because at a higher content, the lignin is more difficult to be dispersed uniformly. Therefore, the dispersion state in the matrix may also plays an important role in determining the overall mechanical properties of the composites [22]. The reinforcing effect of lignin under the influence of compatibilizer was also confirmed by another polar group containing PP (PP-MA), shown in Supporting Information Fig. S2.

UV Stabilities of the PP Composites

As known, PP is prone to free radical-induced degradation, which can therefore easily degrade in outdoor environment, resulting in a severe decrease of material toughness [27,37]. In general, the PP degradation in outdoor environment is mainly due to its exposure to UV light. Since lignin contains abundant phenolic groups, it has been employed as an antioxidant to scavenge free radicals generated by UV-induced degradation [27]. In this study, compatibilizer improves the interaction of the filler and the polymer matrix with much larger contacting areas between the lignin and PP by the smaller particle in the matrix. Thus, with the improved dispersion of lignin in PP matrix, it is highly expected that the lignin may act as a more efficient free radical scavenger to improve the UV stability of PP.

In order to investigate the anti-oxidant function of lignin in PP, tensile test dumbbell-shaped specimens of the composites were exposed to UV light with light intensity of 50 w/m² at 35°C for 240 h. Figs. 5 and 6 show the comparison of tensile properties of the composites as well as neat PP before and after the UV irradiation (the data are also summarized in Supporting Information Table S1). It is observed that the yield strain and the elongation at break of neat PP reduce by 12 and 92%, respectively after the UV irradiation, whereas, its tensile modulus and the yield stress

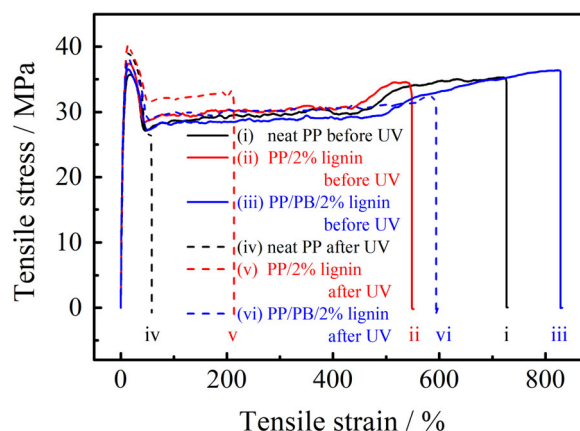


FIG. 6. Typical tensile curves of neat PP, PP/2%lignin, and PP/PB/2%lignin before and after UV irradiation. [Color figure can be viewed at wileyonlinelibrary.com]

increases. For PP/2%lignin, its yield strain and elongation at break drop by 7 and 61%, which is much lower than neat PP. On the other hand, the addition of individual PB even promotes the UV degradation of the composites with the elongation at break of PP/PB blend drop by 98%, that is probably because the UV irradiation causes ring-opening of maleic anhydride group, hence induces the generating of the free radicals and the following degradation. Even on this base, it is much impressing that the PP/PB/lignin composites all exhibit much smaller or even no negative changes in tensile properties after the UV irradiation, revealing the excellent anti-oxidant function of lignin even in the existence of PB. For instance, the tensile modulus, yield stress, and yield strain of PP/PB/2%lignin almost remain the same after the UV exposure, while its elongation at break reduces by only 23%, which is far lower than that of PP/2%lignin composite (61%) and neat PP (92%). In other word, PP/PB/2%lignin retains about 77% of its original elongation at break value after the UV irradiation, which is much larger than that PP/2%lignin with 39%. It also implies that PP/PB/2%lignin is still fairly tough after

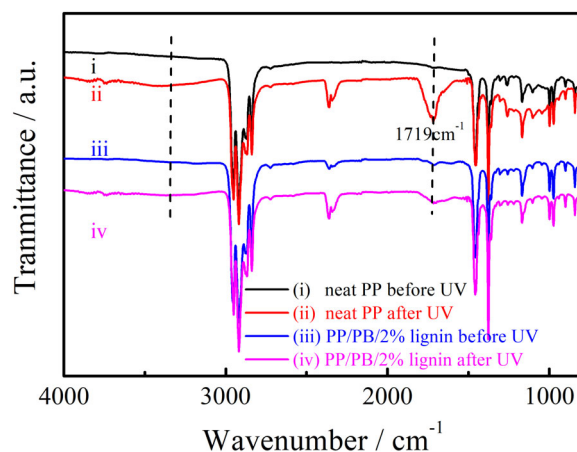


FIG. 7. FTIR spectra of neat PP and PP/PB/2%lignin before and after UV irradiation. [Color figure can be viewed at wileyonlinelibrary.com]

the UV irradiation. More impressively, more lignin addition results in the better anti-oxidant property of the composites, as the PP/PB/4%lignin retains about 85% of its original elongation at break value after the UV irradiation, which is larger than that of the PP/PB/lignin composite containing 2% lignin (77%).

Besides, compared with the composite without compatibilizing agent PB, the composites with cooperative action of compatibilizer show less deterioration of the tensile properties after UV irradiation. For example, PP/2%lignin exhibits a 7% decrease of the yield strain, whereas the yield strain of PP/PB/1%lignin, PP/PB/2%lignin and PP/PB/4% lignin remain almost unchanged after the UV irradiation. As discussed above, PB significantly improves the compatibilities of polar lignin and non-polar PP, and thus, PP/PB/2%lignin have a large contacting area between the antioxidant lignin and PP, allowing the lignin to act as a free-radical scavenger more efficiently.

The effect of compatibilizer acting a great function of the anti-oxidant property of the composites is also confirmed by another compatibilizing agent as PP-MA with lower molecular weight, where, by addition of PP-MA, the PP and lignin composites also exhibits a much obvious lower drop of the mechanical performance especially as the yield strain and the elongation at break after UV irradiation shown in Supporting Information Figs. S3, S4 and Supporting Information Table S2. In summary, by the improvement of the compatibility between filler and polymer matrix under the function of the compatibilizer, lignin can act as an excellent and efficient antioxidant. That is, the enhancement of PP/lignin composites brought by PB is more impressive than that without compatibilizer.

To further confirm the excellent free radical scavenging function of lignin under the influence of compatibilizer, FTIR analysis results are shown in Fig. 7. It can be seen that for neat PP, an intense band at $\sim 1,719\text{ cm}^{-1}$, which can be attributed to stretching vibration of carbonyl (C=O) group, appears after 240 hours UV irradiation. Furthermore, broad absorption in the regions of $\sim 3,100$ to $\sim 3,600\text{ cm}^{-1}$ in the curves of neat PP after UV irradiation indicate the existence of hydroxyl groups (OH). The principal reaction occurring in UV-irradiated PP is chain scission or side-group abstraction. The radicals generated by UV irradiation oxidize the C-H bonds on the PP chains to form the carbonyl groups, which induce chain scission. Thus the intense carbonyl characteristic band indicates that neat PP has under gone severe oxidative degradation. In contrast, PP/PB/2%lignin shows extremely little increase of the characteristic absorption band for carbonyl (C=O) and hydroxyl (OH) group after the UV irradiation, demonstrating that lignin in this composites is able to scavenge the free radicals efficiently.

CONCLUSIONS

In this work, a compatibilization method by using modified polyolefins containing polar maleic anhydride as

compatibilizer was successfully developed to enhance the compatibility of lignin and PP, which significantly improve the corresponding dispersion of the polar filler in the non-polar matrix with more uniform filler dispersion, smaller particle size and much larger interfacial area. The results of tensile mechanical tests show that the Young's modulus, tensile stress and elongation at break are enhanced in comparison with that of neat PP or PP with the same amount of lignin but no compatibilizer. In particular, the elongation at break is drastically increased in the existence of PB when containing only 1 wt% of lignin, revealing the toughness effect of lignin in PP matrix. More impressively, by addition of compatibilizer PB, lignin acts as an excellent free radical scavenger that greatly slows down UV-induced degradation of PP under the influence of the filler dispersion improvement. In a sharp contrast to neat PP, the tensile mechanical properties of the PP/lignin composites show remarkable less drop after 240 h UV irradiation. In conclusion, addition of compatibilizer containing polar functional group is a simple and efficient route to improve the compatibility of polar filler and non-polar matrix and further enhance the multifunctional properties of composites.

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REFERENCES

1. F. G. Calvo-Flores, J. A. Dobado, *Chem. Sus. Chem.* 2010, **3**, 1227.
2. G. Gellerstedt, *Ind. Crops Prod.* 2015, **77**, 845.
3. Y. Qian, H. M. Lou, W. F. Liu, D. J. Yang, X. P. Ouyang, Y. Li, X. Q. Qiu, *Tappi J.* 2018, **17**, 125.
4. M. Norgren, H. Edlund, *Curr. Opin. Colloid. In. Sci.* 2014, **19**, 409.
5. V. K. Thakur, M. K. Thakur, P. Raghavan, M. R. Kessler, *ACS Sustain. Chem. Eng.* 2014, **2**, 1072.
6. B. Imre, B. Pukánszky, *Eur. Polym. J.* 2015, **68**, 481.
7. D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, *Green Chem.* 2016, **18**, 1175.
8. T. Saito, R. H. Brown, M. A. Hunt, D. L. Pickel, J. M. Pickel, J. M. Messman, F. S. Baker, M. Keller, A. K. Naskar, *Green Chem.* 2012, **14**, 3295.
9. J. Sun, C. Wang, J. C. C. Yeo, D. Yuan, H. Li, L. P. Stubbs, C. He, *Macromol. Mater. Eng.* 2016, **301**, 328.
10. B. Xue, J. Wen, R. Sun, *ACS Sustain. Chem. Eng.* 2014, **2**, 1474.
11. P. Cinelli, I. Anguillesi, A. Lazzeri, *Eur. Polym. J.* 2013, **49**, 1174.
12. P. J. Suhas, M. Carrott, M. Ribeiro Carrott, *Bioresour. Technol.* 2007, **98**, 2301.

13. P. Myllytie, M. Misra, A. K. Mohanty, *ACS Sustain. Chem. Eng.* 2016, **4**, 102.
14. Q. Yan, X. Zhang, J. Li, E. B. Hassan, C. Wang, J. Zhang, Z. Cai, *J. Mater. Sci.* 2018, **53**, 8020.
15. W. J. Youe, S. J. Kim, S. M. Lee, S. J. Chun, J. Kang, Y. S. Kim, *Int. J. Biol. Macromol.* 2018, **112**, 943.
16. R. Ding, H. Wu, M. Thunga, N. Bowler, M. R. Kessler, *Carbon* 2016, **100**, 126.
17. Y. Sun, L. Yang, X. Lu, C. He, *J. Mater. Chem. A* 2015, **3**, 3699.
18. C. D. Tran, J. Chen, J. K. Keum, A. K. Naskar, *Adv. Funct. Mater.* 2016, **26**, 2677.
19. Y. Chung, J. V. Olsson, R. J. Li, C. W. Frank, R. M. Waymouth, S. L. Billington, E. S. Sattely, *ACS Sustain. Chem. Eng.* 2013, **1**, 1231.
20. D. Kun, B. Pukánszky, *Eur. Polym. J.* 2017, **93**, 618.
21. F. Chen, H. Dai, X. Dong, J. Yang, M. Zhong, *Polym. Compos.* 2011, **32**, 1019.
22. K. Bula, Ł. Klapiszewski, T. Jesionowski, *Polym. Compos.* 2015, **36**, 913.
23. S. Sen, S. Patil, D. S. Argyropoulos, *Green Chem.* 2015, **17**, 4862.
24. L. Liu, M. Qian, P. a. Song, G. Huang, Y. Yu and S. Fu, *ACS Sustain. Chem. Eng.*, **4**, 2422 (2016), 2431.
25. V. K. Thakur, M. K. Thakur, R. K. Gupta, *Int. J. Polym. Anal. Charact.* 2014, **19**, 256.
26. S. L. Phua, L. Yang, C. L. Toh, D. Guoqiang, S. K. Lau, A. Dasari, X. Lu, *ACS Appl. Mater. Interfaces* 2013, **5**, 1302.
27. H. Sadeghifar, D. S. Argyropoulos, *ACS Sustain. Chem. Eng.* 2015, **3**, 349.
28. Q. Ye, F. Zhou, W. Liu, *Chem. Soc. Rev.* 2011, **40**, 4244.
29. S. R. Yearla, K. Padmasree, *J. Exp. Nanosci.* 2015, **11**, 289.
30. H. J. Lee, H. K. Lee, E. Lim, Y. S. Song, *Compos. Sci. Technol.* 2015, **118**, 193.
31. H. Lei, T. Stevanovic, D. Rodrigue1, *J. Appl. Polym. Sci.* 2014, **131**, 41040
32. J. Yeo, D. Seong, S. Hwang, *J. Ind. Eng. Chem.* 2015, **31**, 80.
33. L. Hu, T. Stevanovic, D. Rodrigue, *J. Appl. Polym. Sci.* 2015, **132**, 41484.
34. S. Laurichesse, L. Avérous, *Prog. Polym. Sci.* 2014, **39**, 1266.
35. F. Chen, W. Liu, S. I. Seyed Shahabadi, J. Xu, X. Lu, *ACS Sustain. Chem. Eng.* 2016, **4**, 4997.
36. B. Bozsódi, V. Romhányi, P. Pataki, D. Kun, K. Renner, B. Pukánszky, *Mater. Des.* 2016, **103**, 32.
37. C. Pouteau, P. Dole, B. Cathala, L. Averous, N. Boquillon, *Polym. Degrad. Stab.* 2003, **81**, 9.