

# Synthesis of a Polypropylene-based Compatibilizer by a Radiation Grafting and an Evaluation of PP/WP Composite Properties

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**Abstract:** The polypropylene-based compatibilizers, polypropylene-g-maleic anhydride (PP-MAH) and polypropylene-g-(styrene-co-maleic anhydride) (PP-St/MAH) were successfully prepared by a high energy irradiation method. The grafting degree of MAH onto PP increased with an increasing dose and MAH content. In addition, the grafting degree of MAH onto PP was enhanced in the presence of styrene as a comonomer. The compatibilizing effect of the newly-prepared graft copolymers on the polypropylene/wood powder (PP/WP) composites was studied by means of the UTM, SEM and DSC techniques. It was observed that the addition of PP-St/MAH enhanced the mechanical properties of the PP/WP composites and increased the crystallization temperature of the PP phase. These results verify that an improved compatibility and interfacial adhesion between the PP matrix and wood powder contributes to an improvement of the mechanical properties.

**Keywords:** radiation-induced grafting, compatibilizer, polypropylene, wood powder, maleic anhydride

## Introduction

Composites based on thermoplastic have received considerable attention due to their many advantages. The mechanical properties of thermoplastics are often required for specific applications, and for this reason, various inorganic fillers such as calcium carbonate, clay, mica and fiberglass have been widely used. Recently, the addition of natural fillers to thermoplastics was performed to reduce the cost per unit volume and improve the stiffness [1-6]. However, there is a poor compatibility between the hydrophobic thermoplastic matrix and the hydrophilic wood powder, which leads to a reduction of the mechanical properties [7-11]. Thus, compatibilizers have been investigated to enhance the resultant interfacial interaction [12]. One of the successful compatibilizers is maleic anhydride grafted polypropylene (PP-MAH), which has been shown to improve the properties of a polypropylene/wood powder (PP/WP) composite [13-16].

These PP-MAH compatibilizers have been prepared by a solution grafting [17], melt grafting [18,19], and a sol-

id state grafting [20,21], in the presence of a peroxide initiator. It has been suggested that the mechanism for the grafting method is the occurrence of MAH incorporation mainly at the chain ends after or before a chain scission reaction, which results in a decrease of the PP molecular weight [18]. Likewise, a radiation-induced graft polymerization could be a radical mechanism, so that the changes in the PP molecular weight could be caused by a radiation grafting of MAH. However, a graft polymerization induced by a high energy irradiation method has several advantages over the previous methods. The previous methods have the following shortcomings: an initiator must be used, which leads to a more complicated compatibilization chemistry, a polymerization is usually not complete under the available thermal conditions, and residual monomers from a thermal polymerization may thus adversely influence the thermal and mechanical properties of the blends. On the other hand, a graft polymerization induced by a high energy irradiation method has advantages: the polymerization proceeds mildly and thoroughly, the chemistry of the reaction system is free of a contamination, and the energy consumption is relatively low [22,23].

In this study, the polypropylene-based compatibilizers, polypropylene-g-maleic anhydride (PP-MAH) and

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polypropylene-g-(styrene-co-maleic anhydride) (PP-St/MAH), were prepared by a high energy irradiation method. The compatibilizing effect of the newly-prepared graft copolymers on the PP/WP composites was studied by means of the UTM, SEM, and DSC techniques.

## Experimental

### Materials

Polypropylene (PP) (B310, MW: 523,000) used in the preparation of the compatibilizers and composites and it was donated from Honam Petrochemical Co. Maleic anhydride (MAH) (Showa chemical) was purified by a re-crystallization by using diethyl ether. Styrene (St) was purchased from Aldrich Chemical Company and used as received. Wood powder, JELUXYL WEHO 120/F, was purchased from JELU-WERK Josef Ehrler GmbH & Co. (Germany). The size distributions of the filler ranged from 70 to 100  $\mu\text{m}$ . The bulk density was 140 g/L.

### Synthesis of PP-based Compatibilizers

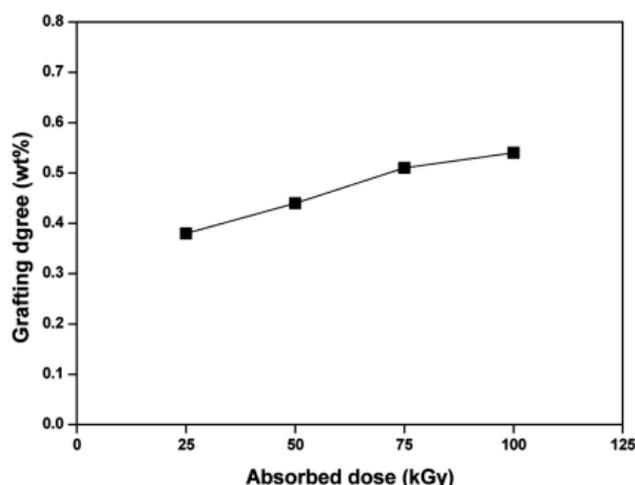
PP was dry blended with MAH (1 ~ 7 phr) or St /MAH mixture with different ratios in a lab-scale Brabender at 170 °C and at a 65 rpm rotor speed for 4 min. The prepared samples were  $\gamma$ -irradiated under various irradiation doses ranging from 25 to 100 kGy at a dose rate of 20 kGy/h and at room temperature. The crude products, PP-MAH and PP-St/MAH, were purified by a refluxing in xylene at 130 °C for 2 h and poured into a large excess of acetone. The products were filtered, washed with acetone, and then dried at 80 °C.

### Preparation of PP/WP Composites

PP/PP-St/MAH composites, containing 10, 20, 30, and 40 wt% WP, were prepared with each of these separated wood samples. Out of the compatibilizers prepared above, the PP-St/MAH with the highest grafting degree, 1.1 wt%, was employed here. Samples were weighed according to the desired ratio to make up a total mass of 40 g and mixed in a lab-scale Brabender at 180 °C, at a rotor speed of 60 rpm for 10 min. Before mixing, the wood powder and PP-St/MAH were dried in an oven at 100 °C for 24 h and 1 h respectively. Composites with and without PP-St/MAH were prepared.

### Characterization

The grafting degree (DOG) was measured by an acid-base titration method. A known weight of a graft copolymer was dissolved in hot xylene, and titrated with alcoholic potassium hydroxide (0.01 N), which had been standardized against potassium phthalate by using 1 % thymol blue as an indicator. The percentage of the func-



**Figure 1.** Effect of absorbed dose on the grafting degree at the fixed MAH content (3 phr).

tionized polymer was estimated using the following equation:

$$\text{Grafting degree (wt\%)} = \frac{V_{\text{KOH}} \times [\text{KOH}] \times W_{\text{eq,MAH}}}{W_{\text{sample}}} \times 100$$

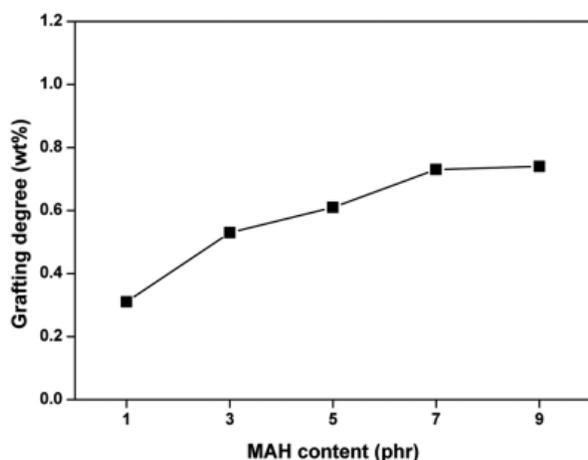
where  $V_{\text{KOH}}$  is the volume of KOH used in mL,  $[\text{KOH}]$  is the concentration of KOH,  $W_{\text{eq,MAH}}$  is the equivalent weight of MAH and  $W_{\text{sample}}$  is the weight of the sample.

The FT-IR spectrum of the graft copolymers was recorded by a Bruker Tensor 37 FT-IR spectrometer. The tensile properties were measured by using an Instron 4206 according to ASTM D638. Thermal analysis was performed with a DSC Q100 differential scanning calorimeter. The test was conducted in a nitrogen atmosphere with a heating rate of 10 °C/min between 30 and 180 °C. The melting temperatures ( $T_m$ ) values were taken from the second heating curve. Crystallinities were calculated by using an extrapolated value of the enthalpy corresponding to a melting of 100 % crystalline samples:  $\Delta H_{PP} = 137.9$  J/g. The fractured surfaces of the various PP/WP composites were examined under a Philips XL30S SEM.

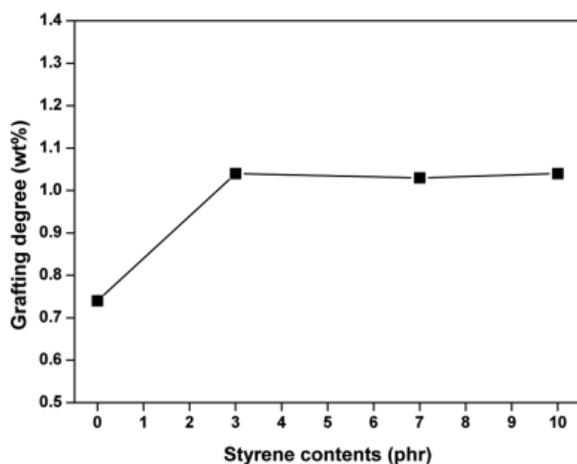
## Results and Discussion

### Synthesis of the Compatibilizers

The effects of the absorbed dose are illustrated in Figure 1. The grafting degrees of MAH on PP increased with the absorbed dose due to a higher formation of free radicals with a dose increase in the grafting system. The highest grafting degree, 0.54 wt%, was obtained at 100 kGy. In addition, the DOG of MAH onto PP with an increase of the MAH content at a fixed dose was investigated as shown in Figure 2. The degree of functionali-



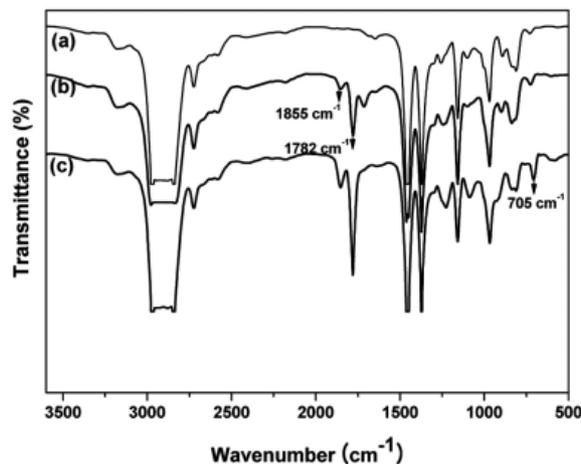
**Figure 2.** Effect of MAH content on the grafting degree at the fixed dose (100 kGy).



**Figure 3.** Effect of styrene content on the grafting degree at the fixed MAH content (7 phr).

zation of MAH increases initially but it reaches a maximum at 0.74 wt% and then levels off. The maximum level of the functionalization did not correspond with the highest level of the initial monomer concentration, indicating that the grafting degree is not exclusively dependent on the monomer concentration [25]. Thus, it is found in this system that the condition for the highest DOG was at 7 phr of MAH with the absorbed dose of 100 kGy.

To enhance the DOG of MAH, a graft polymerization was performed in the presence of various contents of styrene and the results are shown in Figure 3. Increasing the styrene content seems to be ineffective for the DOG because of an evaporation of the styrene at the applied mixing temperature. However, the DOG of PP-St/MAH, 1.04 wt%, was higher than that of PP-MAH. This is due to the fact that the presence of styrene, which is capable of donating electrons, could activate MAH by rendering its structure unsymmetrical as well as its bonding of radical-anion characters [26].

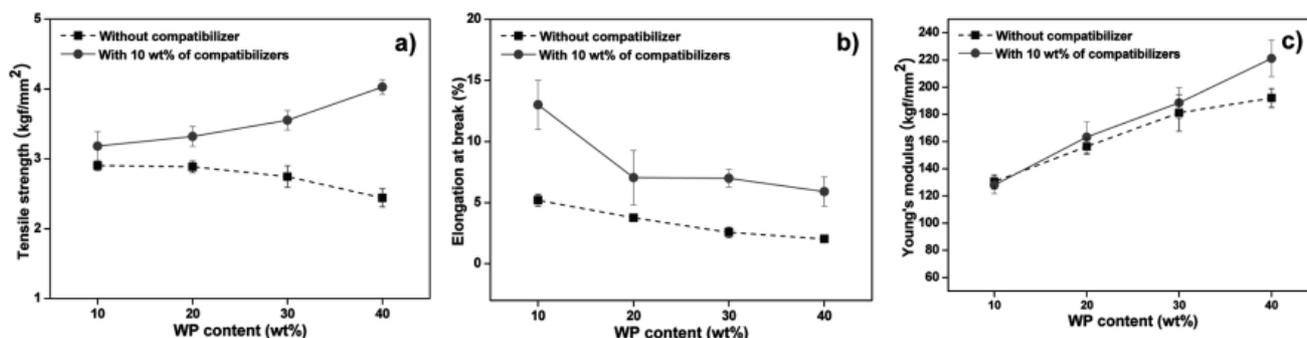


**Figure 4.** FT-IR spectra: (a) atactic PP, (b) PP-MAH and (c) PP-St/MAH.

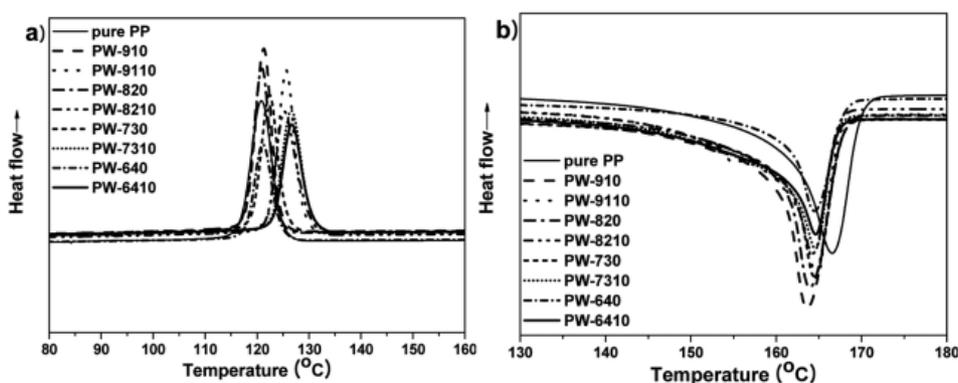
The FT-IR spectra of the pure PP and compatibilizers are shown in Figure 4. After a graft copolymerization of MAH and St/MAH onto PP, the peaks of the carbonyl group of MAH were observed at 1855 and 1782  $\text{cm}^{-1}$ . Also, the peaks of an aliphatic CH group of PP and the out-of-plane bending peaks of a benzene ring in styrene appeared at 2725 and 705  $\text{cm}^{-1}$ . These indicate that the MAH and St/MAH were successfully grafted onto PP.

#### Effect of PP-St/MAH on the PP/WP Composites

PP/WP composites were prepared according to the compositions presented in Table 1. The tensile properties of the PP/WP composites are seen in Figure 5. Compared to the tensile strength of pure PP, 3.19  $\text{kgf/mm}^2$ , those of the non-compatible PP/WP composites decreased for all the compositions, as shown in Figure 5(a). This behavior could result from the fact that the interfacial adhesion is weak and the composite loses its toughness [27]. On the other hand, the tensile strength of the composites compatibilized with PP-St/MAH increased as the WP content increased. This could be attributed to an improvement of the interfacial adhesion between PP and WP by PP-St/MAH, resulting in an improvement of the mechanical properties. Figure 5(b) shows that an elongation of the composites with the compatibilizers is higher than that of the ones without the compatibilizers. In addition, all the composites had a remarkably decrease in their elongations at break for all the composites when compared to that of pure PP, 220%. This means that the mobility of the PP matrix was reduced due to the presence of WP, thus impeding a slip of the segments of the materials. The changes in the Young's modulus with an increasing WP content are shown in Figure 5(c). Young's modulus of all the composites increased regardless of the presence of compatibilizers when compared to that of pure PP, 102  $\text{kgf/mm}^2$ . This behavior is common for a filler-reinforced polymer



**Figure 5.** Tensile properties of PP/WP composites with the contents of WP: a) tensile strength, b) elongation at break, and c) Young's modulus.



**Figure 6.** DSC curves of PP/WP composites: (a) cooling and (b) heating.

**Table 1.** Formulations Used in This Study

Composites	PP	WP	Compatibilizer <sup>a)</sup>
	(wt%)	(wt%)	(wt%)
PP/PP-St/MAH	90	0	10
PW-91	90	10	0
PW-9110	80	10	10
PW-82	80	20	0
PW-8210	70	20	10
PW-730	70	30	0
PW-7310	60	30	10
PW-640	60	40	0
PW-6410	50	40	10

<sup>a)</sup>PP-St/MAH (DOG: 1.04)

[27]. The Young's modulus of the composites with the compatibilizers is higher than that without the compatibilizers. This is due to the same reason as mentioned for the tensile strength.

### Thermal Properties and Morphology

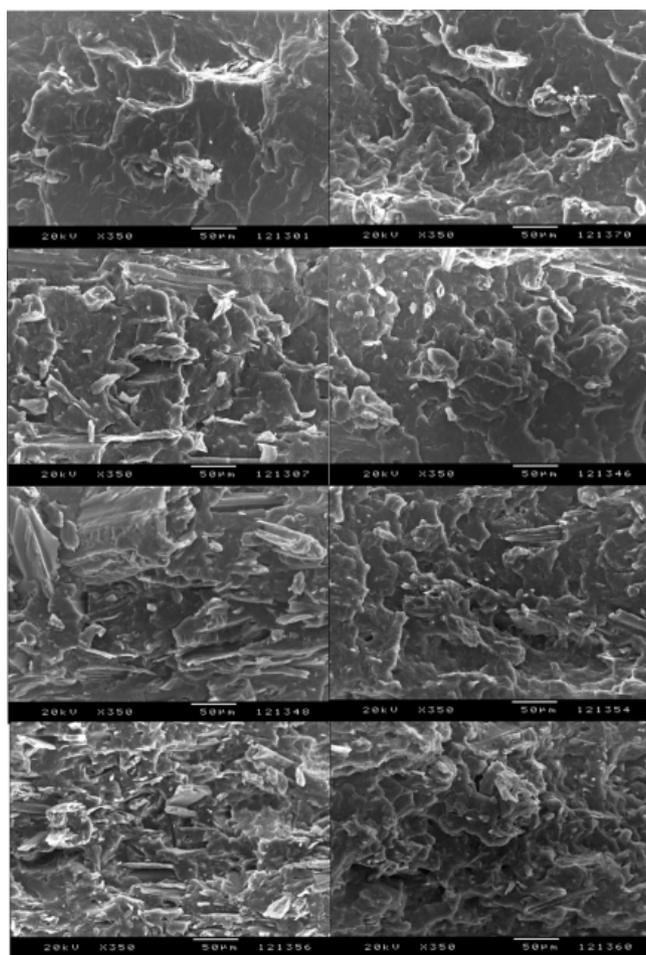
The thermal properties of the composites were characterized by DSC. The results of crystallization temperature ( $T_c$ ), melt temperature ( $T_m$ ), and the crystallinity ( $W_c$ ) of PP are summarized in Table 2 and the DSC cooling and heating curves are shown in Figure 6. For all the

composites, an increase in the WP content resulted in an increase in the  $T_c$  and  $W_c$  of the PP matrix. This could be explained by the nucleating ability of WP for a crystallization of PP. Accordingly, the  $T_c$  of the PP phase was further increased by an addition of PP-St/MAH (Figure 6(a)), which favored the ongoing crystallization process. This behavior could be ascribed to the improvement of the compatibility between the wood particles and PP matrix. Figure 6(b) shows the DSC heating curves of all the composites. The peak temperatures of the  $T_m$  of the composites were somewhat lower than those of pure PP, indicating a decrease in the lamellar thickness, which could also be the result of an epitaxial crystallization on the WP surfaces [27].

Figure 7 shows the SEM micrographs of the PP/WP composites. As shown in Figures 7(a), (c), (e), and (g) without PP-St/MAH, the surfaces were rough with an increase of the WP content and the cleavage between the matrix and wood particles was wider, indicating an enhanced debonding and thus weaker interfaces. On the other hand, for the composites with PP-St/MAH as seen in Figures 7(b), (d), (f), and (g), the surfaces were smoother and the cleavage between the PP matrix and wood particle was tighter. This means that the adhesion between the PP matrix and WP surface was enhanced by adding PP-St/MAH. These results are in line with those

**Table 2.** Thermal Properties of PP/WP Composites

Composites	$T_c$ (°C)	$T_m$ (°C)	$\Delta H_f$ (J/g)	$W_c$ (%)
pure PP	119.8	166.5	80.7	58.5
PP-St/MAH	122.3	165.2	78.4	56.8
PP/PP-St/MAH	121.2	163.2	72.8	58.5
PW-91	121.0	163.6	64.6	52.0
PW-9110	125.6	164.7	63.2	57.2
PW-82	121.2	163.9	57.9	52.6
PW-8210	125.2	164.3	56.4	58.4
PW-730	122.4	164.5	52.3	53.9
PW-7310	126.5	164.6	51.3	62.2
PW-640	121.1	164.5	45.6	54.6
PW-6410	126.7	164.6	44.8	64.1

**Figure 7.** SEM images of PP/WP composites. a) PW-910, b) PW-9110, c) PW-820, d) PW-8210, e) PW-730, f) PW-7310, g) PW-640, and h) PW-6410.

of the thermal analysis and the determined mechanical properties.

## Conclusion

The compatibilizers, PP-MAH and PP-St/MAH, were successfully prepared by a radiation-induced graft polymerization of maleic anhydride onto PP in the presence or absence of styrene. The highest DOG, 1.04 wt%, was obtained in the presence of styrene.

The compatibilizing effect of synthesized PP-St/MAH on PP/WP composites with various compositions was investigated in terms of the resultant mechanical properties, thermal properties, and morphology. WP content and the presence of PP-St/MAH had a considerable effect on the mechanical and thermal properties of the PP/WP composites. The presence of PP-St/MA brings about improvements in all the investigated properties. This could be due to a better interaction between PP and WP in the presence of PP-St/MAH. The composites with PP-St/MAH also showed an improved interfacial adhesion in their morphology.

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