Synthesis of PP-g-MAH and Evaluation of Its Effect on the Properties of Glass Fibre Reinforced Nylon 6/Polypropylene Blends

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SUMMARY: Polymer blends based on polyolefins constitute materials of a great interest owing to their broad spectrum of properties and practical applications. However, due to the poor compatibility of the components, most of these systems are generally characterized by high interfacial tension, low degree of dispersion and poor mechanical properties. It is generally accepted that PP and Nylon 6 are not compatible and that blending of these materials results in poor properties. This compatibility can be improved by the addition of a compatibilizer. In this study, the PP is first functionalised by Maleic Anhydride (MAH) in the presence of an optimized amount of Dicumyl peroxide (DCP). The reaction was carried out in the molten state using an internal mixer. Then, once the compatibilizer (PP-g-MAH) was prepared, it was added at a various concentration (2.5 – 10 wt.%) to 30/70 Glass Fiber Reinforced Nylon 6 (GFRN6)/PP and their mechanical properties are evaluated. It has been found that the incorporation of the compatibilizer enhances the tensile properties (tensile strength and the modulus) as well as the izod impact properties of the notched samples. This was attributed to better interfacial adhesion as evidenced by SEM. The optimum in these properties is reached at a critical PP-g-MAH concentration (5 wt.%).

Introduction

Blending of two or more polymers offers an interesting route to modify the properties of thermoplastics. It is relatively a cost-effective way to produce new materials with desired property combination. The aims can be, for example to improve the properties of commodity of thermoplastics or to lower the cost of engineering high-performance polymers [1].

Polypropylene (PP) and polyamide 6 (PA6) are two important classes of polymers used in the market [2]. PP is widely employed because of its low cost, high barrier properties to moisture, and ease of processing, but its high permeability to oxygen and many organic solvents limits its potential use. On the other hand, PA6 is a good barrier material for oxygen and organic compounds but it is relatively expensive, hygroscopic and thus poor barrier for water [3].

Blends of PP and PA6 are immiscible throughout the whole range of compositions. In the absence of a compatibilizer, such blends lack interfacial adhesion and generally suffer from poor

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mechanical properties. Compatibilization of these polymers using functionalised polyolefins leading to finer dispersion and improved interfacial adhesion.

Maleic anhydride grafted PP (PP-g-MAH) is of considerable importance for application as a compatibilizing agent with PA6, as adhesion promoter with glass or carbon fibers. [4]. The PP-g-MAH has anhydride and carboxyl groups that interact with functional groups such as the amine group of PA6, which are capable of forming covalent or hydrogen bonds therewith. [4]. Generally, functionalisation procedures consist in grafting anhydride in the presence of organic peroxide in the melt state through reactive processing.

Compatibilization is very often used to control the phase morphology, phase stabilization and interfacial adhesion in immiscible polymers blends.

The purpose of the present study is synthesize a compatibiliser by grafting MAH onto PP in the presence of a peroxide. The blends of Glass fiber reinforced Nylon6 /polypropylene (GFRN6/PP) with and without compatibilizers are prepared and their morphology (SEM) and mechanical properties (tensile and impact) are studied.

Experimental Work

Materials

The PP resin used is from DSM and has a melt flow of 3.5 grs/10min (230°C, 2.16kg). The Nylon 6 used is manufactured by BASF under the trade name of Ultramide B3 and contains 33 wt.% short glass fiber. The other ingredients: Maleic Anhydride from Fluka Chemical, Dicymul Peroxide from Merck and a stabilizer Irganox 1010 from Ciba-Geigy.

Sample Preparation

1.1 CONTROLLED DEGRADATION OF PP

PP was melt mixed in Haake Rheometer with different amounts of Peroxide (0-1phr) at three temperatures (180 – 200 – 220°C). The residence time was set equal to the time corresponding to torque stabilization. The critical peroxide concentration was determined using the MFI test.

1.2 PP-g-MAH COMPATIBILIZER SYNTHESIS

In order to synthesize PP-g-MAH, different amount of MAH (0-3.6 phr) were added to PP with the optimized amount of peroxide in the Haake Rheometer under the established operating parameters. The grafting reaction was monitored using MFI, FTIR and titration tests.

2 PREPARATION OF THE BLEND

Prior to blending, PP was first stabilized with Irganox 1010 and the Nylon was dried overnight before use.

GFRN6/PP (30/70) blends with 0, 2.5, 5, 7.5, and 10 wt. % PP-g-MAH were prepared in a Haake Rheometer internal mixer.

Rheological and Mechanical Characterization

MFI

The Melt Flow Index – MFI – test was performed according to ASTM 1238-85 on a TMT melt flow index machine at 230°C under a load of 2160grs

FTIR

Fourrier Transform Infrared (FTIR) spectra of compression molded thin films were recorded on a Perkin-Elmer 1000 Infrared spectroscopy.

Methanol Extraction

A 5-6 grs of PP-g-MAH resulting from the reaction of PP with DCP and MAH was cut into small pieces and then put in contact with methanol using a soxhelet apparatus for 12hrs.

The extracted product was then dried at 80°C for 6 hrs to evaporate any remaining free MAH, poly (MAH) and the solvent.

Mechanical Tests

Tensile properties were measured according to ASTM D638 using an Instron testing machine. The testing speed was set to 10mm/min.

Impact properties were measured using a Zwick Impact tester machine according to ASTM D256.

Results and Discussion

1 Grafting of Maleic Anhydride

Effect of Peroxide on MFI

Peroxide undergoes homolytic cleavage at the oxygen-oxygen bond to form radicals under melt mixing condition applied for grafting. The radicals extract hydrogen preferably from the tertiary carbon of polymer chain. Resulting in a decrease in Mw and in narrowing MWD [3,4].

Figure 1 illustrates the MFI versus peroxide content at 200°C shows that increasing the amount of peroxide increases the MFI prior to leveling off due to a recombination at high peroxide effect. The same trend is observed when an arbitrary amount (2 phr) of MAH is added. The presence of MAH shifts down the MFI values. This is a direct consequence of the grafting reaction taking place. A similar trend is observed when temperature is changed. A slow followed by a sharp rise between 0.4 and 0.6 Phr DCP followed by a leveling off is obtained. The higher the temperature the higher the MFI.

Effect of MAH Content on MFI

Figure 2 shows the variation of the MFI versus MAH content. A sharp decrease in MFI is observed till 2 phr MAH then followed by a leveling off. This is mainly due to the reaction of MAH with the radicals formed by the functionalisation of PP in the presence of peroxide; leading to the grafting of MAH onto PP.

FTIR Analysis

Figure 3 shows FTIR spectra of virgin PP and PP-g-MAH films. One can observe the presence of two new intense overlapping absorption bands at 1785 cm^{-1},1711 cm^{-1} and a low absorption band around 1855 cm^{-1} corresponding respectively to: symmetric, asymmetric C==O stretching and carboxylic acid [4]. This is a clear indication of the grafting of MAH onto PP molecular chain. It is also noted that the absorption increased when the MAH content was increased from 0.4 phr to 2.4 phr and then decreased at higher MAH content.

2 Blend Evaluation

Effect of PP-g-MAH on MFI

Figure 4 illustrates the melt flow index (MFI) of the prepared blend as a function of the compatibilizer content. It can be observed that the MFI decreases at 5 wt. % PP-g-MAH then levels off. This is an indication of the presence of a chemical reaction between PP-g-MAH and the blend constituents.

Mechanical Properties

Table 1 summarizes the tensile properties of the blend (GFRN6/PP) and its constituents as a function of the compatibiliser content.

The blending of PP and GFRN6 in the presence of the synthesized compatibiliser (PPgMAH) indicates several improvements in the compatibility and mechanical properties when compared to the non compatibilized blend.

Table 1. Tensile properties of the GFRN6/PP blends and its constituents.

Formulation	σ_y **[MPa]**	ε_y **[%]**	σ_b **[MPa]**	ε_b **[%]**	**E0.5% [MPa]**
0 (wt .%)	26.34	4.04	23.86	8.1	2381
2.5	31.94	2.51	30.70	3.12	2733
5	34.73	2.77	33.30	3.23	2689
7.5	35.63	2.65	35.03	2.96	2753
10	36.73	2.85	35.14	3.49	2718
PP	30.50	8.36	20.05	374.00	109
GFRN6	No yield	No yield	99.92	5.08	5950

An increase in most tensile properties (tensile strength and modulus) is observed when the compatibiliser in used. This increase levels off at 5 wt. % PP-g-MAH. This seems to corresponds to a critical compatibiliser content.

When compared to the matrix properties, a great improvement is obtained when incorporating an engineering resin such as nylon to a commodity resin such as PP and especially when a compatibiliser is used. 16 % increase in stress at yield, 75 % increase in stress at break and a three fold increase in modulus. This improvement can be attributed to two effects: the compatibilizer locates at the interfaces between the phases and enhances the stress transfer resulting in the enhancement of the mechanical properties, particularly the modulus and the tensile strength (explained mainly by interaction and/or adhesion effect); second upon addition of a compatibilizer, the drop size of the dispersed phase decreases leading to improved properties (emulsifying effect) [4, 5].

Izod Impact Strength

Figure 5 represents the izod impact properties of the blend as a function of PP-g-MAH content. A subtantial increase in impact properties is obtained upon addition of the compatibiliser. A critical compatibiliser content is also observed and corresponding to 5 wt. % PP-g-MAH. This goes along with the tensile properties results.

SEM

Figures 6 and 7 are SEM micrographs of without and with compatibiliser impact fractured samples. In the case of the non-compatibilized blend, the dispersed GFRN6 appears to be loosely attached to the matrix, and their "stress concentration" action can account for the lowering of the ultimate tensile parameters.

However, the addition of PP-g-MAH has improved interfacial adhesion between the two components phases due to low interfacial tension leading to better and finer dispersion and a reduction in the dispersed phase size.

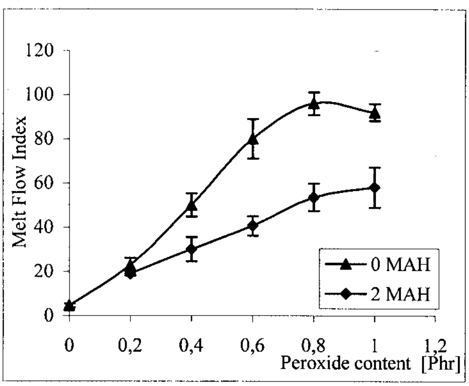

Fig. 1: Effect of peroxide on MFI of PP

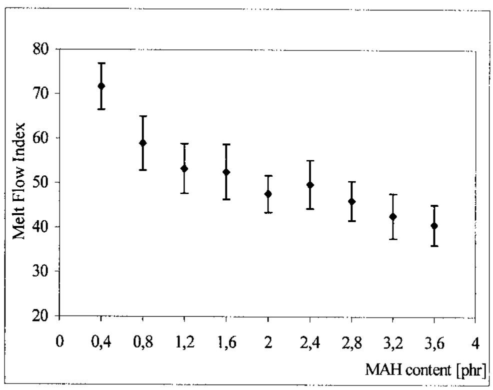

Fig. 2: Effect of MAH on MFI of PP

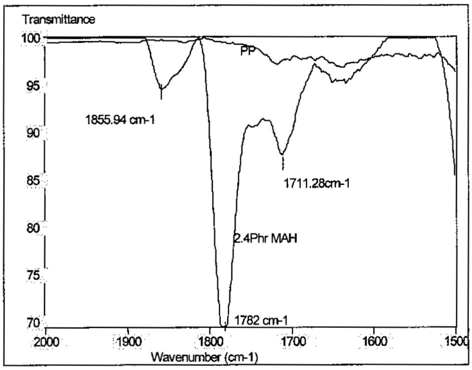

Fig. 3: FTIR spectra of PP and PP+DCP/MAH

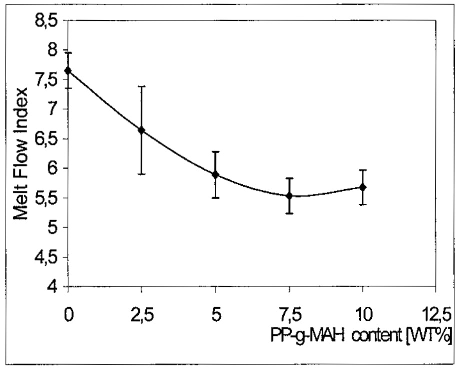

Fig 4: Effect of PP-g-MAH on blend MFI

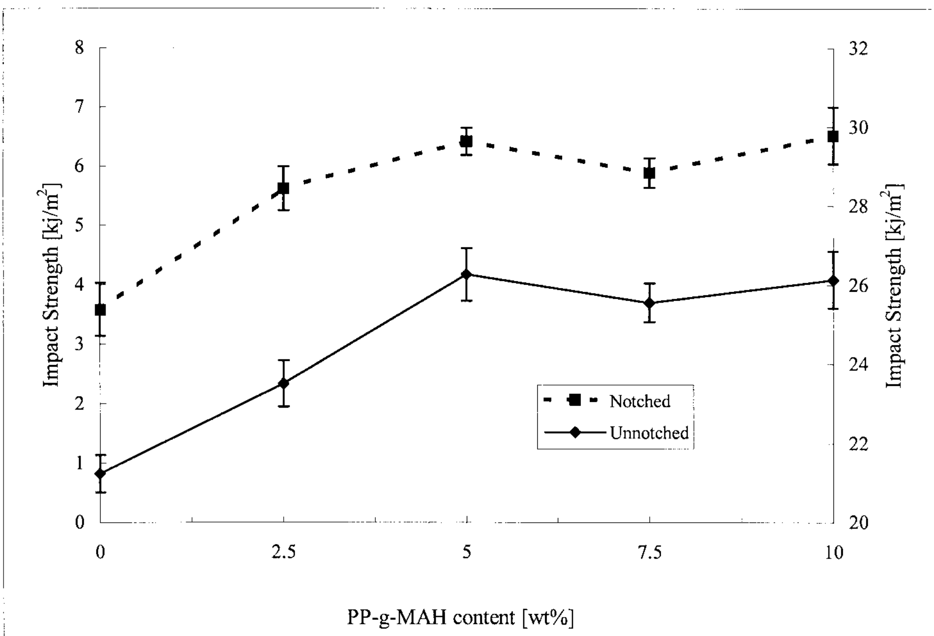

Fig. 5: Effect of PP-g-MAH on impact strength

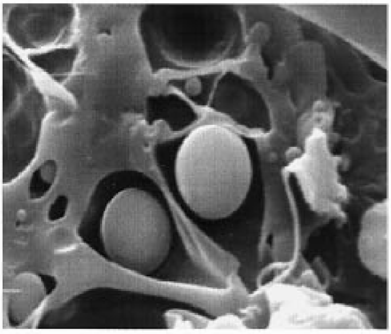

Fig. 6: Non compatibilized GFRN6/PP blend

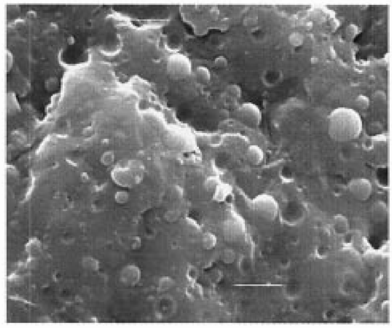

Fig. 7: PP-g-MAH compatibilized blend

Conclusion

A compatibiliser was prepared using reactive processing by grafting Maleic anhydride onto Polypropylene. Addition of this compatibiliser to the GFRN6/PP (30/70) blend was found to improve the tensile properties as well as the impact strength. An optimum in these properties was found to occur at a critical PP-gMAH content corresponding to 5 wt.%. SEM analysis revealed fine dispersion and improved interfacial adhesion between the compatibiliser and the blend components.

References

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