# Advanced Materials from Novel Bio-based Hybrid Resins


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## INTRODUCTION

In the U.S. alone biocompatible material demand is said to approach $3.7 Billion in 2010. Demand for biocompatible polymers is expected to increase at 6.8% annually as of 2006.[1] There are increasing environmental and financial concerns around our dependency on fuel sources. It is critical that polymer blends incorporate materials from natural, renewable, and sustainable resources. The price of oil per barrel is around the US $100 mark! Also disposal of plastic waste poses a major threat to the environment.

The addition of starch as a filler for producing biodegradable composites has been pioneered by Griffin[2] and expanded by many other, such as Gonsalves et al.[3], Thiebaud et al.[4] and Bikiaris et al.[5] The primary focus has been on the relationship of composition and morphology to mechanical properties of polyethylene blends. The function of compatibilizer on the properties of polyolefin blends were investigated in Bikiaris and Panayiotou[6], Prinos et al.[7] and Bikiaris[5]. Recently, the work of Thakur et al.[8] examined the use of starch acetate on morphological properties and the thermo-mechanical properties and degradability of LDPE/starch blends. Also Sailaja[9] examined the use of acetyleated and phthalate starch blends with and without glycidyl methacrylate as a compatibilizer. Pedroso and Rosa [10] examined and saw no variation in mechanical and morphological characterization using virgin versus recycled PE/starch. The work of Azhari and Wong[11] examines the morphology property relationships of PP/starch blends. This paper examines compatibilization of polypropylene and starch blends.

The market size of polypropylene is currently 100 Billion pounds globally.[2] Starch is inexpensive and an abundantly available biodegradable material. It is also a crystalline polymer which has physical properties similar to polyolefins. It is a thermally stable material up to 265°C. The issues around its use have been that it hydrophilic in nature, unlike polyolefins. The uncompatibilized blends therefore suffer from poor adhesion at the interface which leads to poor mechanical properties.

This study looks at a mechanical property comparison of a traditional homopolymer polypropylene against those blended with 50% starch. Two different starches and their effect will be presented. These now commercial novel bio-based blends (Cereplast Biopropylene ™) offer opportunities for end-users spanning a number of industries, from automotive to medical. Other markets include consumer electronics, toys, entertainment packaging, furniture, cosmetic packaging, consumer goods and construction.

## EXPERIMENTAL PROCEDURE

### Materials

The homopolymer polypropylene has MFI (ASTM D1238, 190°C, 2.16kg) of 7g/10min. The starches used were corn starch obtained from ADM and tapioca starch obtained from Asia. The starches were used as received. The compatibilizer used was a functionalized maleic anhydride polyolefin obtained from Chemtura.

### Reactive Extrusion Blending

The 50/50 polypropylene/starch composite was prepared on a 36:1 Length/Diameter co-rotating, intermeshing twin screw extruder of 65 mm diameter, using a temperature profile of between 130 and 170 $^{o}$C, at screw speeds in the range of 200 – 400 rpm. The compatibilizer added was in the 5% range.

### Mechanical properties

Dumb-bell shaped and Izod specimens of 1/8" thickness were injection molded and tested for notched-Izod impact measurements at room temperature (ASTM D 256) and an Instron for tensile and flexural properties according to ASTM D 638 and ASTM D790 test methods. Heat deflection was measured at 264 psi (ASTM D 648).

### Characterization

Differential Scanning Calorimetry (DSC) was used to examine the amount of energy required to melt crystalline regions of starch. The equipment used was Universal V 4.4 TA Instruments and runs were from -40°C to 200 °C at a ramp rate of 20°C/min. Slade et al.[13] has used DSC to determine pre- and post-processing effects on starch swelling, melting, dispersion and retro-gradation.

## RESULTS

The results of the mechanical properties are summarized in Table 1.

Table 1

| Physical Property | ASTM Method | Units | Bio-PP(Corn) | Homo PP | Bio-PP (Tapioca) |
|---|---|---|---|---|---|
| Tensile Strength @ break | D 638 | psi | 2,410 | 1,650 | 2,130 |
| Elongation @ break | D 638 | % | 9.5 | 130.1 | 1.4 |
| Young's Modulus | D 638 | psi | 299,280 | 119,480 | 324,800 |
| Flexural Modulus | D 790 | psi | 139,940 | 101,718 | 143,700 |
| Notched Izod Impact | D 256 | lb-ft/in | 0.57 | 1.81 | 0.51 |
| HDT @ 264 psi | D 648 | $^{o}$F | 140.1 | 129.9 | 145 |
| MFI 230$^{o}$C @2.16 Kg | D 1238 | g/10 min | 1.80 | 7 | 2 |
| Density | | g/cc | 1.04 | 0.9 | 1.04 |

Impact strength data shows that the 50% corn starch filled with compatibilizer is lower than the straight homopolymer PP. These values were also comparable with the tapioca starch. The impact strength is however higher by about 50% with the compatibilizer as compared to the binary blend without compatibilizer. This decrease in impact values has been reported by Sailaja[9] amongst many others.

The tensile strength at break is 46% higher for the compatibilized 50%starch/PP blend as compared to the pure homopolymer PP. The tensile strength of the binary blend is 2,650 psi, showing significant interaction of the maleic anhydride in the adhesion process across the PP/starch interface. The tensile strength at break of the compatibilized tapioca blend is about 23% higher than the pure homopolymer PP. The difference between the two starches may be related to the starch functionality, type, source, structure and or pretreatments. In previous work the theoretical model of Halpin-Tsai[14] for tensile strength fit the experimental data best for Sailaja et al.[9]

$$\sigma_b/\sigma_{PP} = (1+G\,\eta_T\varphi)/(1-\ \eta_T\varphi)$$

where $\eta_T$ is given by

$$\eta_T = (R_T - 1)/(R_T + G)$$

where $R_T$ is the ratio of filler tensile strength to PP tensile strength.

The values of elongation at break are much lower as compared to the homopolymer PP. This drop in elongation at break and even more significantly was reported at lower starch filler levels (15%) by Azahri and Wong.[11]

The effect of both starches on the stiffness, that is Young's modulus, increases by 56% over the pure homopolymer PP and with the compatibilizer by 150%. The difference between the tapioca and corn starch is due to the number of interactions of the methacrylate with the hydroxyl groups present in the starch. The traditional theoretical model of Kerner do not fit the experimental data well as the model assumes that the filler modulus is much higher than that of the matrix and that the filler will have no effect on matrix performance. Again the Halpin-Tsai model fits the experimental data best.

$$E_b/E_{pp} = \{(1 + G\,\eta\varphi) / (1-\ \eta\varphi)\}$$

Where $\eta = (R - 1)/(R + G)$, $G = \{7 - 5\nu\}/(8 - 10\nu)\}$ and R is the ratio of filler modulus to the matrix modulus.

The melt flow index (MFI), a measure roughly of the inverse of its viscosity, decreased with the addition of both tapioca and corn starch fillers, making the viscosity increase. Previously Griffin[15] had advised to keep levels of starch around 6% for polyolefin blends to maintain MFI values. From the compatibilized blend we note that the MFI is approximately 25% of the homopolymer PP.

The Heat Deflection Temperature is higher with the starch blends than as compared with the homopolymer PP.

Figure 2 & 3 contains the melting point data of the blends with the compatibilizer. A is corn (Figure 2) and C is tapioca (Figure 3). By adding 50% starch to polypropylene, this lowers the melting point of the polypropylene by about 3°C. With the addition of the maleic-anhydride grafted polyolefin as the compatibilizer there is a slight effect on the melting point of the polypropylene and the melting temperature of starch of around 100°C is no longer observed.

Figure 2 DSC Scan of 50% corn/PP Compatibilized Blend

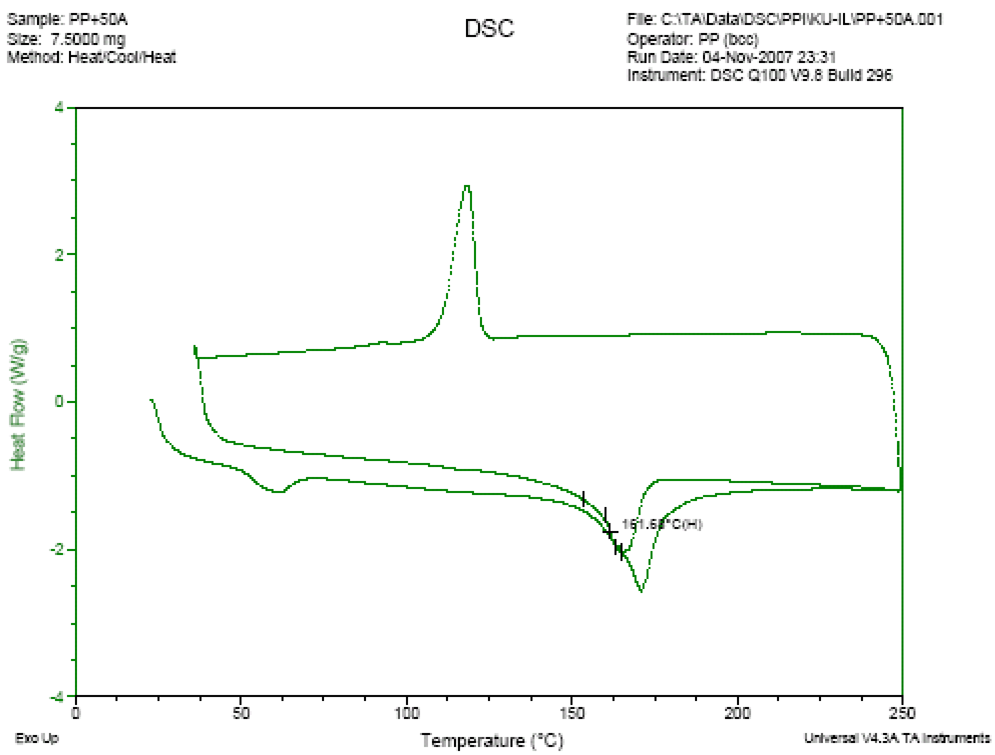
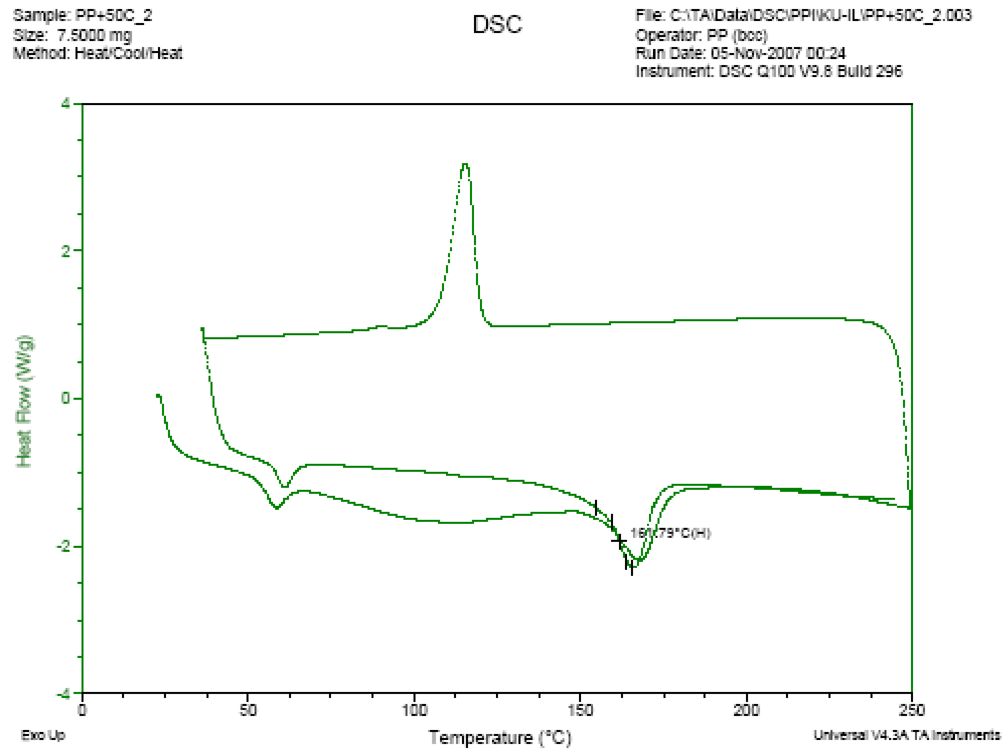
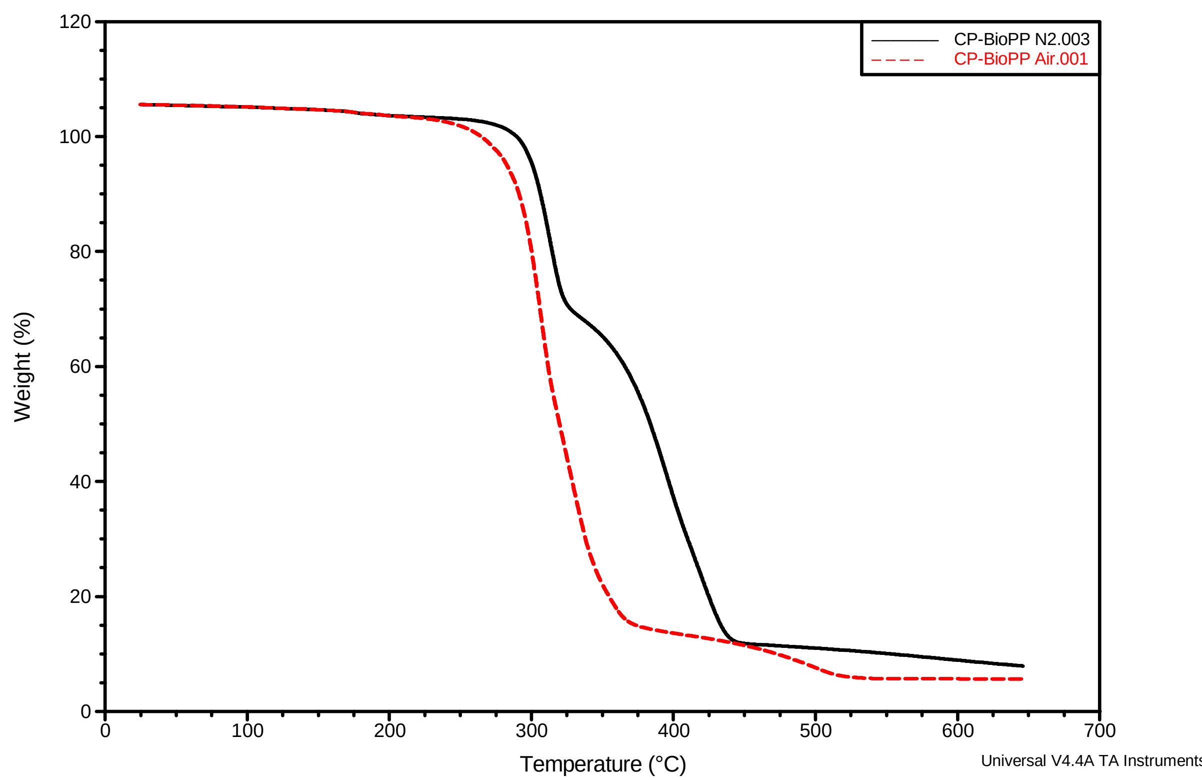


Figure 3 DSC Scan of 50% tapioca/PP Compatibilized Blend




Further based on TGA scans these Hybrid resins™ are stable up to 225° C.



## CONCLUSION

The results show that the compatibilized 50% corn/tapioca starch/PP blends perform better than the homopolymer PP in tensile strength at break, Young's modulus, flexural modulus and HDT.

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