BIOBASED FILLERS FOR POLYPROPYLENE FOR INTERIOR APPLICATION

Ayse Ademuwagun & Joel Myers, Hyundai America Technical Center

Abstract

Coconut shells and torrefied wood are bio-sourced and renewable materials that can be used as fillers in various polymer matrices. These bio-fillers would replace talc and glass bubbles which are not a renewable resource. The implementation of torrefied wood and coconut would reduce the carbon footprint and improve sustainability of Hyundai and Kia vehicles. In this study, coconut and torrefied wood filled polypropylene properties are tested for a HVAC Case application. Weight savings (7-10%) achieved by replacing talc with coconut or torrefied wood. Lower coconut and torrefied wood concentration (10-20%) is preferred for optimum of mechanical properties.

1. Introduction

Part of Hyundai's vision is to improve sustainability, which can be accomplished by using bio-sourced materials. Torrefied wood and coconut shell materials would replace talc which is currently mined and not a renewable resource. Glass bubbles are an expensive additive that is used to reduce weight of plastic materials. Due to low density, torrefied wood and coconut shells can reduce the weight of the plastic materials at a lower cost than glass bubbles. Additionally, the implementation of coconut and torrefied wood would reduce the carbon footprint of Hyundai and Kia vehicles which will improve customer perception of our product line.

Torrefication is a controlled decomposition of biomass in the absence of oxygen, where the wood fiber is heated to approximately 220-300°C. Upon heating, the hemicellulose (polar parts of the fiber) within the biomass will decompose. The remaining parts of the wood fiber, lignin and cellulose, will remain. The resulting composition is called a torrefied fiber. Torrefied wood material can be produced from numerous cellulose based materials, such as wood, sunflower hulls, flax shive, hemp and oat hulls. Torrefication decreases the polarity of the wood fibers and improves filler-polypropylene matrix compatibility. Furthermore, the torrefication process reduces the variation that would typically be different types of wood filler (i.e. oak, pine, etc.).

Coconuts are multi-use staple fruits grown in tropical regions. Approximately 60 million tons of coconut is produced worldwide per year. After all the edible parts and husks are removed, the coconut shells are currently either discarded for natural decomposition or burned to produce charcoal.[1, 2]

Coir, a natural fiber extracted from the husk of coconuts, is currently used in automotive applications such as trunk load floors, rear package trays, textiles and carpets.[3] No materials have been developed using the hard shell portion of the coconut. Natural Composites Inc., founded by researchers at Baylor University, is the ground coconut shell supplier.

Coconut fibers with greater surface roughness enhance adhesion when used in a polymeric matrix. Coconut fiber is porous, similar to a honeycomb structure, and has a low mass density due to long tube-like structures inside the coconut fiber. Coconut particles are 60% solid material and 40% voids.[4]

Natural fillers are hydrophilic which generates incompatibility with hydrophobic thermoplastic resins. The lack of interaction between the hydrophilic filler and hydrophobic polymer matrix generally leads to a seen when using decrease in mechanical properties. In an attempt to address this issue, chemical compatibilizers such as maleic anhydride grafted polypropylene (MAPP) are added to these composites. The functional groups in MAPP alter the surface of the natural filler by hydrogen-bonding with the natural filler's hydroxyl groups. This modification of the interface between natural filler and polymer increases mechanical properties of the composite.[5, 6]

The scope of this material development project was to develop and evaluate thermoplastic biocomposite materials for use in HVAC Case applications. Current HVAC materials are talc filled PP (low cost) or talc/glass bubble filled PP (lightweight but high cost). Performance evaluation methods and criteria were designated based on part requirements.

2. Torrefied Wood Filled Polypropylene

2.1 Methodology

A Zeiss EVO 50 Scanning Electron Microscope (SEM) was used to evaluate the microstructure of the biocomposites. Due to partial vacuum settings on the SEM, the test samples did not require sputter coating to reduce the charging effect typically seen when analyzing polymers under high vacuum conditions. Additionally, copper tape was placed on the specimens near the evaluation area to allow any electrical charge to transfer to the grounded stage in the electron microscope. The mechanical properties of the composites were evaluated by the testing conditions outlined in Table 1.

Table 1. Material test methods.

Tests	Method	Comments
Melt Index	ASTM D1238	230°C, Load: 21.2N
Specific Gravity	ASTM D792	
Tensile Strength	ASTM D638	Specimen: ASTM Type 1 Tensile Bar Test Speed: 50 mm/min
Elongation		
Flexural Strength	ASTM D790	Specimen: 12.7x127x6.4mm Test Speed:30 mm/min
Flexural Modulus		
Izod Impact 23°C	ASTM D256	Specimen: 63.5 x 12.7 x 6.4mm Hammer: 2.94 J
Izod Impact -10°C	ASTM D256	
Rockwell Hardness	ASTM D 785	
HDT	ASTM D648	Stress Load: 0.455 Mpa Specimen: 12.7x127x6.4mm
Scratch Resistance	Hyundai Spec	Evaluation Grain: HT-74A and KM-403
Odor	Hyundai Spec	

2.2 Coupling Agent Affect on Mechanical Properties

MAPP was used to improve adhesion between the natural fiber and synthetic PP resin. As seen in Figures 1, the addition of a 2% concentration of MAPP significantly improved both tensile and flexural strength versus similarly filled composites without MAPP.

In our previous TWF PP study, MAPP at a 3% concentration produced the best notched Izod impact while maintaining both tensile and flexural properties of the 2% MAPP formulation (Figure 2).

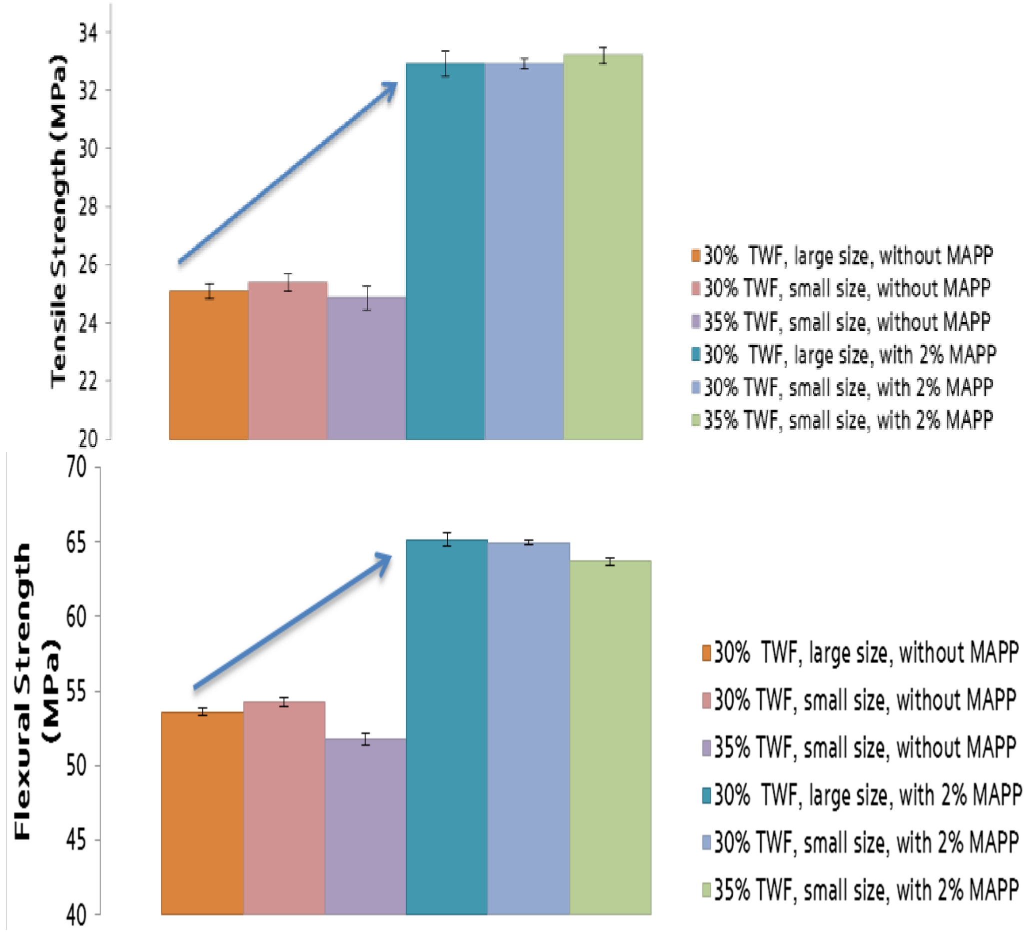

Figure 1. Effect of the MAPP on Tensile Strength.& Flexural Strength

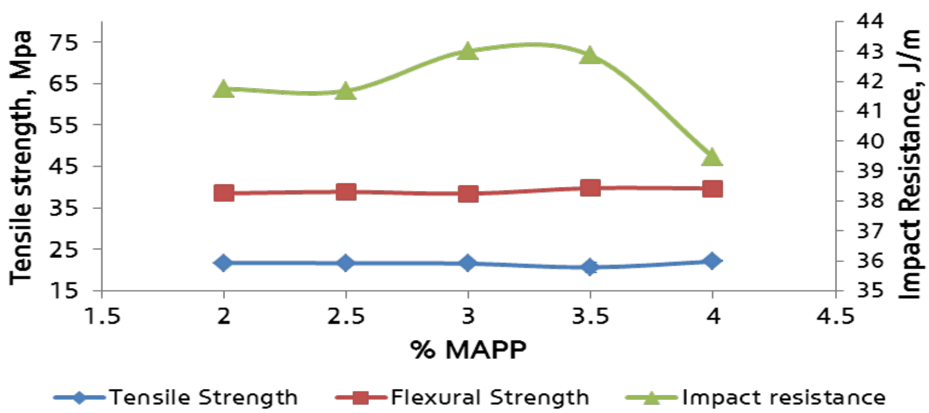

Figure 2. Effect of the MAPP concentration on mechanical properties.

2.3 Microscopy Analysis of TWF PP

The torrefied wood particle sizes were between 10-150μm in diameter with aspect ratios of 1:3-1:5 (Figure 3). TWF has a brownish black color and therefore, can only be used in dark colored plastic applications.

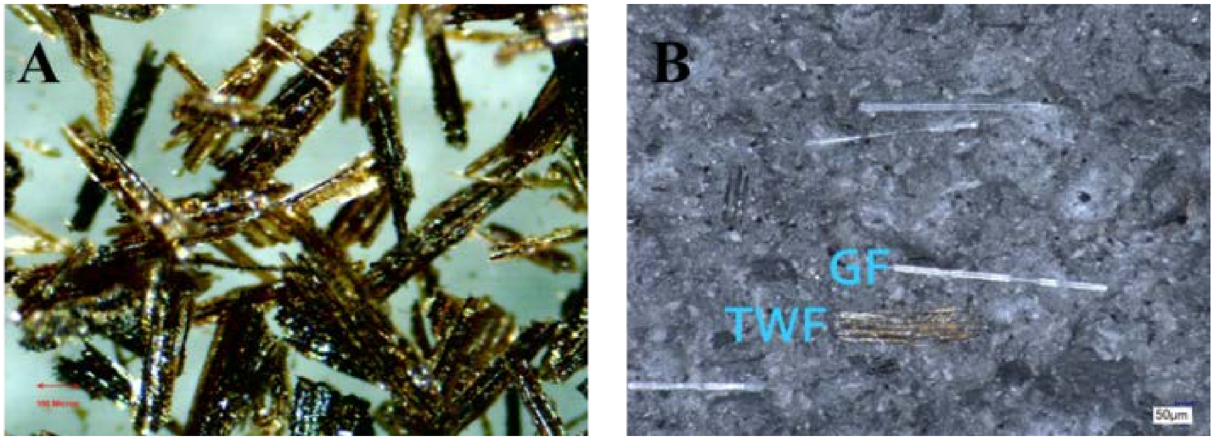

Figure 3. Optical microscope images: A) TWF, B) TWF/GF PP polymer matrix (200x).

SEM images showed that torrefied wood particles had very good adhesion to the polymer matrix due to low polarity of both the torrefied wood and MAPP coupling agent which can be seen in Figures 3B and 4. Optical microscopy of tensile fracture surfaces showed that many of the torrefied wood particles were imbedded in the polymer matrix. (Figure 3B). In Figure 4, good bonding between the torrefied wood particle and PP matrix can be clearly seen.

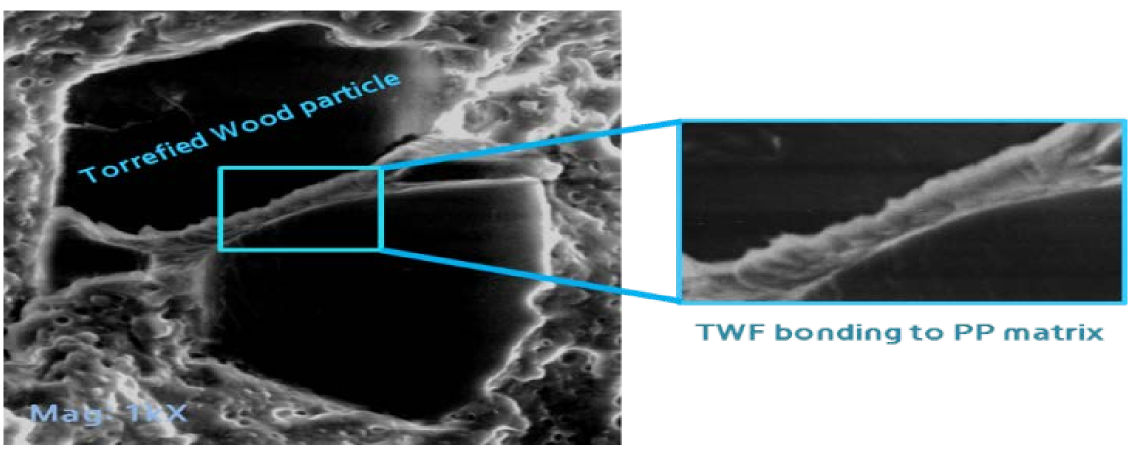

Figure 4 SEM of torrefied wood adhesion to polypropylene matrix (tensile tested specimen).

2.2. Results and Discussions

In order to meet the glass bubble specification, 10% torrefied wood was formulated with short glass fiber. The results of this testing are shown in Table 2, the mechanical properties are within the recommendations for part performance. The HVAC Case is not considered a structural or load bearing component.

Table 2. Material test data for (TWF/GF) PP

Test	**10% Torrefied Wood & Glass Fiber Filled PP**
Melt Index	17 g/10min
Specific Gravity	0.96 g/mL
Tensile Strength	34 MPa
Elongation	5%
Flexural Strength	51 MPa
Flexural Modulus	2065 MPa
Izod Impact 23^{0}C	59 J/m
Izod Impact -10^{0}C	41 J/m
HDT (0.45 MPa)	94 ^{0}C
Rockwell Hardness	145 R
Scratch	Excellent
Odor	Pass

As torrefied wood fiber content increases: flexural modulus, flexural strength, HDT and Rockwell hardness increases while melt flow, elongation and Izod impact decreases. No significant change in tensile properties was observed. (Figure 5)

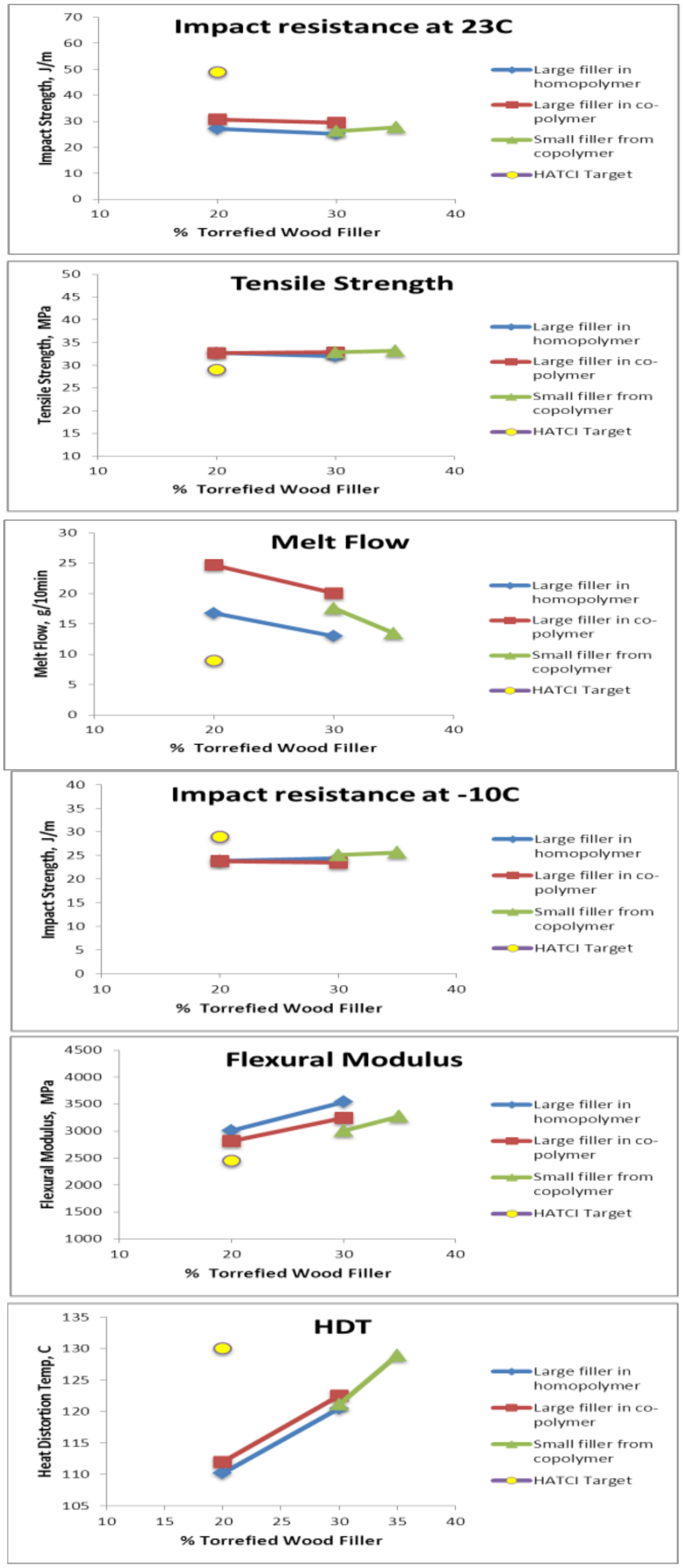

Figure 5. Affect of torrefied wood fiber on mechanical properties.

3. Coconut Shell Filled Polypropylene

3.1 Microscopic Analysis of Coconut filled PP

The fine ground coconut particle sizes were between 80-150 μm in diameter with an aspect ratio of 1:3. Coconut particles have a layer like structure that is porous at the surface and tube-like when viewed in cross section (Figure 6). The tensile tested samples provided the most visible particle to matrix failure interaction versus the other methods such as multi-axial impact and cryogenically frozen flexural fractures.

Coconut particles have good adhesion to the polymer matrix due to MAPP coupling agent. Coconut particles were imbedded in the polymer matrix after tensile testing. In Figure 7, good bonding between the coconut particle and PP matrix can be clearly seen.

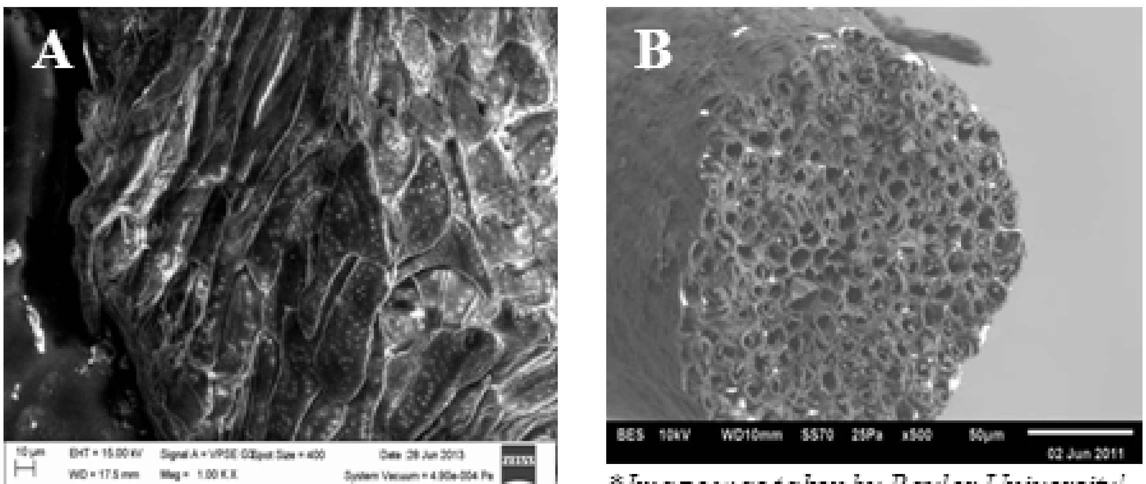

*Image was taken by Baylor University[1]

Figure 6. Scanning Electron Microscopy (SEM) images of coconut shell A) Surface and B) Cross section

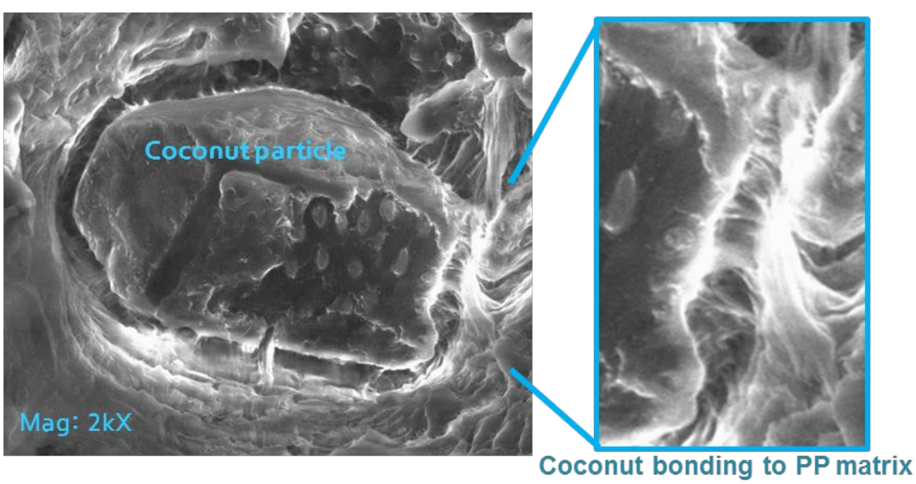

Figure 7. SEM of tensile fractured coconut particle showing adhesion to polypropylene matrix.

3.2. Results and Discussions

In order to meet the talc reinforced PP specification, various coconut formulations are tested. The results showed that 10% and 20% coconut filled PP performed better than 30% coconut filled PP. The 10% coconut filled PP had mechanical properties that were within the recommended part performance criteria (Table 3).

Table 3. Material test results for 10% -30% coconut filled PP

Test	Units	10% coconut filled PP	20% coconut filled PP	30% coconut filled PP
Melt Index	g/10min	16	16	10
Specific Gravity	-	0.94	0.97	1.02
Tensile Strength	MPa	27	27	27
Elongation	%	28	22	12
Flexural Strength	MPa	40	42	45
Flexural Modulus	MPa	1730	1902	2212
Izod Impact 23°C	J/m	54	52	40
Izod Impact -10°C	J/m	34	36	27
HDT (0.45 MPa)	°C	126	132	139
Rockwell Hardness	R	87	91	92
Flammability	mm/min	41.0	45.0	46.0
Odor	Rating	Pass	Pass	Fail
Scratch	Rating	Excellent	Excellent	Excellent

As coconut content increases: flexural modulus, flexural strength, HDT, Rockwell hardness and specific gravity increases while melt index, elongation and Izod Impact decreases (Figure 8). 10% and 20% coconut filled PP show better cold temperature IZOD impact resistance than talc filed PP. However, talc filled PP showed better elongation properties than coconut filled PP. Coconut as a filler improved scratch resistance since its color is dark brown. On the other hand, natural white color of talc is easily seen on PP matrix when it is scratched.

Odor failed Hyundai specification when 30% coconut used as filler. The odor-neutralizing/masking agents can be used to improve odor of coconut PP materials, but this increases the cost of the material. The odor-neutralizing/masking agents are made of either micro porous structures that absorb odors/VOC's or works as a micro foam absorbing the VOC and that is then removed in the venting system on an extruder.

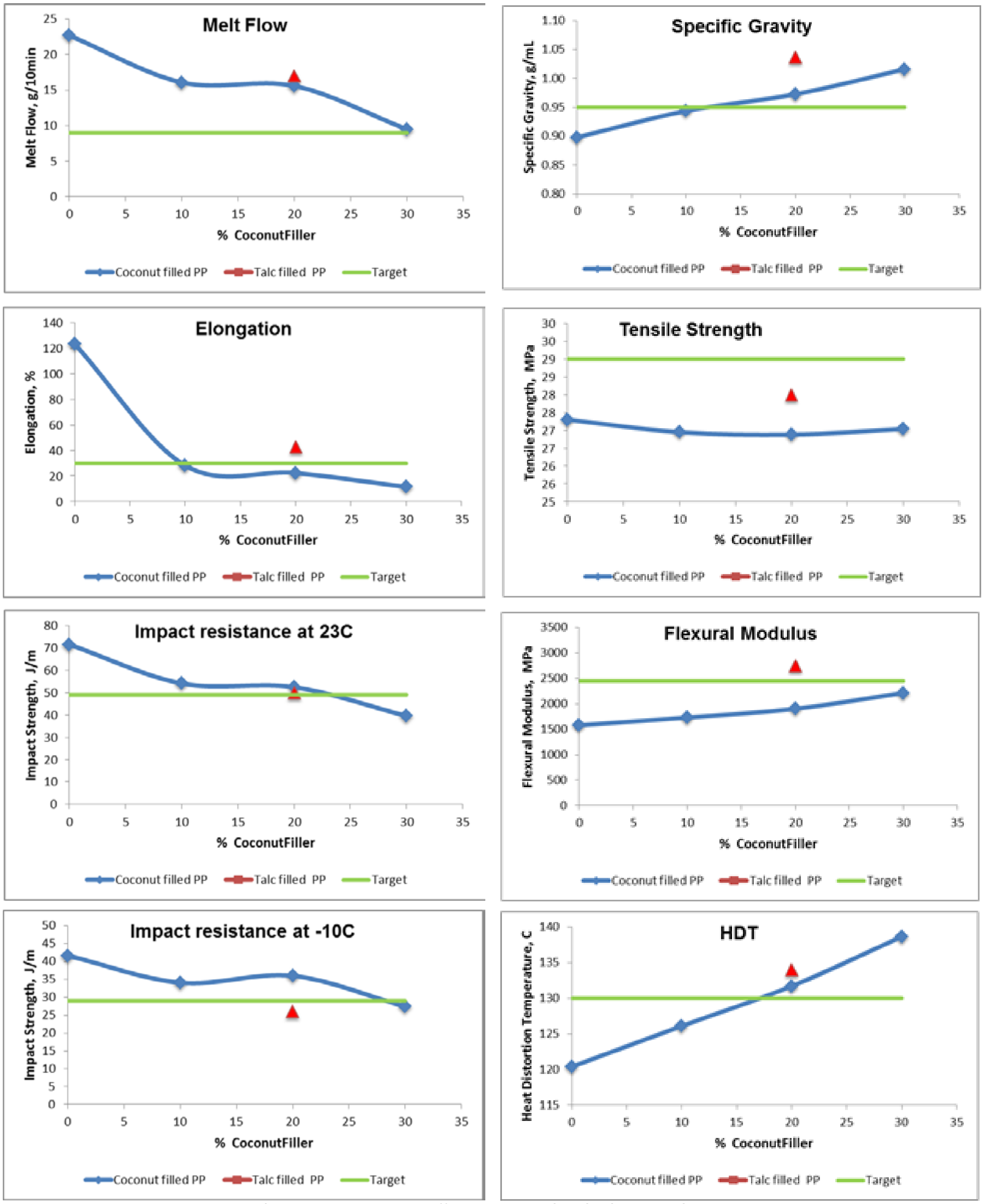

Figure 8. Coconut's effects on mechanical properties

4. HVAC Case Molding Trials

HVAC (Heat Ventilation Air Conditioning) units (Figure 9 & 10) were successfully molded for both coconut and torrefied wood filled PP. Current HVAC materials are talc filled PP (low cost) or talc/glass bubble filled PP (lightweight but high cost). The best formulas were selected for HVAC part trial and bio filler content for both materials kept at 10%.

The current product, talc filled PP, is molded at 450F; whereas, coconut filled PP needs to be molded at 380F which can reduce the power usage. Torrefied wood-glass fiber PP (TWF/GF PP) used current production settings at 450F, but could be run at lower temperature.

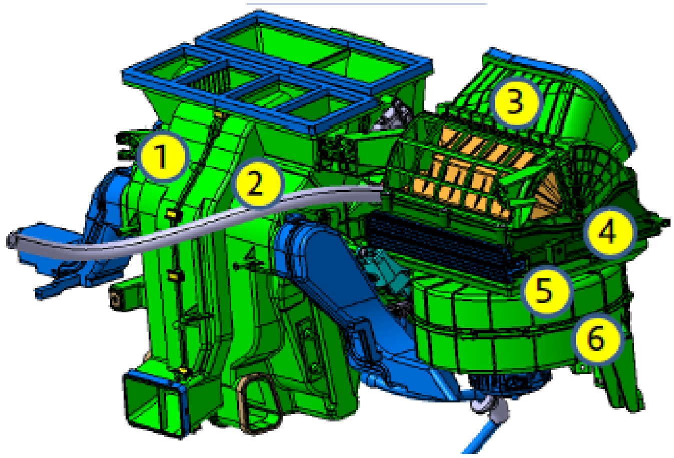

Figure 9: HVAC case (green indicates molded parts)

During molding, both bio-materials gave off a minor burnt wood odor which faded when the parts cooled. Both materials assembled easier than current production & passed the part function test.

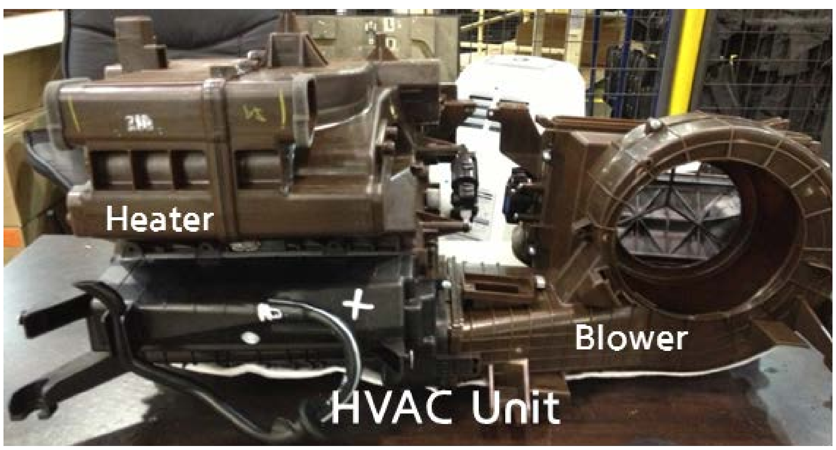

Figure 10. HVAC unit that made of Coconut PP

5. Light Weighting Possibilities

The weight of an SUV HVAC case was evaluated for bio-filled PP versus the current talc filled PP (Table 4). The calculation was done by using the density difference between talc and the bio-fillers. The results showed that, both coconut and torrefied wood fiber would decrease the weight of HVAC case by 7-10%. All of the selected materials can potentially pass the current specification for the HVAC case and can therefore be used rather than the current material regardless of filler content.

Table 4: SUV HVAC case weight comparison

Material	Density, g/mL	SUV HVAC Weight, grams	Weight Savings Compare to 20% Talc filled PP
20% Talc Filled PP	1.04	5151	-
10% TWF & GF Filled PP	0.95	4705	9%
10% Coconut Filled PP	0.94	4656	10%
20% Coconut Filled PP	0.97	4804	7%

6. Conclusions

Light weighting (7-10%) is possible by replacing talc with coconut and torrefied wood. Both coconut and TWF improves flexural modulus, flexural strength, HDT, and Rockwell hardness, but reduces melt flow, elongation and Izod impact resistance. Lower coconut and torrefied wood concentration (10-20%) is preferred for optimum of mechanical properties. To maximize natural filler particle adhesion to the polymer matrix, MAPP coupling agent is required.

Molding trials for HVAC case with TWF and Coconut filled PP were successfully completed and part durability testing is underway. Both materials have opportunities to replace current materials if the part durability test shows promising results.

7. References

1. Singh, RH, " The Regional Coconut Industry". CARICOM Regional Transformation Programme for Agriculture. Web. Dec. 2007. http://www.caricom.org/jsp/community/agribusiness_forum/coconut_industry_market_intelligence.pdf
2. Saman, H, "Coconut Shell And Its Ash As A Replacement Of Aggregate Or Cement In Producing Concrete and Particleboard". http://eprints.uitm.edu.my/6980/1/LP_DR%20%20HAMIDAH%20MOHD%20%20SAMAN%2002_24.PDF
3. S. N. Monteiro, L. A. H. Terrones and J. R. M. D'Almei, "Mechanical Performance of Coir Fiber/Polyester Com-posites," Polymer Testing, Vol. 27, No. 5, 2008, pp. 591- 595. doi:10.1016/j.polymertesting.2008.03.003
4. Bradley, Walter, "Coconut Waste Changes to Grace for Poor Farmers". *Baylor University*. JEOL legacy. Web. 04 Jan. 2014. http://www.jeolusa.com/APPLICATIONS/REALab/BaylorUniversity/tabid/826/Default.aspx
5. W. Wang and G. Huang, "Characterization of Natural Coconut Fibers Composites," Materials & Design, Vol. 30, No. 7, 2009, pp. 2741-2744.
6. M. Sapuan and M. Harimi, "Mechanical Properties of Epoxy/Coconut Shell Filler Particle Composites," The Arabian Journal for Science and Engineering, Vol. 28, No. 2B, 2003, pp. 171-181.