

## ***Toughening Glass Filled Polyamides using Low Molecular Weight Functional Polybutadienes***

### **Abstract**

The use of low molecular weight polyfunctional polybutadienes as toughening agents for glass filled nylon 6/6 was studied. Both a maleic anhydride grafted, and in-chain epoxy functional polybutadiene were evaluated for this purpose by measuring improvements in both tensile modulus and impact strength. It was demonstrated that using additive quantities of the aforementioned additives increased both the tensile modulus and notched Izod impact strength in a manner that contradicts glass only addition. A polybutadiene TPU was also evaluated for the same purpose, and provided similar, yet less dramatic toughening.

### **Introduction**

Short glass fibers can increase the range of properties, and applications of nylon (PA)<sup>1-2</sup>. Consequently, glass-filled nylon is used increasingly in automotive and small appliance applications that were historically metal components. The function of glass fibers is to enhance the structural properties of the compound, in particular properties such as modulus, strength and the retention of these properties at higher temperature. Generally speaking however, the addition of glass fiber to nylon 6/6 can improve the initial modulus of the compound, however the toughness is compromised. In applications where a balance of rigidity and toughness are required a combination of glass fiber and impact modifier are employed<sup>3</sup>. Up to 20% by weight of a rubbery additive may be required to elicit a morphology that is capable of dissipating energy, in addition to the 20% by weight or more glass fiber content. In this instance the resulting

properties are derived by a calculated compromise between modulus, and toughness.

The objective of this work was to evaluate low molecular weight rubbery functional additives in a glass filled polyamide 6/6 compound. The polybutadiene based additives had either maleic anhydride or epoxy functionality to react with the chemistry of polyamides and generate a network structure that imparts toughness. Each additive was multi-functional and can therefore interact with multiple nylon chains. Eliminating a second rubbery phase should lessen the reduction in modulus, while promoting a tougher material. In addition, the functional additives can serve as coupling agents, whereby the adhesion between the nylon phase and the glass fiber is improved. It is difficult to delineate the property improvements induced by formation of the network structure versus any improvements in coupling efficiency. Consequently, the results in this paper are presented as manifestations of both schemes. Neither scheme was given unequal weighting.

### **Materials**

Commercial nylon 6/6 (Solutia Vydne 50BW) was used as received. The nylon was dried in a vacuum oven for 20h prior to extrusion. Glass fiber evaluated in this study were (PPG HP 3540) chemically sized for adhesion to polyamides.

Functional polybutadienes were supplied by Cray Valley Company, with low molecular weights and high functionality, as show in Table 1. Both Ricon and Poly bd additives described in Table 1 are high viscosity liquids, and were prepared as dry liquid carriers (DLC) on porous silica in a 70:30 ratio. The liquid polybutadienes were added drop-wise onto silica at room temperature in an industrial blender, and blended until homogenous.

**Table 1: Properties of the polybutadiene based additives used in this study. Note that the Ricon 131MA5 is graft modified with maleic anhydride, and Poly bd 605E contains in-chain epoxy functional groups.**

Material	Mw	Functionality	Funct %
Ricon 131MA5	5.3k	Maleic anhydride	6
Poly bd 605E	1.5k	Epoxy	5
PRO 7840 TPU	114k	N/A	N/A

In addition, a polybutadiene based thermoplastic urethane was evaluated. Although it does not possess the functional groups to be reactive with nylon, previous studies have revealed value in improving the interface between organic and inorganic substrates.

### Experimental

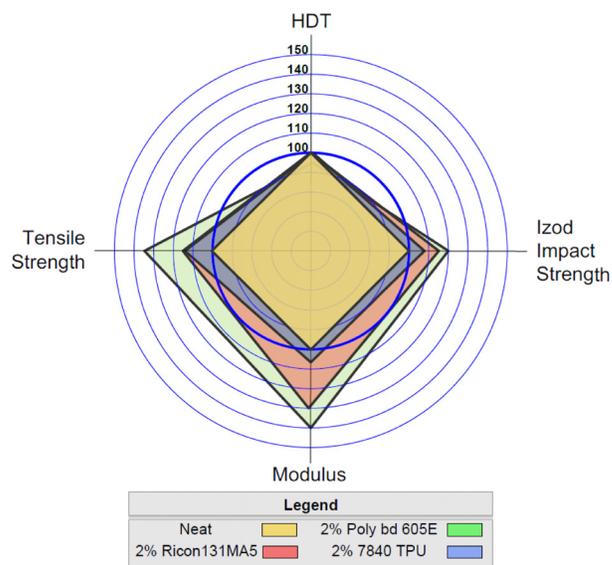
The nylon was pre-dried in a vacuum oven for 20h prior to compounding. All formulations were dry blended with approximately 0.5% by weight mineral oil to eliminate separation during feeding. Glass fibers were metered separately, and passively top fed into the extruder at 20D. The extruder was equipped with a single strand die, which was cooled in a water trough prior to granulating. A constant temperature profile of 260°C was used from feedthroat to die.

A ladder study was employed to define the effect of the functional additives. Loading levels were 2, 4, and 6% by weight, with a constant glass fiber loading of 30% by weight. HDT measurements were conducted on a DMA, following a method that scales the ASTM method. Tensile measurements were conducted on a Thwing-Albert tensile tester in accordance to ASTM D638. Impact data was collected using an Instron POE2000 impact tester with hammer weight of 8lbs in accordance with ASTM D256.

### Results

Figure 1 depicts the relative results of the mechanical test data in the modified glass filled systems as compared to a neat system. The absolute increases are presented in Appendix A. Notice the constant HDT for each of the four systems, which includes the benchmark. Previous results in unfilled PA6/6 demonstrated an improvement in HDT with subsequent addition of MA functional additives. This

result indicates that the glass fiber governs the modulus at temperature dynamic despite the presence of a network macrostructure within the nylon 6/6.



**Figure 1: Relative response in modulus, notched Izod impact, tensile strength and heat distortion temperature as compared to the 30% glass filled unmodified material.**

Changes in tensile properties suggest that the modified composites are both stronger and stiffer as indicated by improvements in tensile modulus and tensile strength respectively. Gains in tensile modulus are consistent with the formation of a network structure that inhibit the polymer chain mobility in response to strain. Both the Ricon 131MA5 and Poly bd 605E yielded 50% improvements over the neat benchmark. Conversely, the TPU provided only modest improvements consistent with improving the interfacial adhesion of the fibers without any bulk modification of the PA6/6 phase. Equating the tensile strength to ultimate strength, the results indicate that the epoxy functional polybutadiene has greater efficacy in generating the network, with maleic anhydride functional and non-functional TPU following.

The crux of this investigation was however not just to stiffen an already stiff material, but to improve the applicability by introducing toughness. A material's ability to absorb energy as opposed to breaking can be characterized by impact energy. Both functional

additives provided greater than 30% gains in Izod impact energy. Nylon chains were tethered together by the functional polybutadienes that prevented the chains from conforming to a chronic tension. However, it is believed that the acute impulse of energy applied by a hammer weight was sufficient to allow the polybutadiene crosslinks to deform elastically and absorb the energy of impact. The TPU again provided modest improvements in this property, and likely was in a more traditional energy absorbing impact mechanism.

Additional formulations employing higher loadings of the functional additives were conducted to better understand to the property landscape. Increasing the loading to 4 or 6% by weight did not achieve significantly higher properties, as compares to 2% by weight. A comprehensive optimization study was not conducted, however the aforementioned results suggest that 2% by weight in a 30% glass filled system balances cost versus performance.

### Conclusion

Introducing low molecular weight Ricon 131MA5 and Poly bd 605E at 2% by weight to nylon 6/6 glass filled composites yielded a toughening effect. This effect was manifested as substantial improvements in both tensile strength and modulus, in addition to notched Izod impact strength. Epoxy and maleic anhydride functionality created a network like structure within the nylon phase that limited the mobility of the polymeric chains. The elasticity of the polybutadiene permitted energy absorption in response to acute energy impulses giving rise to a toughened material.

### References

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### Appendix A

**Table 2: Tabulated data. All additives were loaded at 2% by weight.**

Material	HDT (°C)	Modulus (GPa)	Tensile Strength (MPa)	Notched Izod (kJ/m <sup>2</sup> )
Neat	258	4.77	141	8.27
Ricon	260	6.10	158	9.49
Poly bd	260	6.27	189	9.69
TPU	259	5.06	158	8.93