

Proprietary Engineering Resins as Additives to Polypropylene

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ABSTRACT

To extend the performance of polypropylene, additives manufacturers have developed a variety of products (light stabilizers, antioxidants, nucleating agents, etc.) to enhance specific material properties. However, to bridge the gap between polypropylene and engineering resins, converters must improve its impact resistance and also its elevated temperature dimensional stability, and do so economically. PPO* resin, a proprietary polymer of poly(2,6-dimethyl-1,4-phenylene ether) available from GE Plastics, is a unique product which may be utilized as a low level additive in polypropylene to achieve such property enhancements.

INTRODUCTION

Polypropylene resins have been used in applications ranging from food packaging to power tools and from carpet fibers to automotive components. Combined with polypropylene's low density around 0.9 g/cm³, the resin's mechanical properties, excellent chemical resistance, low viscosity in molding processes, and relatively high melting temperature (165°C) make it an attractive resin for a wide variety of applications. In the food packaging market, these properties have enabled polypropylene applications in flexible retort pouches fabricated from multi-laminate films, blow molded bottles, semi-rigid thermoformed trays, and even thick-walled injection molded reusable components. Even with its wide acceptance in the food packaging market, areas for property improvements still remain.

Many applications require both heat and impact resistance, especially in the evolving food-packaging segment. Hot-fill foods, retort sterilization, and reheating processes have continued to put pressure on the temperature resistance of polypropylene based packaging. In addition to these high temperature requirements, freezer storage, shipping, and handling demand a high level of durability and impact resistance to keep breakage loss to a minimum and to avoid compromising the freshness seal protecting packaged foods.

Although a wide variety of polypropylene compounds have been commercialized over the years, the need for the combination of high heat and high impact remains. Figure 1 plots the data-sheet properties of notched-Izod resistance and heat deflection temperature for over 1,000 commercial grades of polypropylene. Although highly crystalline homopolymer polypropylene grades offer high temperature and copolymer grades offer durability, both properties are rarely present together.

Talc, glass fiber, and other inorganic fillers used to boost the high temperature stiffness of polypropylene have been noted to also increase impact strength in some situations. Often, this increase in impact strength is due to the increase in flexural strength and stiffness and not an increase in ductility or elongation-to-failure properties. On the contrary, elongation-to-failure and ductility are often reduced by inorganic fillers in PP. In applications where elongation is important and brittle failure is undesirable, these fillers may not be attractive options. Additionally, inorganic fillers generally increase the density of the PP compound and may complicate molding processes with differential shrinkage and decreased mold flow.¹

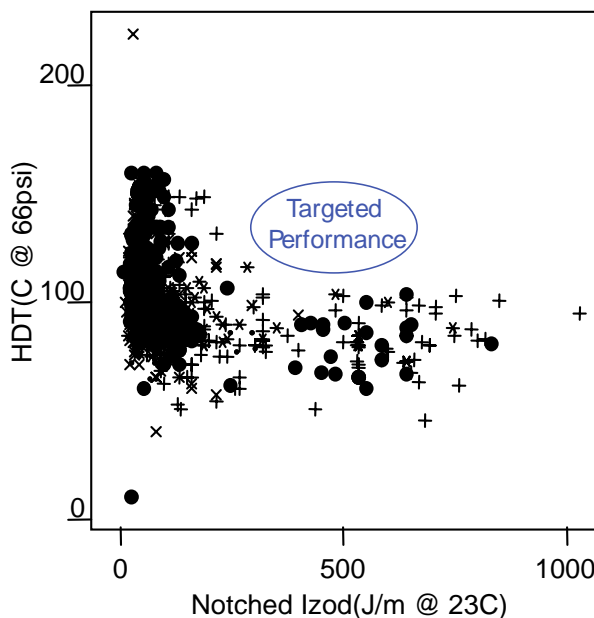


Figure 1: Commercial unfilled polypropylene grades constructed from publicly available datasheets.

Proprietary formulations of modified polyphenylene ether resin (“mPPE”) have been shown to provide both heat and impact resistance benefits to polypropylene.

MODIFIED POLYPHENYLENE ETHER RESIN BLENDS

Modified polyphenylene ether resin, offers several attractive features for addition to polypropylene:

- + High glass transition temperature (215°C)
- + High ductility
- + High load carrying ability at elevated temperatures
- + Low density relative to other engineering resins
- + Increased melt strength
- + Excellent electrical properties
- + Immiscible yet partially compatible with polyolefin resins

Of course, these benefits come with some trade-offs. The proprietary additive formulations of mPPE may also bring to polypropylene:

- Opacity
- Increased density versus pure polypropylene yet significantly lower density than mineral filled resins
- Increased odor in processing
- Increased cost

A more detailed review of the properties of mPPE has been given in prior literature. [ⁱⁱ, ⁱⁱⁱ]

Readers familiar with NORYL PPX* resin, an alloy of mPPE and PP released to the market by GE Plastics in 2001, may wish to understand the differences between those grades and the additive materials presented in this paper. These mPPE/PP alloys were designed as finished, “ready-to-mold” compounds bringing stiffness, dimensional stability, and temperature resistance to bridge the gap between polypropylene and traditional modified PPE resins. Unlike the mPPE additives for PP discussed in this paper, these mPPE/PP alloys do not contain high concentrations of mPPE and therefore are not the most economical way of introducing mPPE into PP as an additive. As a finished compound, mPPE/PP alloys were designed for manufacturing within GE’s production facilities and therefore these grades do not provide the flexibility and stability desired to dial in specific impact and temperature performance in a wide variety of applications. New developments in optimizing mPPE for use as an additive to PP have expanded the breadth of performance available from mPPE/PP alloys.^{iv}

These newly formulated additive grades of mPPE, optimized for polypropylene, are proprietary and therefore specific formulations will be referred to only as formulations A and B in this paper. Additionally, it is important to note that many specific questions about the performance of these additives in advanced conversion processes and specific end-use applications remain to be answered through additional testing and collaboration with our customers.

INCREASING TEMPERATURE RESISTANCE

Driven by the need for higher temperature retort capable packaging (increased to 132°C from 115°C), initial attempts at modifying polypropylene using mPPE concentrates focused on improving the temperature resistance of PP. In this paper, we will address the melting temperature and stiffness at elevated temperature without considering time effects such as creep and stress relaxation. Since amorphous mPPE and semi-crystalline PP are immiscible and we are concerned with low concentrations of PPE as an additive, the continuous phase in the resin alloy is PP. [Figure 2] Since polypropylene loses most of its load bearing capability at its melting temperature, the PP+mPPE blended system will also lose much of its mechanical usefulness at the same temperature. In other words, there will be no improvement in the melting temperature of the PP when blended with mPPE.

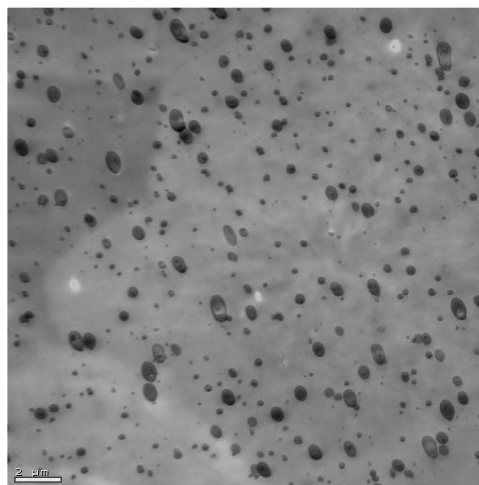


Figure 2: mPPE dispersion in PP

However, these mPPE additives do improve stiffness of polypropylene at elevated temperatures below the melting point of the PP. For example, a hot-fill food packaging application filled at 82°C will require that the container maintain its shape without warping or distorting. Even though 82°C is below the melting temperature of most polypropylene grades, the stiffness of PP at those temperatures is very low relative to an amorphous resin such as mPPE. [Figure 3] For this reason, we expect blends of mPPE and PP to have increased stiffness at elevated temperatures up to near the melting point of the PP. Figure 4 shows the stiffness versus temperature produced by one such additive formulation referred to here as formulation A.

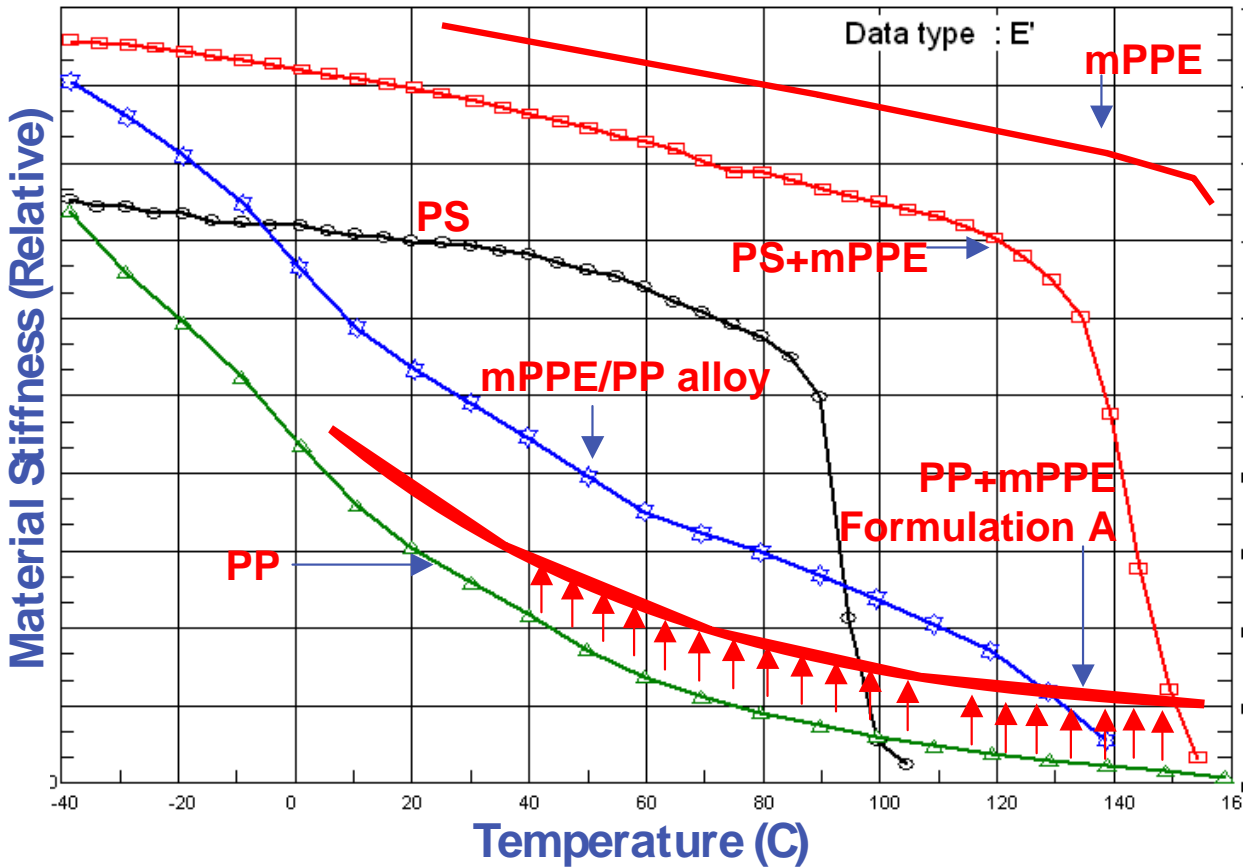


Figure 3: General stiffness vs. temperature profiles of PP, PP+mPPE additives, mPPE/PP alloys, PS, PS+mPPE, and PPE

Another more common measure of stiffness at elevated temperature is Heat Deflection Temperature (HDT) or Deflection Temperature Under Load (DTUL). Although HDT is not generally very useful for predicting end-use performance, it is very common on product datasheets and is often useful in comparing performance of relatively similar resins such as PP and PP modified with low concentrations of mPPE. In the case of similar resins, shifts in HDT may indicate shifts in the entire stiffness-temperature curve as illustrated in Figure 3 and observed in Figure 4. As with the full stiffness-temperature profile, we again see the benefits of mPPE formulation A on HDT. [Figure 5]

By applying the mPPE additive formulation A to high impact copolymer, it is possible to produce a polypropylene based compound with both relatively high impact resistance and high temperature resistance [see Figure 10 below]. These improvements are expected to manifest themselves in end use testing of the deflection of a part under load at elevated temperature. Figure 6 illustrates visually the difference in softening observed in a thermoformed tray after 10 minutes at 115°C when modified with mPPE additive formulation A. Further validation of these results in a wide variety of conditions and applications is still necessary.

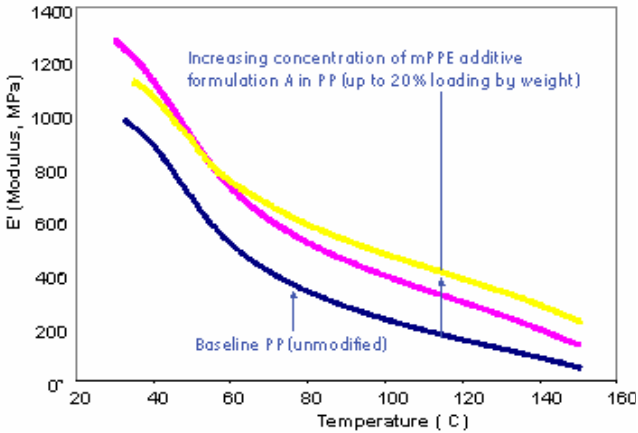


Figure 4: Stiffness vs. temperature for PP+mPPE additives

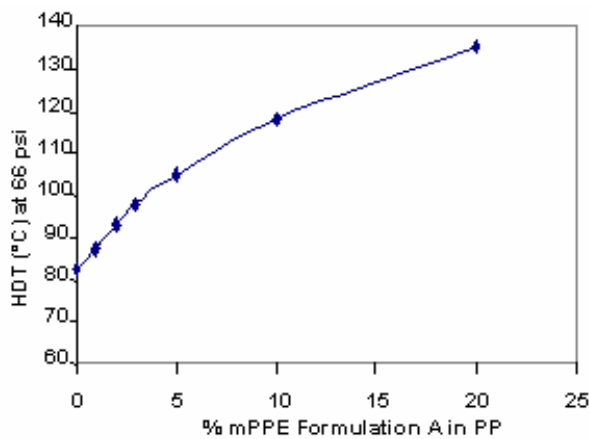


Figure 5: HDT vs. loading of mPPE formulation A in PP

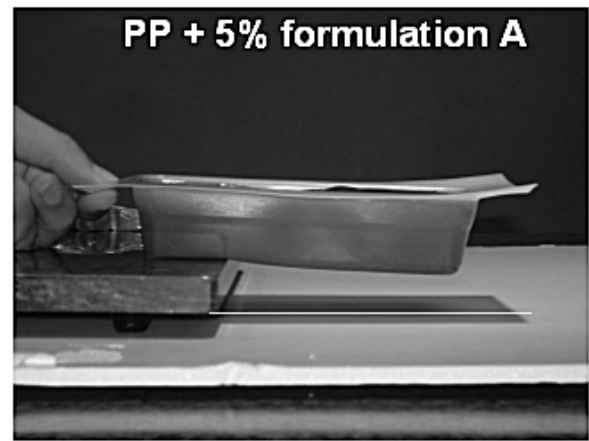
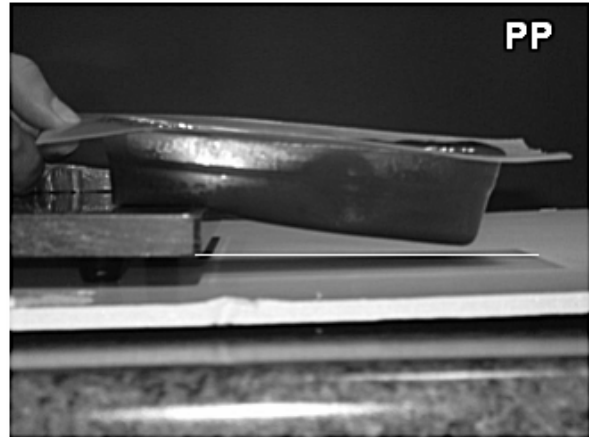


Figure 6: Example application testing.

INCREASING IMPACT RESISTANCE

As we introduced above, improved stiffness at elevated temperature may be achieved in copolymer PP by introducing low levels of mPPE additives. However, copolymer polypropylene has other differences such as higher cost, reduced stiffness, and lower strength that may make it an unattractive alternative to homopolymer in some applications. Therefore, we have explored the direct impact modification of homopolymer polypropylene by using a second mPPE formulation. We will refer to this version as formulation B in this paper.

Impact resistance is a very complicated engineering topic where the speed of impact, the geometry, the amount of preexisting damage, temperature, and other factors may have a dramatic effect on the part's actual performance. In order to simplify the qualitative ranking of materials modified with mPPE additives, we relied on two common tests available to the industry: dynatup falling-dart and notched-Izod tests. Improvements in a material's performance in dynatup and notched-Izod tests may indicate that there will be real world benefits to durability and impact resistance. However, given the complexity of an impact event, the results reported here should not be considered as a guarantee of performance in a specific impact event. The material's performance will need to be validated in each application through end use testing.

Of these two impact tests, dynatup falling-dart testing has been found to provide the closest correlation to an impact event resulting from dropping a thin-walled container, especially a thermoformed container with very wide radius on every corner.^v Dynatup testing standard homopolymer PP at room temperature often results in what would be considered a brittle failure like the one shown in figure 7a. Figure 7b shows the same homopolymer PP modified with mPPE additive formulation B at 10% loading. Under the same conditions, the failure of the modified

polypropylene was clearly ductile and the impacting dart punched through without shattering the sample. Quantifying our visual observations, the total energy absorbed in by the sample was 42 J versus only 10 J absorbed by unmodified PP homopolymer. The load and energy versus time plots are included in Figure 8. The brittle behavior of the PP is clearly visible in the steep drop of the load versus time curve after initial failure. The modified materials continued to bear load long after the initial failure while the material plastically deformed at the impact location.

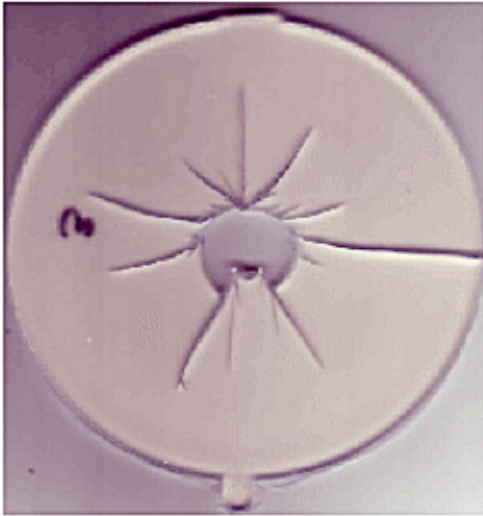


Figure 7a: Brittle performance of homopolymer PP

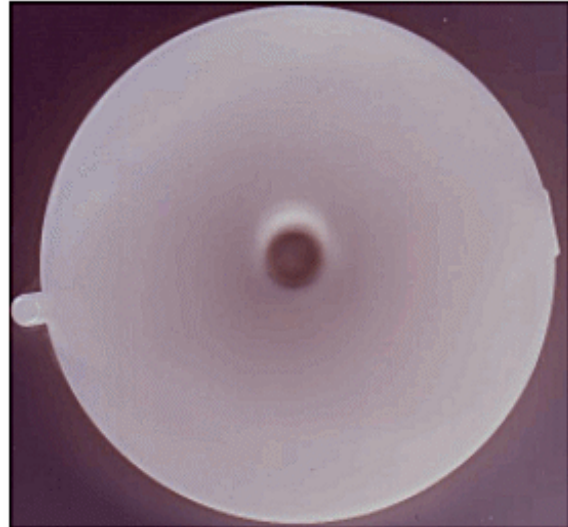


Figure 7b: homopolymer PP + 10% with formulation B

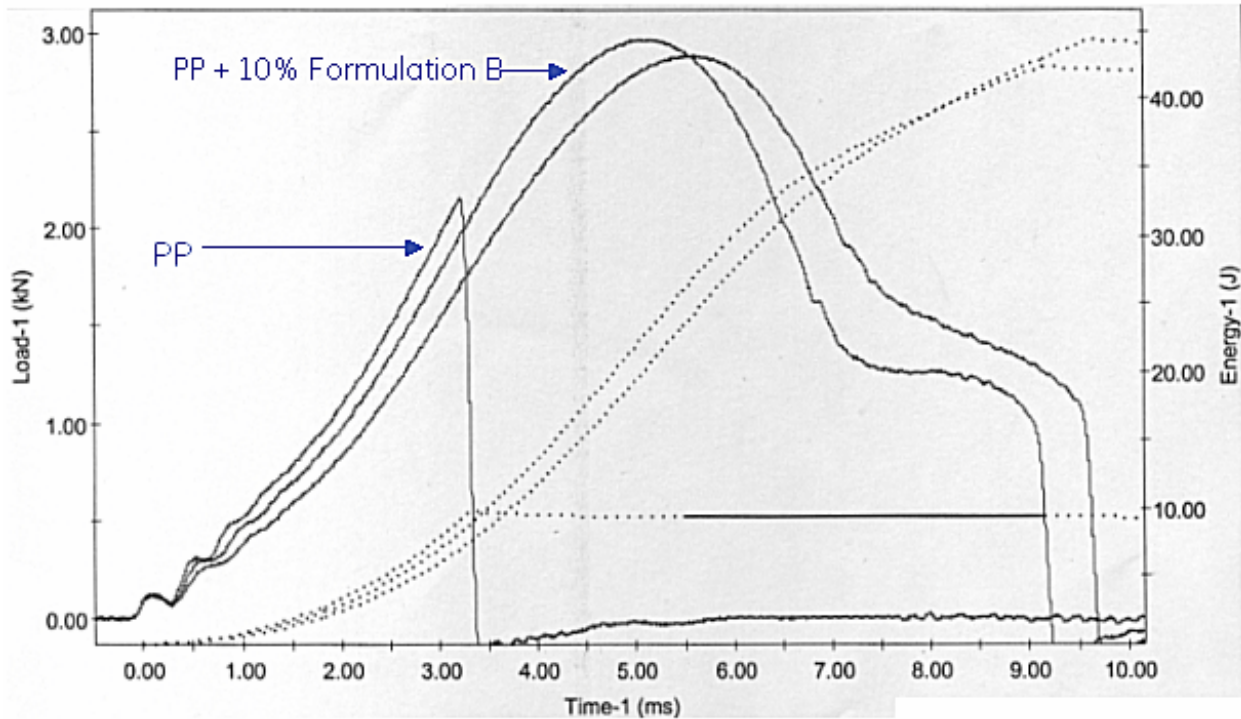


Figure 8: Load and energy plots for dynatup testing of both modified and unmodified homopolymer PP

Notched-Izod testing is a much more aggressive impact event and tends to correlate more closely with very complicated injection molded or machined parts with many sharp corners.^{vi} Reviewing the notched-Izod results for mPPE formulation B in PP, we observe that Notched-Izod is also improved significantly over the baseline polypropylene homopolymer. [Figure 9] Additionally, elongation-to-failure of homopolymer PP in standard static loading (non-impact events) is also significantly improved using mPPE additive formulation B. The complete property profile of several variants of formulation B may be reviewed in Table 1.

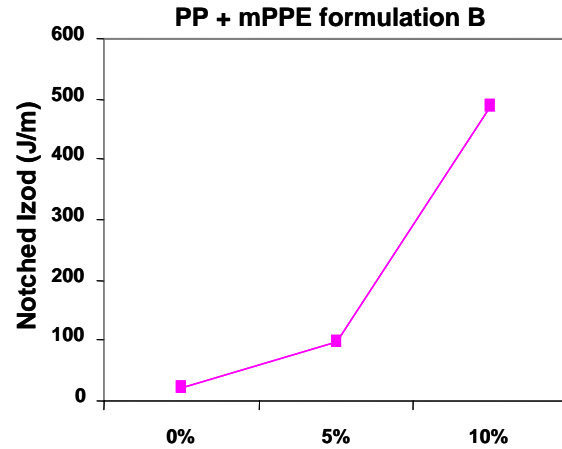


Figure 9: Notched-Izod and PP+ mPPE formulation B

The reason for the two formulations (A and B) is clearly observed in Figure 10. As we discussed above, formulation A is efficient at increasing the temperature resistance of polypropylene. The modified polyphenylene ether additive formulation A is not as useful in improving the impact resistance of PP as formulation B. This characteristic has been observed in both homopolymer and copolymer polypropylene. On the other hand, formulation B has been optimized to have the greatest effect on the impact resistance of homopolymer PP and has either a small positive or small negative effect on the temperature resistance of PP depending upon the grade of polypropylene and the exact variant of the mPPE additive formulation. Therefore formulation B is not an effective heat extender for PP.

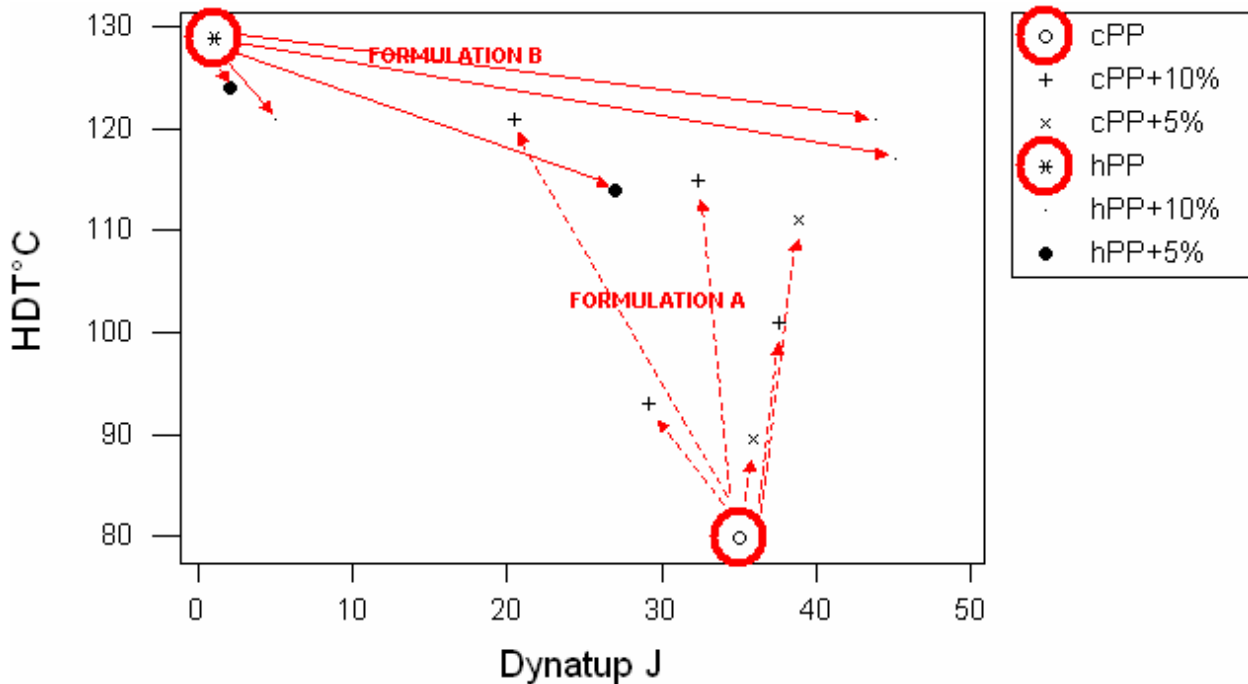


Figure 10: Combining higher temperature with higher impact: the effects of variants of Formulation A and Formulation B on two representative grades of homopolymer (hPP) and copolymer polypropylene (cPP).

Formulation		cPP	cPP + A	cPP + A	cPP + A	cPP + A	hPP	hPP + B	hPP + B	hPP + B	hPP + B
Loading		0%	5%	5%	10%	10%	0%	5%	5%	10%	10%
Flexural Modulus	MPa	1120	1140	1220	1160	1240	1960	1670	1690	1540	1580
HDT 66psi	°C	79.7	89.5	111	115	121	129	114	117	117	114
Notched Izod	J/M	795	744	728	256	238	21.4	98.7	82.5	487	288
Notched Izod -20C	J/M	56.7	26.7	36.1	19.1	21.4	17.8	18.5	17.2	20.4	20.4
Dynatup (Energy to Failure)	J	35.0	35.9	38.9	32.3	20.4	1.06	27	28.7	45.2	44.2
Dynatup (Energy to MaxLoad)	J	19.2	19.5	21.9	20.4	16.4	0.88	19.6	22.4	26.1	25.4
Elongation-at-break	%	150%	120	90	*	*	9.8	64	43	26	37
Tensile Modulus	MPa	1550	1576	1647.5	1603.3	1650	2994	2260	2312	1904	1964
Yield Strength	MPa	30	30.1	30.9	30.2	31.1	42.5	37	37.7	34.4	35.4

Table 1: Selected pairs of PP modified with variants of mPPE additive formulations A and B. hPP=homopolymer. cPP = copolymer. * data unavailable at the time of publishing.

CONCLUSIONS AND NEXT STEPS

The modification of PP using mPPE engineering resins is a viable path to combined improvement in impact and heat resistance of polypropylene, especially in applications where brittle behavior is unwelcome and inorganic fillers are difficult to use. A wide range of performance may be obtained through variations on the exact composition of the mPPE additive as illustrated by formulation A and B in this paper. In addition, it is possible to achieve similar temperature and impact resistance from both homopolymer and copolymer PP in combination with mPPE additives. Much more work must be done to understand the complete advantages and disadvantages of modifying polypropylene with mPPE including advanced processing studies, optimization the additive formulation, and the exploration of other properties such as creep, rheology, fatigue, and chemical resistance.

ACKNOWLEDGEMENTS

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* NORYL PPX and PPO are trademarks of the General Electric Company.

Figures and data presented are for general information and are not for the purposes of warranty and specification. Any questions may be directed to Robert McKay at (401) 270-6359 or robert.mckay@ge.com.

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- ⁱⁱ *Engineering Plastics Handbook*, edited by J. Margolis, McGraw-Hill, 2005
- ⁱⁱⁱ *Commercial Polymer Blends*, Springer – Verlag, 1998, Chapter 20
- ^{iv} A. Adedeji, J. Haylock, T. Hartle, and J. Parmer, "NORYL PPX* resin: A new polymer alloy offering advanced performance properties for the automotive industry," GE Plastics, 2001
- ^v R. Nimmer and G. Trantina, *Structural Analysis of Thermoplastic Components*, McGraw-Hill, 1994, Chapter 6
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mPPE + PP

Proprietary engineering resins as
 additives to polypropylene

Presented by:
Robert McKay
 Industry Manager – Performance Additives
 GE Advanced Materials

Engineering Resins as Additives

	PS	PP	PE	EVOH	APET	CPET	PA	PVDC
mPPE	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>				<input checked="" type="radio"/>	
PBT		<input checked="" type="radio"/>	<input checked="" type="radio"/>			<input checked="" type="radio"/>	<input checked="" type="radio"/>	
PC			<input checked="" type="radio"/>		<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	

Immiscible, Useful Blends Possible Miscible, Single Phase Possible

Today's presentation: mPPE+PP

Polyphenylene Ether as an Additive to PP

2,6-Dimethyl-1,4-Phenylene Ether

- ✓ Heat
- ✓ Melt Strength
- ✓ Non-halogenated FR
- ✓ Mechanical Properties
- ✗ Clarity
- ✗ Polarity

Opacity

Extruded samples, 0.6mm thick

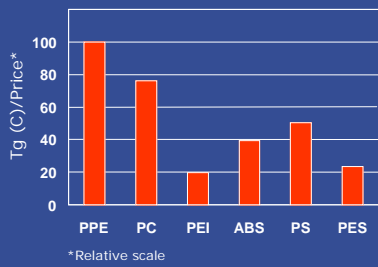


PP

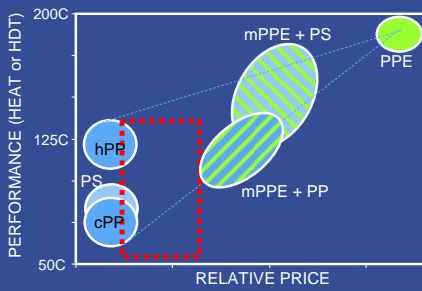
PP+5% mPPE

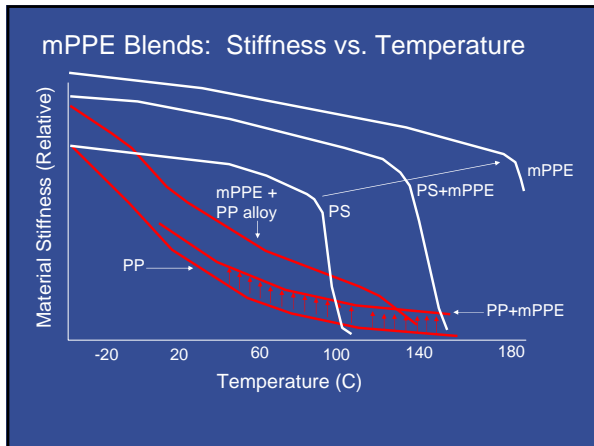
PP+10% mPPE

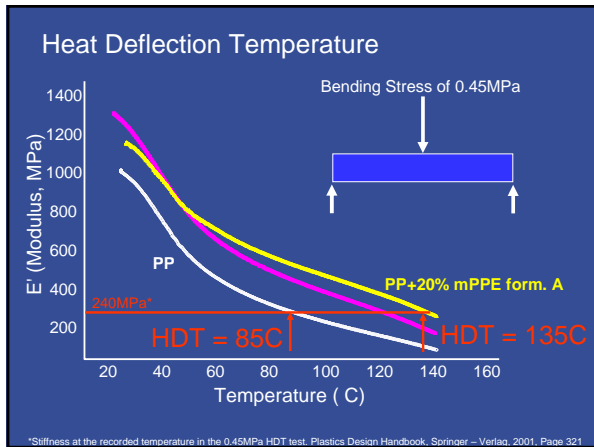
PPE: Most heat resistance per dollar spent

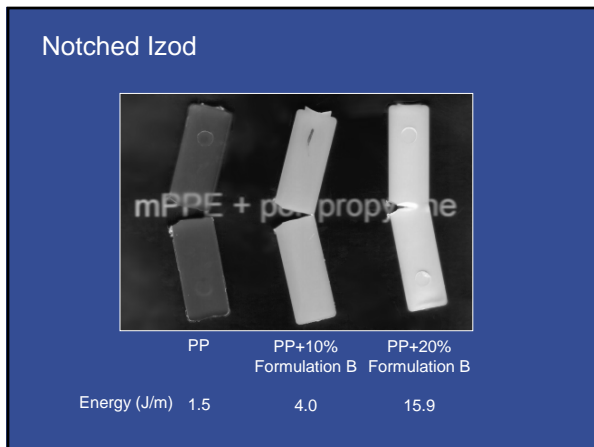


mPPE Blends

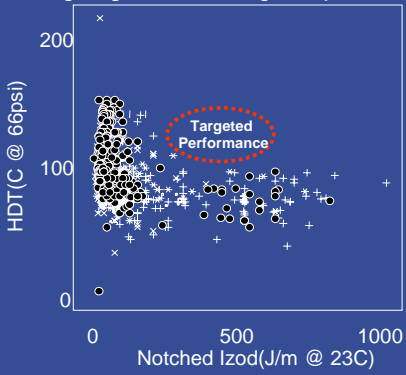




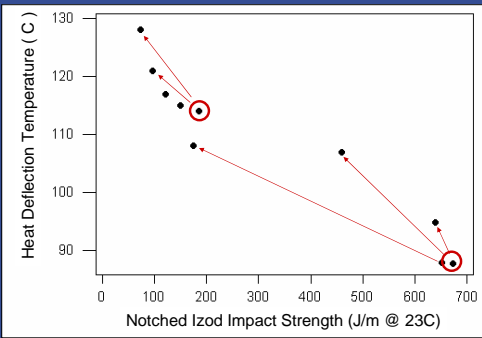




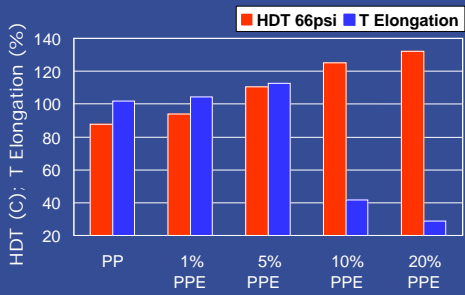
Enabling High Heat & High Impact in PP



Early Progress

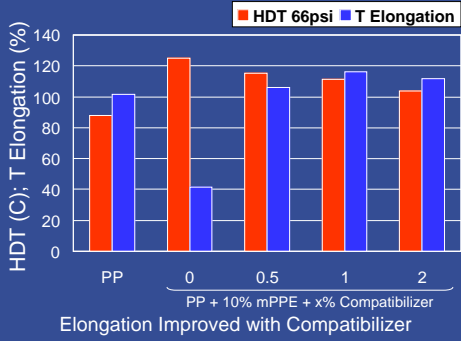


Early Progress

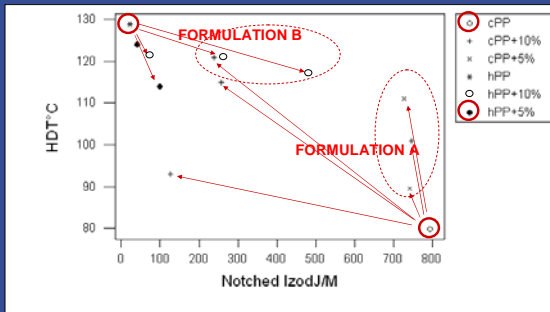


HDT improved; Elongation compromised

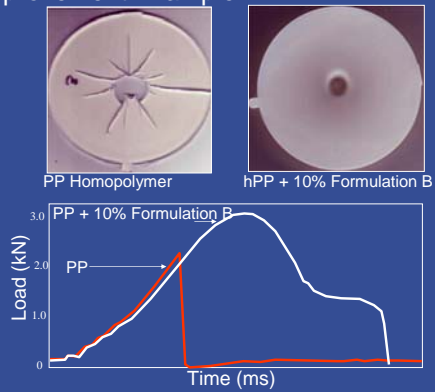
Effect of Compatibilizer



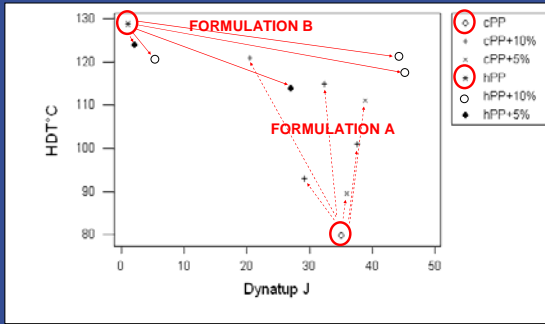
Development of Improved Formulations



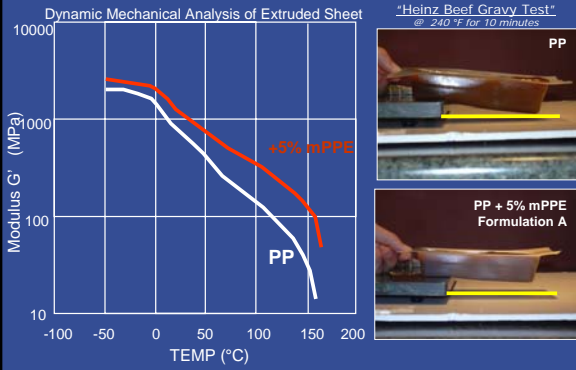
Improvement Example



Development of Improved Formulations



Extruded/Thermoformed Example



Biaxial Oriented PP+mPPE



HDPE + mPPE (> 20% mPPE)

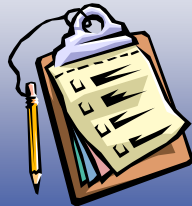
Parameter	Unit	Neat HDPE	Blend 1	Blend 2	Blend 3
Flexural Modulus	MPa	817.00	978	1260	1400
HDT 0.455 Mpa	°C	70	120	133	137
Impact Strength 23C	J/M	451	500	762	854
Impact Strength -30C	J/M	332	445	337	316
Tensile Stress at Yield	MPa	31.2	36.9	42.0	45.8
Tensile Stress at Break	MPa	25.4	32.3	35.7	37.8
Tensile Elongation at Yield	%	8.6	17.0	12.0	9.8

HDPE grade: MI=0.29, Density=0.962



Thank You

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 in your evaluation sheet...*
