Polypropylene Based Olefin Block Copolymers for Clear Cold Tough Application

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Abstract

INTUNE™ Olefin Block Copolymer (OBC) builds upon Dow's proprietary catalyst chain shuttling technology. INTUNE OBC is a block copolymer that contains both polypropylene and polyethylene connected together within one polymer chain. INTUNE OBC is the ideal compatibilizer to connect and balance the properties of blends of polyethylene and polypropylene.

PE and PP each have a material advantage when used alone. PE has toughness and flexibility while PP has stiffness and clarity. With OBCs, a new balance of properties of where one no longer has to choose between toughness and clarity or flexibility and stiffness. OBC technology can provide better dispersion that this correlates to better homogeneity, less stresses, better part esthetics, and more consistent part performance. As an impact modifier, OBC technology can offer balanced solutions of clarity, impact, and flow. This study shows that INTUNE 10510 OBC offers high flow, good dispersion, good optics, and good impact and INFUSE™ 9817 OBC offers moderate optics and excellent impact over the leading high clarity impact copolymer.

Introduction

PP homopolymers or PP random copolymers provide the desirable stiffness and clarity for many applications, but suffer from poor impact properties due to PP's high Tg of 0°C and high degree of crystallinity. To overcome this deficiency, PP homopolymer is blended with PP copolymers and/or elastomers to improve toughness, but often at the expense of clarity, impact properties, and modulus (1-2). Conventionally, to achieve high clarity and impact of PP, the modifier needs to be refractive indexed matched. However clarity can also be achieved using non-refractive index polymer, as long as it is a high flow elastomer where fine dispersion of elastomer domains can be achieved. The performance at freezing temperature is still lacking with these approaches.

INTUNE™ OBC, a polypropylene-based OBC comprising iPP hard blocks and ethylene-propylene soft blocks offers a compatiblization solution to reduce the domain sizes (100-500 nm) of the elastomer phase when blended in PP. These novel compatibilized blends of PP and elastomers offer a wider range of thermodynamically-stable compositions with morphologies finer than those achievable with classical blends (3), resulting in unique combinations of properties.

The purpose of this study was to compare the relative performance of an RCP impact modified with olefin block copolymers and polyolefin elastomers, targeted for use in a clear freezer application. Impact modifiers based on OBC technology can offer balanced solutions of clarity, impact, and flow that outperforms a leading high clarity impact copolymers (4).

Materials

A 40 MFR, random copolymer (next gen clarified), was impact modified with polymers listed in Table 1.
These materials were dry-blended with the PP random copolymer (40 MFR) at 20wt% concentration and then injection molded in a KraussMaffei KM110-390 injection molding machine. The conditions were as follows: injection parameters of 40 mm/s at 2000 bar for 0.78s, hold pressure of 300 bar for 20 s, and cool time of 20s.

INTUNE™ 10510 OBC, is a new PP based olefin block copolymer. INFUSE™ OBC 9817 is an ethylene-based olefin block copolymer containing polyethylene hard segments and ethylene-octene soft segments. ENGAGE™ 8402 Polyolefin Elastomer (to be referred to as POE 1), ENGAGE™ 8200 Polyolefin Elastomer are random copolymers containing ethylene and octene (to be referred to as POE 2). VERSIFY™ 4301 Polyolefin Elastomer is a random copolymer containing propylene and ethylene (to be referred to as PBE).

For comparison, a clarity ICP that is typically used for cold food and storage applications was also tested.

<u>Property Testing</u>

<u>Optical Properties</u>
Plaques of 1.6 and 0.75 mm thickness were compression molded. Clarity, transmittance, and haze was measured using BYK Gardner Haze-gard as specified in ASTM D1746. 60° gloss was measured using BYK Gardner Glossmeter Microgloss 60° as specified in ASTM D-2457.

<u>Tensile Testing</u>
Stress-strain behavior in uniaxial tension was measured using ASTM D638. Injection molded tensile specimens are used (approx. 16.5mm 19mm x 1.6mm). Samples

were stretched with an Instron at 50mm/min at 23ºC. Tensile strengths and elongation at break are reported for an average of 5 specimens.

Izod Impact

The notched Izod impact tests were performed on injection molded specimens (63.5 mm x 12.7 mm x 1.6 mm) was used with a milled notch and confirmed according to ASTM D256. The samples were notched using a notcher to produce a notch depth 2.54 +/- 0.05 mm. Ten specimens of each sample were tested using ASTM D256 at room temperature, 23°C, and 0°C.

Transmission Electron Microscopy

Image Collection **-** TEM analyses were performed on a JEOL JEM-1230 operated at 100kV accelerating voltage and collected on a Gatan-791 and 794 digital cameras.

TEM Sample Preparation - The compression molded films were trimmed so that sections could be collected near the core of the films. The trimmed samples were cryopolished prior to staining by removing sections from the blocks at -60°C to prevent smearing of the elastomer phases. The cryo-polished blocks were stained with the vapor phase of a 2% aqueous ruthenium tetraoxide solution for 3hrs at ambient temperature. Sections of approximately 90 nanometers in thickness were collected at ambient temperature using a diamond knife on a Leica EM UC6 microtome and placed on 600 mesh virgin TEM grids for observation.

Discussion

The development of PP impact modifiers to meet the requirements for clear freezer applications is an on-going challenge. Containers and articles for frozen foods or storage are challenged by the balance of toughness and stiffness while having clear optics for consumer appeal. Containers made from polyethylene can certainly meet the needs of toughness but are not clear. Containers made from polypropylene random copolymers have excellent clarity (with the addition of clarifiers and nucleators) but are not tough. Hence, the introduction of elastomer modifiers to toughen the PP to meet the impact requirements is needed. Reactor grade PP impact copolymers can offer a good balance of clarity and stiffness, but the impact properties are limited due to the miscibility of the ethylene-propylene rubber phase and dispersion. To obtain the best impact performance, additional elastomers are compounded and blended with RCP's or ICP's to increase the rubber phase volume and increase the impact toughness. The loading of modifier varies depending on the performance that is required in the given application. Typically, ~3-10 wt% loading of the modifier is sufficient for room-temperature applications, ~10 wt% for refrigerator applications, and greater than 20 wt% for cold freezer applications.

In this work, solutions for the freezer application was targeted and 20 wt% of modifier was blended and tested. The optical and physical properties of blends containing a RCP matrix and 20% dispersed elastomer phase were evaluated (refer to Table 1). It was hypothesized that olefin block copolymer with its Compatibilization attributes, could improve the balance of clarity and toughness. For cold freezer applications, the stiffness is less of a requirement due to the increase in modulus at low temperatures but viscosity build and crystallization setup is important for quick processing and demolding of articles for injection molding.

Table 2 shows the clarity, and haze measurements for plaques from the blended components. Two part thicknesses were tested for optics; thin 0.75mm and thick 1.6mm. At 0.75 mm thickness, the thickness used for thin-wall food containers, all of the parts looked transparent and clear as a stand-alone RCP. At 1.6 mm thickness which is typically used for storage containers, the best optics, highest clarity and lowest haze % was observed with PBE and POE 1, 99% clarity, and 13-14% haze. Next, the INTUNE™ 10510 OBC exhibited a clarity of 99% and 22% haze. Poorer optics were observed with INFUSE™ 9817 OBC and the clarity ICP. The worst optics was with the POE 2, with a reduction in clarity to 90% and greater than 50% haze.

The optical results are in-line with the composition of the modifiers. For the non-refractive index matched polymers, INTUNE 10510 OBC, INFUSE 9817 OBC, POE 2, Clarity ICP, TEM micrographs of the samples were recorded to understand the relationship of optics and the dispersed morphology of the rubber domains. Figure 1 shows the TEM micrographs of the blends at the 1μm scale. The micrographs show that the size and dispersion of the rubber domains are related the optical properties observed. The clarity ICP and the POE 2 modified blend showed the poorest dispersion with large bands in the flow direction. Similarly, the INFUSE 9817 show bands in the flow direction but shows some evidence of droplet break-up; it is suspected that the long and thick domain bands, contributed to higher haze. Unlike the other modifiers, INTUNE 10510 shows the rubber domains been finely dispersed into the matrix with droplet sizes less than 200 nm. Note due to the compatibilization effect of the iPP-EP nature of the polymer, a very fine dispersion results and relates to the lower haze observed in the molded plaques that shows better dispersion is good for optics. However the next question is how the balance of performance changes with the improvement in optics?

Table 3 summarizes the physical properties of the blends. All mechanical testing was completed on the 1.6 mm thickness parts. The tensile modulus (2% secant) of the modified blends ranged from ≈ 1300 – 1500 psi. The

PBE resulted in the lowest modulus while POE 1, the highest. The INTUNE™ 10510 OBC, INFUSE™ 9817, and POE 2 were all around 1400 psi. However, at the 20 wt% loading of these modifiers, the modulus is lower than that of the clarity ICP. As mentioned, for cold/freezer temperatures, the toughness is more critical than the modulus since the modulus increases with decreasing temperature. The more important factor is the impact strength and failure mode at low temperatures.

Figure 2, 3, and 4 compares the IZOD impact strength and failure type at 23°C, 0°C, and -20°C, respectively. These testing temperatures were chosen to understand the impact performance at room temperature, refrigerator, and freezer conditions.

At room temperature, the INTUNE 10510 and INFUSE 9817 modified blends, and clarity ICP exhibited ductile behavior with high impact strength and partial breaks of the specimens. At room temperature, these materials exhibit high toughness sufficient for storage and food/pantry applications. Conversely, the other modifiers exhibited lower impact strength and brittle behavior, with PBE and POE 2 being similar and POE 1 the lowest.

As expected, the impact strength of all the materials decreased when tested at subambient temperatures. The data shows that the INTUNE 10510 and INFUSE 9817 outperformed the clarity ICP, exhibiting higher impact energies and some partial breaks (indicating more ductility) than the clarity ICP which showed brittle behavior with 100% complete breaks. The observed trend for these three examples is consistent at both 0°C and -20°C. In comparison of the INTUNE 10510 and INFUSE 9817, the INFUSE 9817 exhibited higher impact strength at these subambient temperatures; the increase is attributed to its block architecture and high levels of incorporated octene which results in a low Tg and high flexibility. The INTUNE 10510 and its compatibilization approach for a propylene-based OBC resulted in not only an improvement in impact strength, but in rubber dispersion and homogeneity to result in better optics.

In application to clarity freezer applications, each modifier solution can be tailored to provide a unique feature balance. Figure 5 depicts the property balance and comparison to the clarity ICP. The INTUNE 10510 exhibited the fine particle sizes and excellent dispersion, to result in good optics, room temperature ductility, and an improvement in low temperature toughness. The INFUSE 9817, offers a significant improvement in low temperature toughness (due to its low density, ethylene-octene soft segments), a slight improvement in dispersion but poorer optics than the clarity ICP. Therefore, depending on the processing and application constraints, a unique and tailored solution can be provided. High flow, good dispersion, good optics, and good impact with INTUNE 10510 or moderate optics and excellent impact with INFUSE 9817, all out performing the clarity ICP.

Conclusions

The olefin block copolymers can used to modify RCP PP, to improve the performance compared to a clarity ICP. INTUNE™ 10510 OBC compatibilizes the polymer where it results in the fine particle sizes and excellent dispersion, to result in good optics, room temperature ductility, and an improvement in low temperature toughness. INFUSE™ 9817 OBC offers a significant improvement in low temperature toughness with a slight improvement in dispersion, but poorer optics. The processing plays a part in the final performance in the parts, however the OBCs out performs clarity ICP.

INTUNE 10510 and INFUSE 9817 outperformed the clarity ICP, exhibiting higher impact energies and some partial breaks. INFUSE 9817 exhibited higher impact strength at these subambient temperatures of 0 and -20 °C. INTUNE 10510 resulted in not only an improvement in impact strength, but in rubber dispersion and homogeneity to result in better optics than the clarity ICP. INTUNE 10510 rubber domains have been finely dispersed into the matrix that relates to the lower haze observed in the molded plaques that shows better dispersion is good for optics. The benefits of dispersion by the OBCs results in better homogeneity, less stresses, better part esthetics, more consistent part performance.

References

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Table 1 – Properties of Matrix Blending Components

	MFR (230°C) or MI (190°C) (g/10 min)	Density (g/cm^3)	Description
Clarity RCP	40	0.902	Random copolymer, PP (clarified)
Clarity ICP	30	0.900	PP Impact copolymer (clarified)
INTUNE™ 10510	90	0.890	Olefin Block Copolymer, propylene-based
INFUSE™ 9817	15	0.890	Olefin Block Copolymer, ethylene-based
POE 1	30	0.902	Random copolymer, ethylene-octene
POE 2	5	0.870	Random copolymer, ethylene-octene
PBE	25	0.868	Random copolymer, propylene-ethylene

Table 2 – Physical and Optical Properties

	Clarity ICP	INTUNE™ 10510 OBC	INFUSE™ 9817 OBC	PBE	POE 1	POE 2
Ten. 2% Sec. Mod. (psi)	1650	1400	1460	1290	1500	1430
Clarity % (1.6mm)	99	99	97	99	99	90
Haze % (0.75mm , 1.6 mm)	13, 31	11, 22	15, 36	6, 14	7, 13	21, 50
Izod (23°C), kJ/m^2	20	21	23	16	5	15
Izod (0°C), kJ/m^2	8	13	20	5	4	7
Izod (-20°C), kJ/m^2	7	7	11	3	3	7

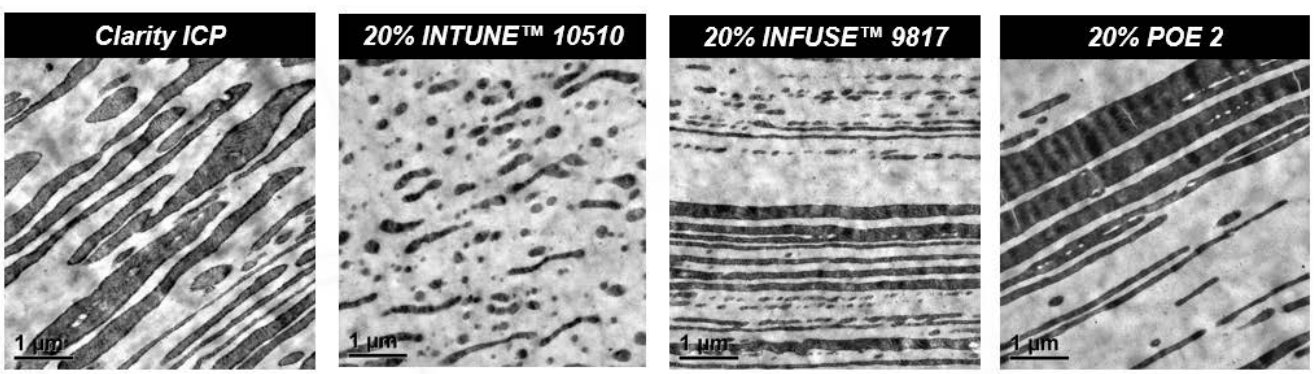

Figure 1 – TEM comparison of RCP modified blends to clarity ICP

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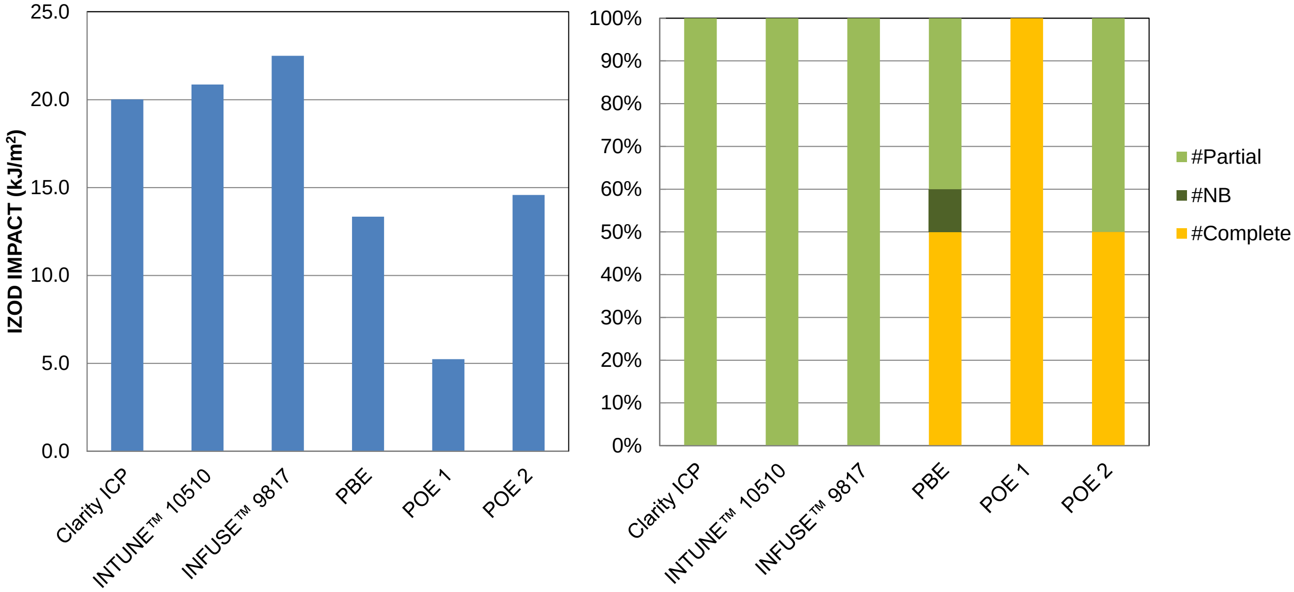

Figure 2 – Izod Impact and Failure type at 23°C

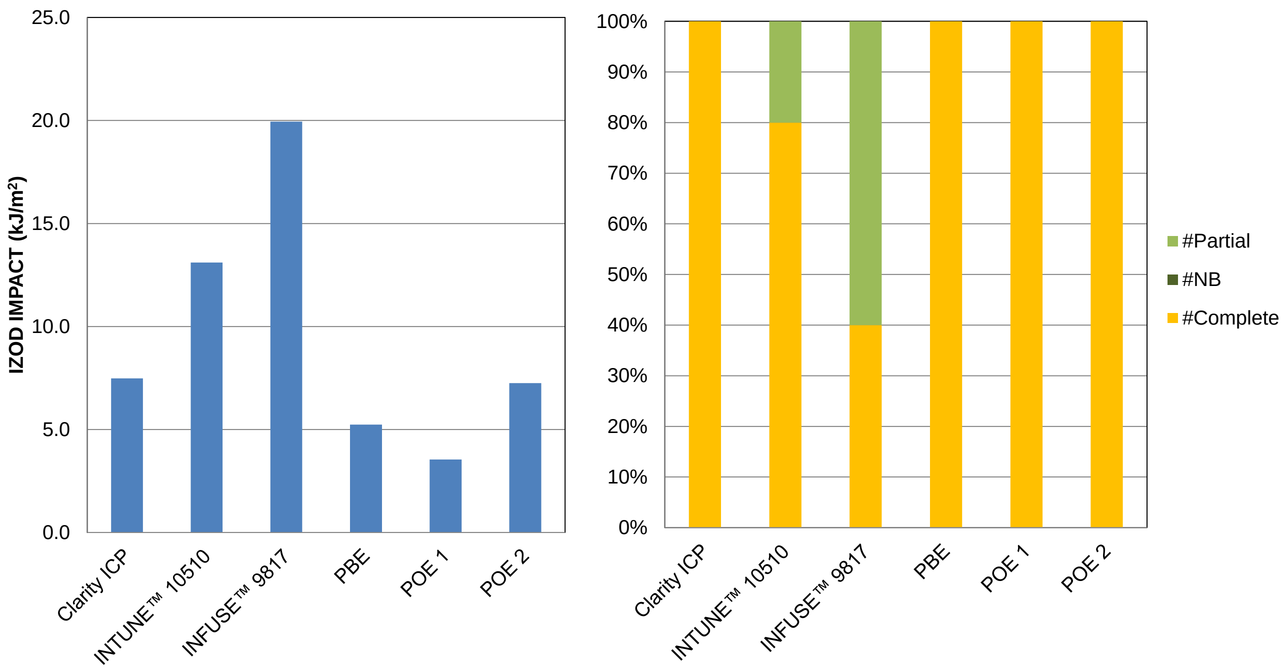

Figure 3 – Izod Impact and Failure type at 0°C

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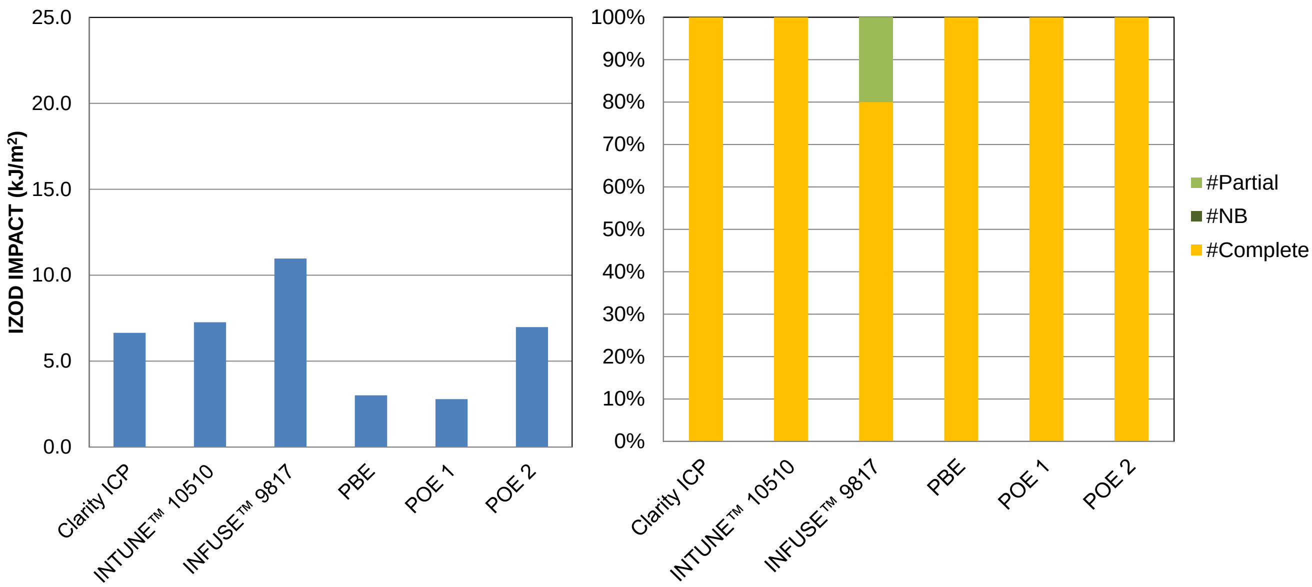

Figure 4 – Izod Impact and Failure type at -20°C

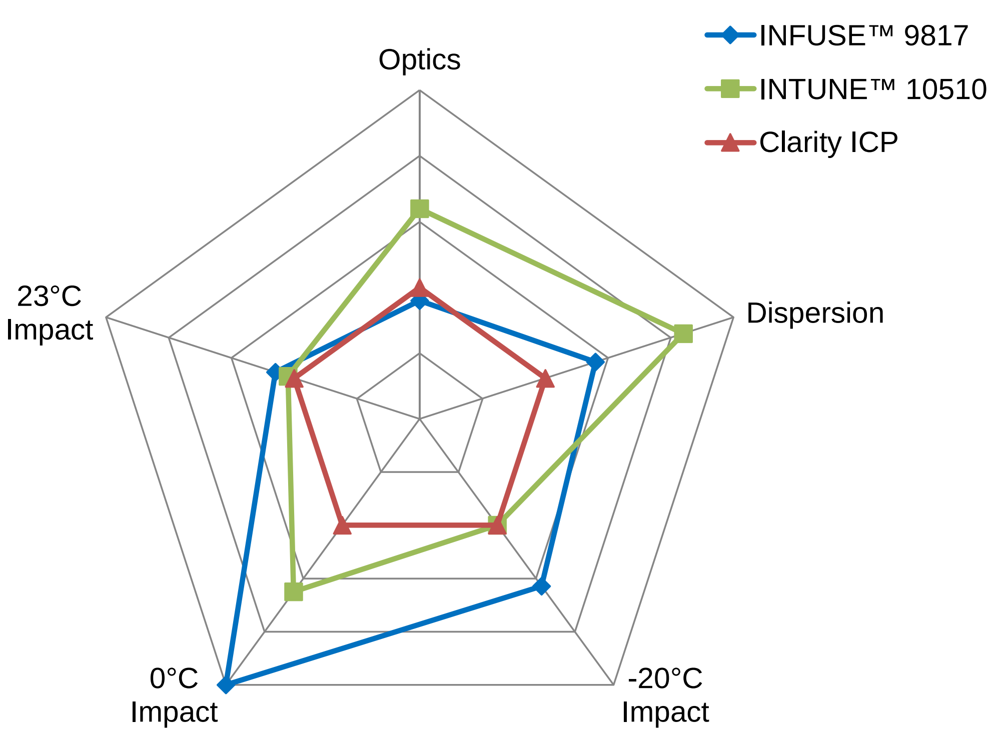

Figure 5 – Performance advantages of INFUSE™ 9817 OBC and INTUNE™ 10510 OBC compared to the clarity ICP.

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