

CLARIFIED POLYPROPYLENE – OLD TECHNOLOGY VS. NEW CHEMISTRY

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ABSTRACT

RiKA International Limited, a subsidiary of New Japan Chemical Company Limited (NJC), presents a review on the acetal-sorbitol based clarifying agents currently available and explains why their failings, mainly low thermal and chemical stability and poor organoleptic properties, are spurring a shift in the polypropylene industry towards the endorsement of a new type of product. This paper demonstrates how new chemistry addresses these shortcomings and data presented will show how this new compound, RiKACLEAR PC1, will become the new benchmark in clarified technology.

BACKGROUND

In late 1960's, New Japan Chemical was the first to introduce GEL ALL D (dibenzilidene sorbitol, DBS) as a gelling agent. By the 1980's, the addition of DBS to polypropylene enabled much higher clarity levels than those previously achieved with the additives used at that time (e.g. sodium benzoate), mainly due to the spherulite size being smaller than the wavelength of light. DBS became then known as the First Generation Clarifying Agents. Although excellent clarity and organoleptics were achieved, "plate-out" problems were their main drawback, due to their low thermal stability. This first generation remains, however, of interest for certain markets where economical clarity will suffice. Continuous research efforts led way to the introduction of the Second Generation Clarifiers (p-methyl dibenzilidene sorbitol, MDBS). With improved thermal stability, higher processing temperatures were allowed and better clarity achieved, at the expense of poor organoleptics. The distinctive sweet, almond odour characteristic of the aldehyde (p-tolualdehyde) used in the manufacturing of MDBS, has somewhat restricted their use in clarified PP for food contact applications. Their main use has focused on medical applications, such as disposable syringes. The latest generation based on the acetal-sorbitol chemistry is the Third Generation or 3,4-dimethyl dibenzilidene sorbitols (3,4-DMBDS). Although this generation achieves good clarity, the organoleptics issue is still not solved, due to their intrinsic acetal-sorbitol nature.

The poor organoleptic properties of the acetal-sorbitols are primarily caused by very small amounts of free aldehyde. There are two main sources of aldehyde:

- Residual aldehyde from the manufacturing process.
- Aldehyde released due to the intra-molecular rearrangement during the breakdown of the acetal-sorbitol molecule during resin processing.

Changing from one aldehyde to another may bring about small changes in the properties of clarified polypropylene but the inherent flaws of acetal-sorbitols will still be present.

In light of this, NJC, a company regarded by many as the pioneer in the clarifiers field, has taken on board the high demands of the polypropylene industry, producing an alternative to the current acetal-sorbitols in order to circumvent the issues that their use generates. This new chemical has been developed to meet all the requirements of the PP industry, which are transparency, stiffness, impact strength, heat resistance and organoleptics: RiKACLEAR PC1, a new non acetal-sorbitol based clarifying agent, which was successfully launched at K2007 in Düsseldorf, (Germany) in October 2007.

Extensive comparative data has already been presented elsewhere^{1,2}, as well as its performance in controlled rheology grades, regrind and aging studies^{3,4}.

The focus of this paper will turn to the cost-effectiveness of the product, its wide processing window, which allows its use in any fabrication process and its comparative performance against conventional clarifiers in the market.

CONCENTRATION STUDY OF RiKACLEAR PC1 IN RANDOM POLYPROPYLENE

Polypropylene (PP) is a semi-crystalline material. PP normally crystallizes slowly, and when the molten polymer cools down, the growth of these crystals is generally initiated around microscopic “defects” naturally present in the material. These crystals with spherical structure called spherulites, grow until they meet another crystal, their size being dependent on the number of nucleation sites within the crystallizing polymer^{5,6}. Since the spherulites scatter light, un-nucleated polypropylene manifests poor see-through clarity. The addition of a clarifier to PP is equivalent to introducing “artificial defects” around which spherulites can initiate their growth. Consequently, adding a high performance clarifier results in the formation of spherulites smaller than the wavelength of light, so that the light scattering is considerably reduced and the clarity of the material is significantly improved.

In random copolymer, the presence of ethylene monomer in the polypropylene chain as a defect decreases the melting temperature of the resin to a relatively low value of 145°C⁷. The ethylene content present inhibits the crystallization of the chain, giving way to lower melting and less perfect crystals. Moreover, since the size of the crystals is quite small (generally lower than the wavelength of visible light) high levels of clarity can be achieved.

In the current uncertain economic conditions with rising oil prices and inevitable increase costs in production, it is essential to adapt quickly to the changing market. RiKA and NJC are very aware that the polypropylene industry requires a cost-effective product that can successfully improve the properties of the material at a limited cost.

With a view to assessing the optimal dosage of RiKACLEAR PC1 in random copolymer, a concentration study was carried out with loadings of the additive ranging from 1000 to 2000ppm and the results are shown below.

Figure 1 shows haze vs. concentration data. Both sets of results for plaques of 0.5 and 1mm thicknesses show that the plateau of haze is reached about 1400-1600ppm of concentration of the additive, which is significantly lower compared to the 2000ppm mark of conventional clarifiers.

The mechanical properties were also investigated. Figure 2 shows the crystallization temperature where the addition of 1000ppm of product already achieves a T_c similar to that of the sample at 2000ppm. Figure 3 confirms again that for heat distortion values, 1000ppm of product will provide excellent heat resistance for hot-fill applications, for example. The flexural modulus (Figure 4) shows also

that with certain variations, 1200ppm will provide good stiffness for the final moulded article with no loss of impact strength (Figure 5).

This concentration study confirms that RiKACLEAR PC1 is a cost-effective product with an optimum dosage that can vary from 1200-1600ppm, depending upon the requirements of the final article.

PROCESSING WINDOW OF RiKACLEAR PC1 IN RANDOM POLYPROPYLENE

A well-known feature of the sorbitol based clarifiers is that owing to their sugar-based chemical structure, they suffer from thermal decomposition, leading to a phenomenon called “plate-out”. In this case, a white residue appears on the surface of the mould during the injection moulding process, leading to increased downtime and production costs. The thermal instability of acetal-sorbitols has restricted their processing conditions to very narrow range of temperatures to avoid any “plate-out” problems. This issue, however, can be overcome with the incorporation of RiKACLEAR PC 1 into the polypropylene grade.

In order to assess the processing window of RiKACLEAR PC1, random copolymer containing 2000ppm of the additive was extruded at temperatures ranging from 180°C to 260°C and each extruded material compounded at injection moulding temperatures from 200°C to 260°C.

Haze values were measured in 0.5mm and 1mm thickness plaques and the results are shown in Figures 6 and 7. For both sets of results, 0.5mm and 1mm, it can be observed that for all the extrusion and injection moulding temperatures, the haze values show no variations across the whole set of temperatures, showing that RiKACLEAR PC1 has a wide processing window, which ensures reliable performance of the product during processing. In addition, no signs of “plate-out” (white residue) were found during the study.

Therefore, it is clear from these results that previous processing restrictions can be easily avoided when using this new type of chemistry.

RiKACLEAR PC1 AS A CLARIFIER IN CONTROLLED RHEOLOGY AND POLYPROPYLENE HOMOPOLYMER GRADES

Controlled rheology (CR) PP is produced by vis-breaking process (viscosity breaking): peroxides are mostly used and they are added with stabilizers and other additives prior to extrusion and pelletization. These CR resins have higher melt flow rate (MFR), lower molecular weight (MW), narrower molecular weight distribution (MWD)

and consequently they exhibit an easier and more consistent flow. When peroxide and a PP polymer mixture is heated, the peroxide will produce free radicals that react with the PP molecules. In the CR process the peroxide attacks randomly, and statistically the longest molecules are most susceptible to be attacked. This results in a narrow MW distribution and increased MFR. Controlled rheology grades (CRG) are designed to combine very high fluidity while maintaining a high stiffness-impact balance.

To evaluate the robustness of PC1 in the presence of peroxide, and if degradation of the clarifier could take place in these circumstances, 300ppm of Trigonox 101 were added to a homopolymer base resin of MFR of 12g/10min. The optical and mechanical properties of the controlled rheology material (MFR 55) were compared against those of the homopolymer base resin (MFR 12).

Figure 8 shows the increase on the melt flow rate when 300ppm of peroxide were added to the formulation, leading to a material with MFR of 55g/10min.

It is also essential in homopolymer PP to achieve a high level of clarity in the presence of peroxide. Figure 9 shows the haze values obtained for 0.5mm plaques upon the addition of peroxide. All products increase their haze values, with PC1 at 2000ppm showing the lowest increase and the lowest haze value of all, about 50% lower than that of 3,4-DMDBS. In the case of 1mm plaques (Figure 10), haze values also increase for all products, with PC1 showing much lower haze than the phosphate salt and a similar or lower haze compared to DMPAB and 3,4-DMDBS.

In terms of crystallization temperature (Figure 11) PC1 shows no signs of degradation on addition of peroxide.

HDT values of the grades are shown in Figure 12. At both concentrations, 1500 and 2000ppm, PC1 exhibited the best performance compared to DMPAB and 3,4-DMDBS, (with 15% increase compared to the latter) and also against the phosphate salt.

One of the drawbacks associated with peroxide addition is that it could lead to a significant decrease of the stiffness of the material due to the rupture of the polymer chains. It is clear, however, from Figure 13 that the stiffness conferred by PC1 is not affected by the presence of peroxide, achieving the highest flexural modulus of all 4 products, including the nucleator phosphate salt. Nonetheless, the impact strength seems to be affected by the addition of peroxide, with all materials including the blank showing a similar loss of both Charpy (Figure 14) and Izod (Figure 15) impact strengths in the MFR 55 grade.

Once again, the results shown above confirm that the performance of RiKACLEAR PC1 is not affected in controlled rheology grades.

EXPERIMENTAL

MATERIALS

All formulations contained a standard base stabilization system.

In the controlled rheology grades, the peroxide Trigonox 101 (2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane) by Akzo Nobel Polymer Chemicals was added with the stabilizers and nucleating agents prior to extrusion.

An unnucleated sample (Blank), an organophosphate metal salt, bis(3,4-dimethyl benzylidene) sorbitol (3,4-DMDBS) and 1,3,5-tris(2,2-dimethylpropanamido)benzene (DMPAB) were used to compare with the newly developed clarifying agent RiKACLEAR PC1.

A polypropylene random copolymer of MFR 13g/10min and ethylene content of 3.9wt% was used for the concentration study. For the processing window study, a random copolymer of MFR 8 g/10min was used.

The polypropylene homopolymer base used in the CRG evaluation of PC1 was of MFR of 12g/10min.

PROCESSING

All samples were mixed with a specified amount of nucleating agent using a Thermo Prism Pilot 5 high speed mixer with a rotating blade, followed by extrusion with a Thermo Prism twin-screw extruder (L/D=28) and pelletization. In these evaluations the extrusion temperature was held at 250°C, unless specified. Similarly, the injection moulding was performed at a melt temperature of 230°C (unless specified) and a mould temperature of 40°C.

MEASUREMENTS

The crystallization temperature of polypropylene was determined by using a Mettler Toledo DSC 822 differential scanning calorimeter (DSC) under nitrogen. Samples of 3-5mg were heated up to 240°C, held for 3 minutes, and cooled at -10°C/min to 25°C.

Mechanical and optical tests for injection moulded parts were carried out according to the relevant ISO and ASTM (Haze measurements) methods.

CONCLUSIONS

RiKA International Limited presents an overview on acetal-sorbitol based clarifying agents and shows why their weaknesses are favouring the incorporation of new chemistry based products into polypropylene clarified grades. Data obtained with RiKACLEAR PC1, a new non acetal-sorbitol clarifier, clearly illustrates that this product is highly cost-effective, with optimum dosage in the range of 1200-1600ppm. Also, its wide processing window and high thermal stability eliminates any “plate-out” risks and allows its use in any manufacturing process. Moreover, comparative data show that its performance is not influenced by peroxide addition, showing superior optical and mechanical properties in both random and homopolymer, including controlled rheology grades.

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Key Words: Polypropylene, Clarifier, Non Acetal-Sorbitol, Dosage, Haze, Stiffness, Processing Window, Peroxide, CRG

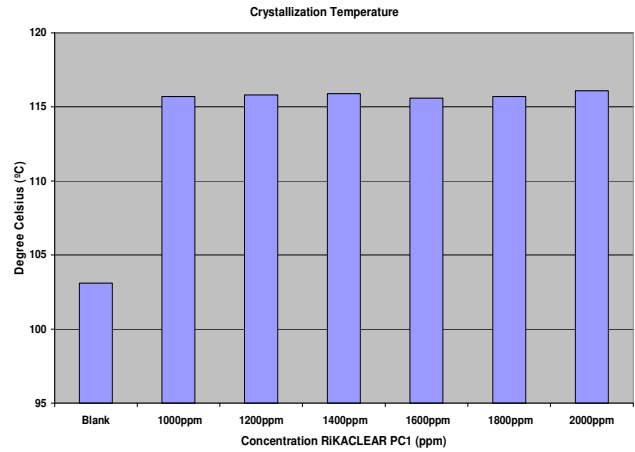
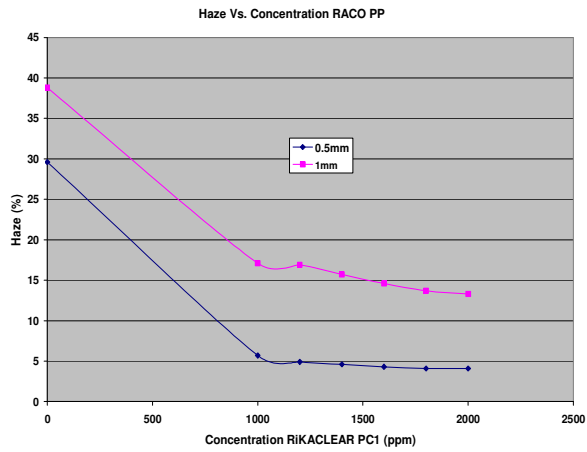


Figure 1. Haze vs. Concentration in 0.5mm and 1mm plaques

Figure 2. Crystallization temperature of PC1 in RACO

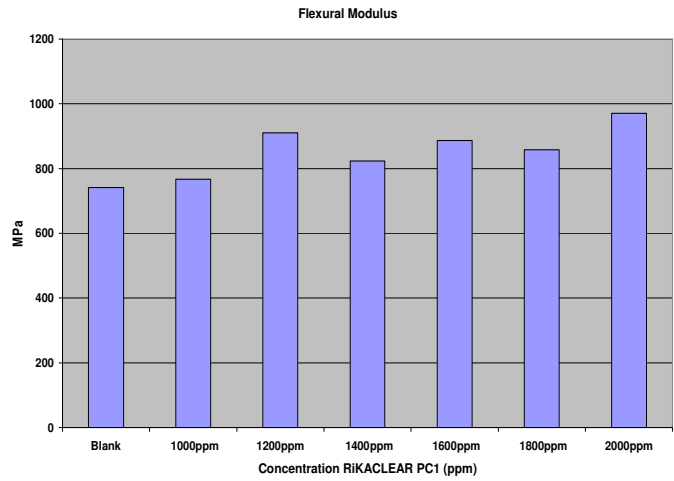
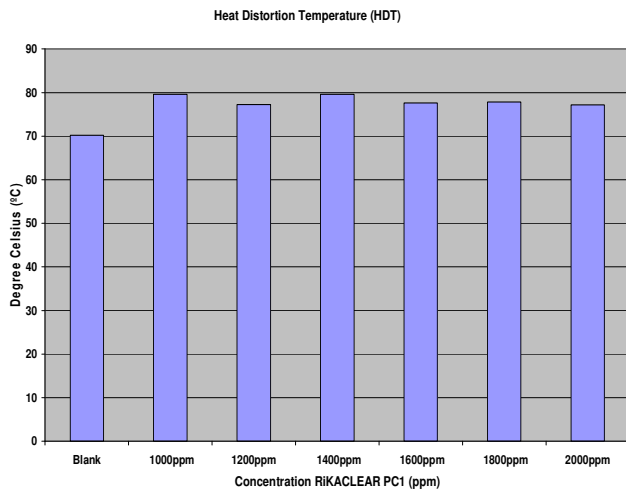


Figure 3. HDT values of PC1 in RACO PP

Figure 4. Flexural Modulus of PC1 in RACO PP

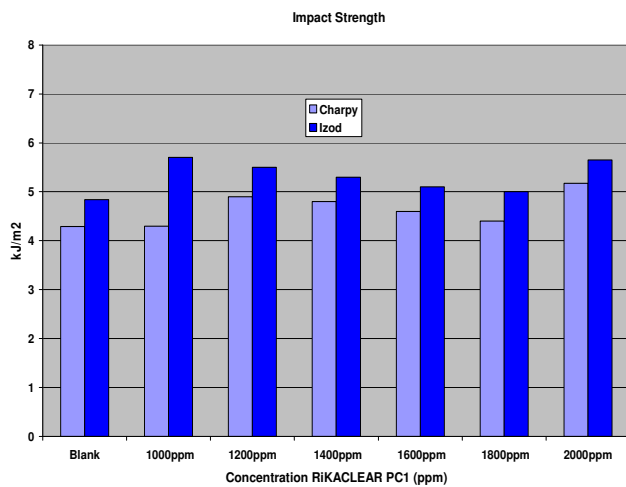


Figure 5. Impact strength of PC1 in RACO PP

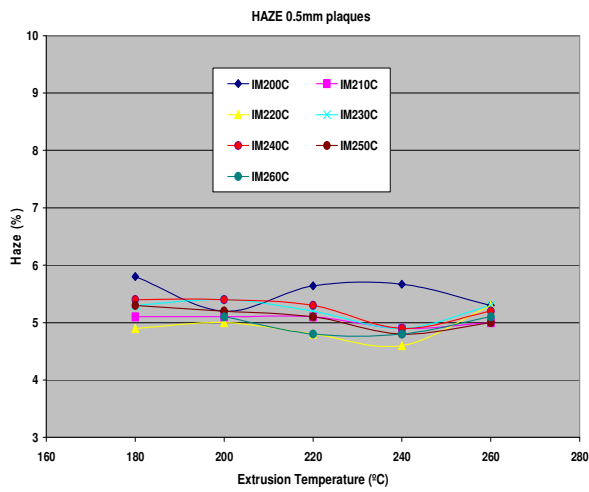


Figure 6. Haze values in 0.5mm (Processing Window)

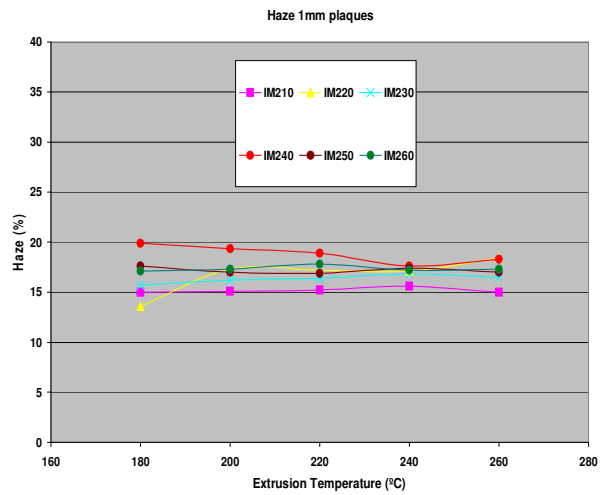


Figure 7. Haze values in 1mm (Processing Window)

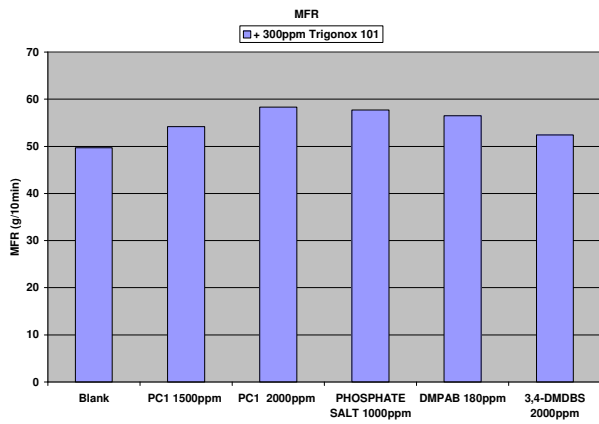


Figure 8. MFR when adding 300ppm of Trigonox 101

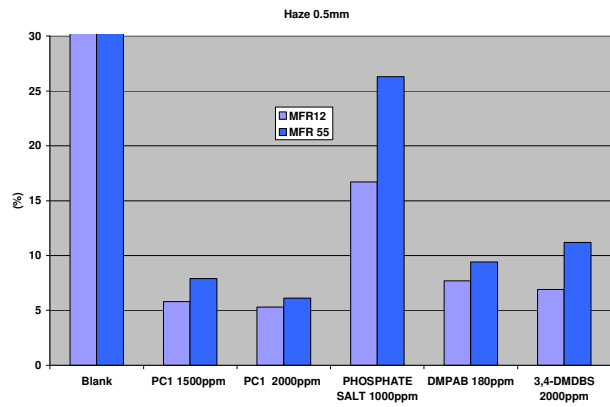


Figure 9. Haze value in 0.5mm plaques in HOMO+CRG

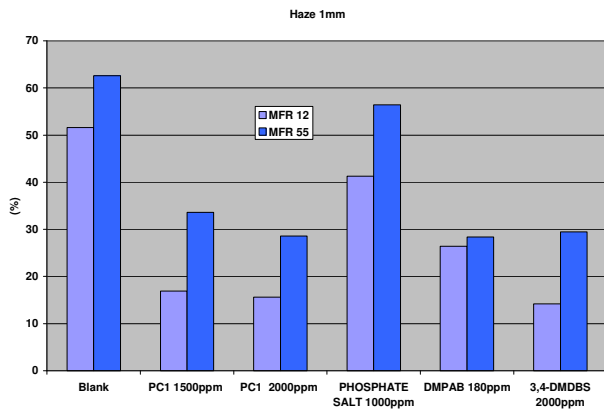


Figure 10. Haze value in 1mm plaques in HOMO+CRG

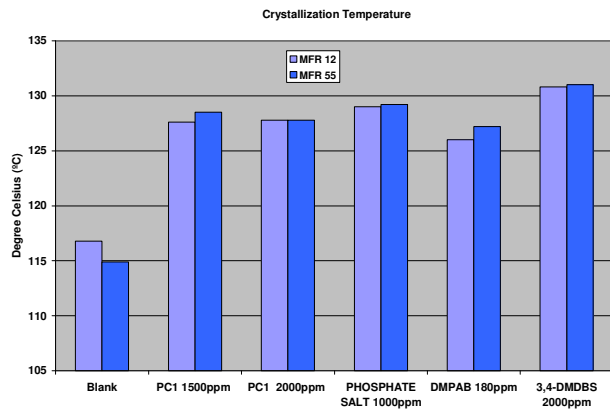


Figure 11. Crystallization temperature in HOMO+CRG

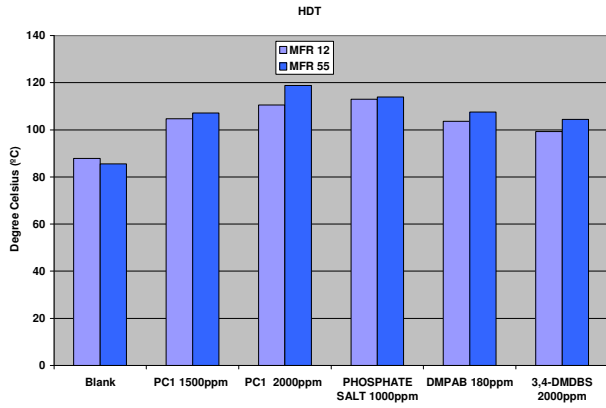


Figure 12. HDT values in HOMO+CRG

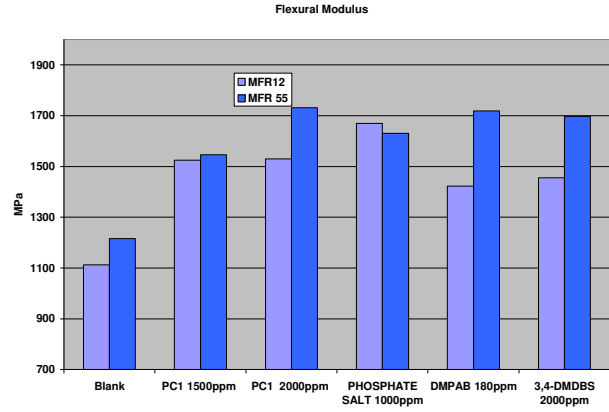


Figure 13. Flexural Modulus in HOMO+CRG

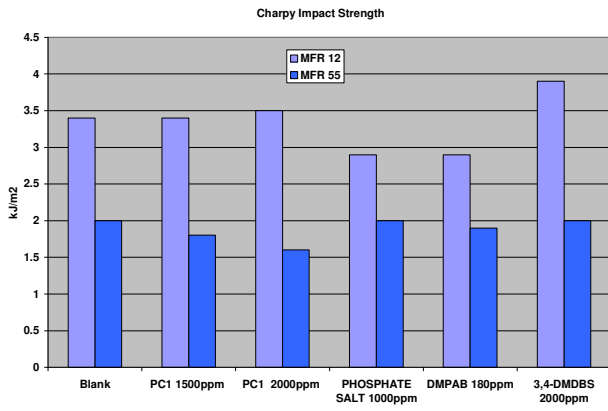


Figure 14. Charpy Impact Strength in HOMO+CRG

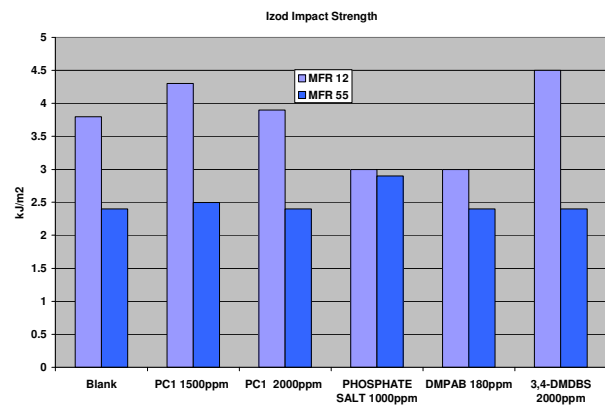


Figure 15. Izod Impact Strength in HOMO+CRG