



CLARIFIED POLYPROPYLENE – A NEW BENCHMARK

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ABSTRACT

RiKA International Limited, a subsidiary of New Japan Chemical Company Limited (NJC), presents a new clarifier for the polypropylene industry. For the first time, a non-acetal sorbitol product namely **RiKACLEAR PC1** has become the new benchmark in clarified polypropylene. Haze values in random copolymer are extremely low and the stiffness-impact balance is vastly improved at very low addition levels. Based on new technology, this new product has no taste and odour issues. This new chemical is also an extremely effective nucleator in non-clear applications. Data presented demonstrates that RiKACLEAR PC1 achieves high stiffness values in block polypropylene, as well as high impact strength at both ambient and zero degrees temperatures. Moreover, aging and multiple pass extrusion studies show that RiKACLEAR PC1 is the best and more stable long-term clarifier in the market.

RiKACLEAR PC1

RiKACLEAR PC1, a newly developed clarifying agent, is the first non-sorbitol based clarifier that meets all of the polypropylene industries' requirements: transparency, stiffness, impact strength, heat resistance and organoleptics. PC1 provides superior transparency compared with the current industry standard and higher stiffness is also achieved by using this clarifier without lowering impact strength and heat resistance. Therefore PC1 gives an exceptional balance between clarity and stiffness. In addition, the inclusion of PC1 in all polypropylene systems, including rheology grades, shows no signs of degradation and does not affect the organoleptics of the finished articles.

During development, RiKACLEAR PC1 was given the designation Perfect Chemical (PC) by the R&D staff at NJC, as it was their intention to design the perfect chemical as a clarifier/nucleator for polypropylene. The main goals of the development project were high clarity, high stiffness, high impact strength, high heat resistance and no taste and odour. As the inventors of acetal sorbitol chemistry, the R&D staff at NJC were only too aware that the mono-substituted molecule and indeed, the di-substituted molecule had a tendency to degrade under certain

conditions, which caused taste and odour problems especially in thin walled articles. It was therefore a cornerstone of the development project to identify a chemical compound that was not based on old technology.

RiKACLEAR PC1 AS A CLARIFIER IN POLYPROPYLENE RANDOM COPOLYMER


Polypropylene is a semi-crystalline material that as the molten polymer cools down, the polymer chains begin to form crystals at foreign particles in the melt [1]. In random copolymer, due to the presence of ethylene monomer in the polypropylene chain as a defect in the chain regularity, the melting temperature of the resin is a relatively low value of 145°C. 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.

As can be clearly seen from Figure 1 PC1 significantly reduced the haze levels in 0.5mm plaques at 1500 and 2000ppm, compared to 3,4-DMDBS and a commercial phosphate salt. This improvement in haze using lower levels of PC1 will enable cost-effective improvements in the design of clarified polypropylene. In the case of 1mm plaques, haze levels for PC1 were slightly higher than that of 3,4-DMDBS.

An important feature of PC1 along with its clarifying properties is the higher stiffness that confers to the material. Figure 2 is an excellent example of what can be achieved using PC1 in random copolymer. All addition levels showed a significant improvement compared to 3,4-DMDBS, and 1500 and 2000ppm exhibited a similar or better performance than that of the phosphate salt. Consequently, PC1 can improve not only the transparency, but also the stiffness of the material.

Furthermore, the high stiffness that PC1 evidenced was also counterbalanced with a high heat resistance (HDT) (Figure 3). All HDT values of PC1 were higher than that of 3,4-DMDBS and similar to the phosphate salt.





In addition, Figure 4 demonstrates that there was no loss in impact strength associated with the high stiffness and heat resistance conferred by PC1 to the material. All impact strength values for PC1, both Charpy and Izod, were superior to those of 3,4-DMDBS, with similar Izod values obtained for the phosphate salt containing material. Charpy values were, however, lower compared to that of the phosphate salt.

The crystallization of PP from the melt can be improved with the addition of foreign nuclei to the polymer melt. In Figure 5 PC1 reflected a high increase in the T_c which proved that, in addition to providing a reduction in the moulding cycle time, PC1 is an excellent clarifier with superior mechanical properties and with no taste and odour issues.

RiKACLEAR PC1 AS A CLARIFIER IN POLYPROPYLENE HOMOPOLYMER

Homopolymer polypropylene is the most widely used polypropylene material in industry. Its high stereoregularity leads to high levels of crystallinity of around 60-70%, with a melting point of about 160°C. As a result of this high crystallinity, homopolymer PP shows excellent rigidity at room temperature and high heat resistance [2].

To assess the effect on the clarity of PC1 in homopolymer PP, plaques of 0.5 and 1mm thickness were injection moulded and their haze measured (Figure 6). All PC1 addition levels reduced the haze in the material compared to that of 3,4-DMDBS and the phosphate salt in 0.5mm plaques. Moreover, at half the concentration of 3,4-DMDBS, PC1 at 1000ppm showed a similar haze improvement. In the case of 1mm plaques, PC1 at 2000ppm exhibited a similar performance to that of 3,4-DMDBS.

As mentioned before, one of the most important features of PC1 is the high stiffness associated with this excellent clarifier. In Figure 7 the stiffness of the injection moulded parts containing different levels of PC1 was evaluated. Substantial improvement in the stiffness of all PC1 concentrations was observed, when compared to the blank and 3,4-DMDBS, including a higher rigidity value for the PC1 concentration at half of the addition level of 3,4-DMDBS. However, the stiffness provided by the phosphate salt was slightly higher than that of PC1 at any given concentration.

These results confirm again that, PC1 perfectly balances transparency and stiffness compared to 3,4-DMDBS and the phosphate salt.

Another important characteristic associated with the high stiffness-clarity balance that PC1 offers is its superior heat resistance. The HDT performance of PC1 was reflected in

Figure 8. It is important to note that PC1 at 1000ppm achieved a similar HDT value to that of 3,4-DMDBS at 2000ppm. 1500 and 2000ppm of PC1 recorded higher values than 3,4-DMDBS, with 2000ppm of PC1 showing a similar performance to the phosphate salt.

For a successful clarifier like PC1 it is vital that the impact-stiffness balance is high. Figure 9 shows that the Charpy impact strength for PC1 at 1500 and 2000ppm was higher than that of the phosphate salt and slightly lower than the value obtained for 3,4-DMDBS. Moreover, at 1000ppm PC1 achieved a similar impact performance at half the concentration of the phosphate salt. In the case of the Izod impact strength, low concentration levels of PC1 exhibited higher impact values than that of the phosphate salt and also similar values to that of 3,4-DMDBS. At 2000ppm, the Izod impact was similar to that of the phosphate salt and slightly lower than 3,4-DMDBS.

These results demonstrate that PC1 is an excellent clarifier with a high impact-stiffness balance that can also achieve much improved heat resistance.


RiKACLEAR PC1 AS A NUCLEATOR IN POLYPROPYLENE BLOCK COPOLYMER

Impact copolymers are physical mixtures of homopolymer and random copolymer, with the overall mixture having ethylene contents of 6-15%. The random part of the mixture, due to its high ethylene content (45-65%), is termed the rubber phase. As the rubber content of the mixture is increased, so too is the impact resistance, but at the expense of the reduction of the stiffness of the material [3]. The impact strength in this type of copolymers is not only a function of the rubber content, but also of its size, shape and distribution. Therefore, it is of the utmost importance to obtain a material with much improved stiffness in order to achieve an impact-stiffness balance.

Two of the most important industries where impact copolymers are widely used are the automotive and packing applications industries, where excellent impact strength, especially at temperatures below freezing point, is a much sought property.

Figure 10 shows that PC1 significantly increased the stiffness of the material compared to the blank, especially at concentrations up to 1500ppm. In addition, PC1 containing material achieved a similar or even superior performance to that containing the phosphate salt. Associated with this excellent stiffness, PC1 also exhibited superior heat resistance in block copolymer when compared to the blank and the phosphate salt (Figure 11).

As pointed out before, impact copolymers are characterised by high impact strength as can be observed in Figure 12. Both Charpy and Izod impact strength values were high and hardly any improvement was observed upon the



addition of PC1 or the phosphate salt at any concentration level.

Nevertheless, the increase in impact strength provided by PC1 when the testing was carried out at 0°C was quite remarkable. It is important to note that all PC1 concentrations highly improved the impact strength compared to the blank and to the phosphate salt, with PC1 at 1500ppm achieving a notable 25% increase (Figure 13).

Therefore, the experiments showed that in addition to being an excellent clarifier with superior stiffness in clear applications, RiKACLEAR PC1 can provide excellent stiffness in non-clear applications and superior impact strength even at zero degrees temperatures.

RiKACLEAR PC1 AS A LONG-TERM CLARIFIER COMPARED TO 3,4-DMDBS

A well-known feature of the sorbitol based clarifiers is that owing to their sugar-based chemical structure, they appear to suffer from thermal decomposition, leading to a phenomenon called “plate-out”, where a white residue appears in the surface of the mould during the injection process. As a result, running times are shortened and costly delays in production, due to the cleaning process, arise.

To assess the compatibility of PC1 with the resin and its long-term stability, the haze and gloss of samples containing PC1 in a low ethylene content PP resin were compared against 3,4-DMDBS. The haze and gloss of 0.5 and 1mm thickness plaques were measured over a two months period.

Figure 14 shows clearly how the haze in 0.5mm plaques increased considerably overtime for 3,4-DMDBS compared with PC1 at any given concentration. Similarly, the gloss also decreased significantly overtime in the case of 3,4-DMDBS, compared with PC1 (Figure 15). This fact confirms, on one hand, the long-term stability of PC1 as clarifier and on the other hand, its superior long-term performance when compared with 3,4-DMDBS.

A similar trend was observed when the haze and gloss were measured in 1.0mm plaques thickness (Figures 16 and 17). It was especially interesting the dramatic loss of gloss of around 20% (Figure 17) of 3,4-DMDBS after just one week compared to PC1.

This feature, in addition to the excellent balance between transparency and mechanical properties such as stiffness, heat resistance and impact strength compared to the common commercial nucleating agents and clarifiers make PC1 the new benchmark for the polypropylene industry.

STABILITY OF RiKACLEAR PC1 DURING MULTIPLE PASS EXTRUSION

Another way to assess the stability of PC1 is by regrinding it in a multiple pass extrusion process and measuring the haze of the finished article afterwards.

Figure 18 shows the haze values obtained during a 5 pass extrusion process of a low ethylene content random copolymer at 250°C. It can be clearly identified that 3,4-DMDBS showed the highest deterioration of optical properties throughout the whole process compared to PC1 and the phosphate salt. In contrast, PC1 at both concentration levels of 1500 and 2000ppm exhibited consistently lower haze values with increasing number of passes for 1mm plaques, which confirms once more, the stability and robustness of this non-sorbitol product.

CONCLUSIONS

RiKA International Limited presents its innovative product to the polypropylene industry: **RiKACLEAR PC1**, the new benchmark in clarified polypropylene; a non-acetal sorbitol product with low haze values and a high stiffness-impact balance with no taste and odour issues. In addition, owing to high stiffness and impact strength achieved at room and zero degrees temperatures, it is considered a highly effective nucleator in non-clear applications. Moreover, aging and multiple pass studies carried out showed that **RiKACLEAR PC1** is the best and more robust long-term clarifier in the market.

EXPERIMENTAL

MATERIALS

All formulations contained a standard base stabilization system.


A polypropylene random copolymer of MFR 10g/10min and ethylene content of 3.9wt% was used. In the aging study, a low ethylene content random copolymer with a MFR of 12g/10min was used.

The polypropylene homopolymer used in the evaluation of PC1 was of MFR of 12g/10min. A polypropylene block copolymer of MFR 18g/10min and ethylene content of 11wt% was used.

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. Similarly, the injection moulding was performed at a melt temperature of 230°C and a mould temperature of 20°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.

The aging study was carried out on the 0.5mm and 1.0mm injection moulded plaques at 80°C.

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

ACKNOWLEDGMENTS

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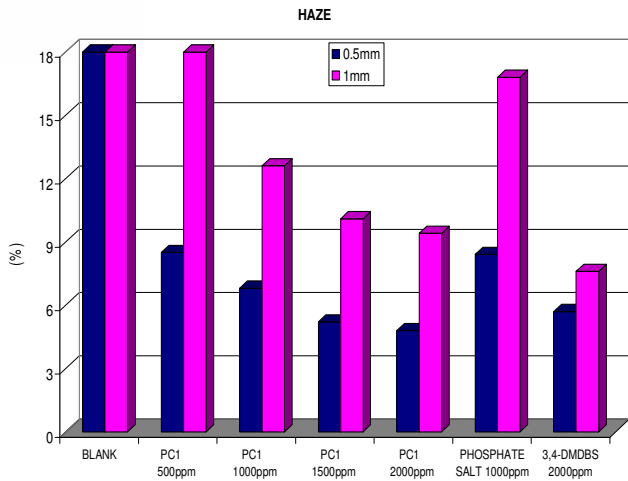


Figure 1. Haze measurements in Random Copolymer

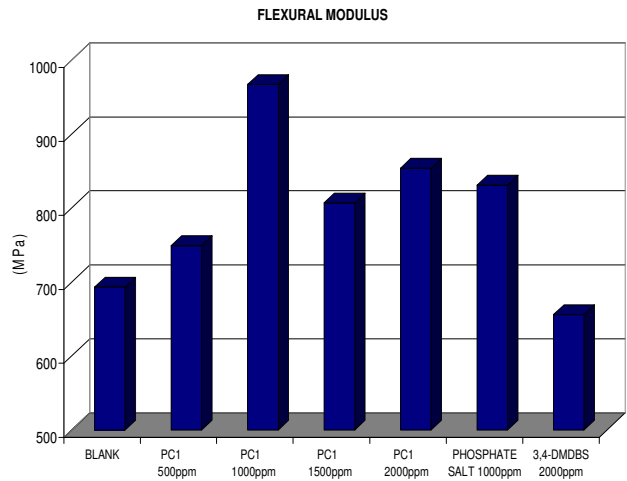


Figure 2. Flexural modulus in Random Copolymer

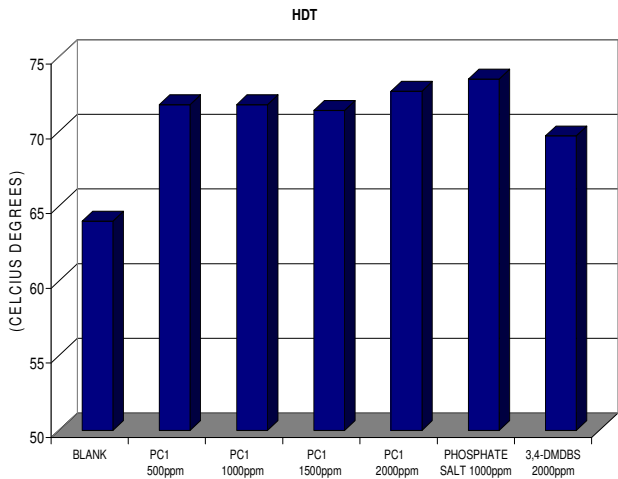


Figure 3. Heat Distortion Temperature in RACO

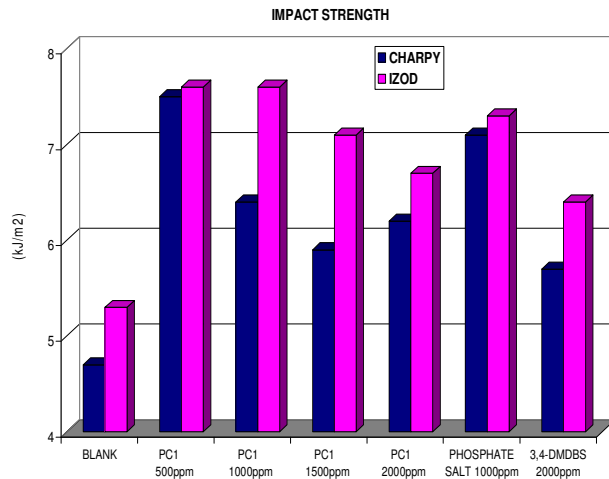


Figure 4. Impact strength at RT in RACO -notched

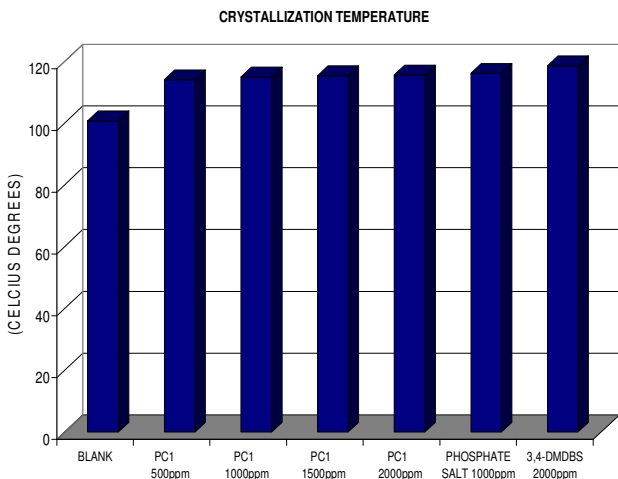


Figure 5. Crystallization temperature in RACO

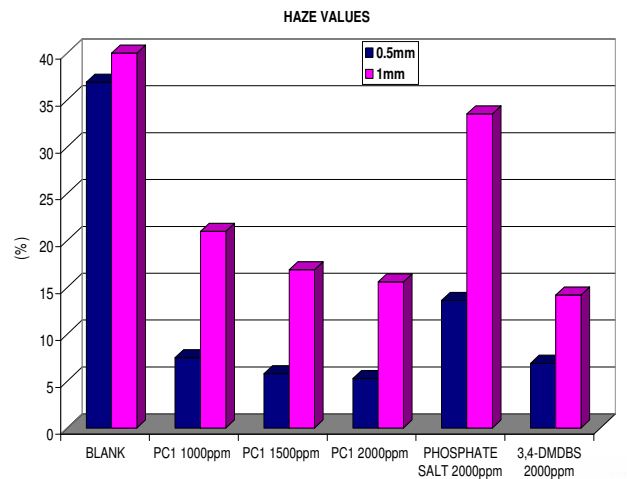


Figure 6. Haze measurements in Homopolymer PP



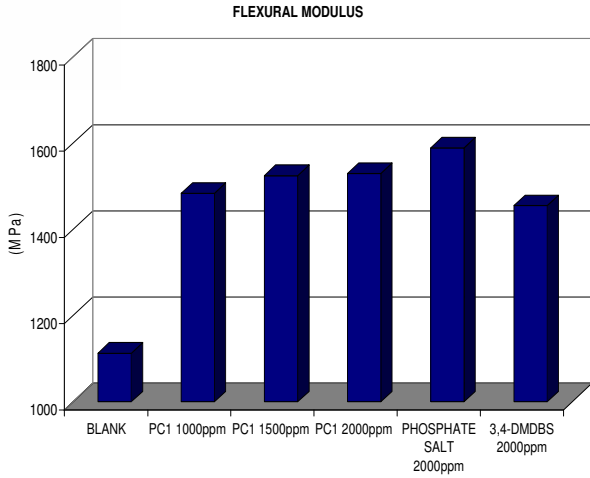


Figure 7. Flexural modulus in Homopolymer PP

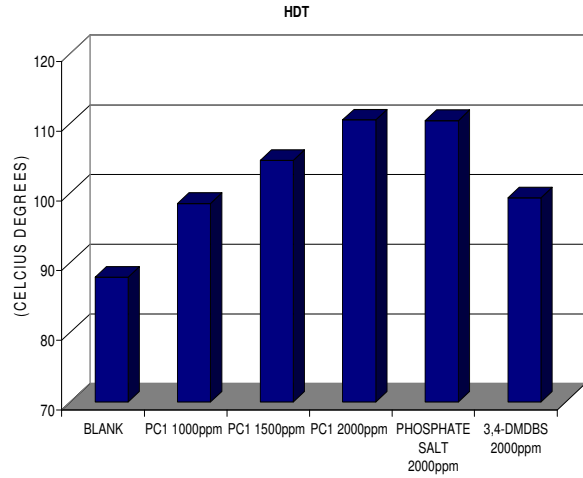


Figure 8. HDT in Homopolymer PP

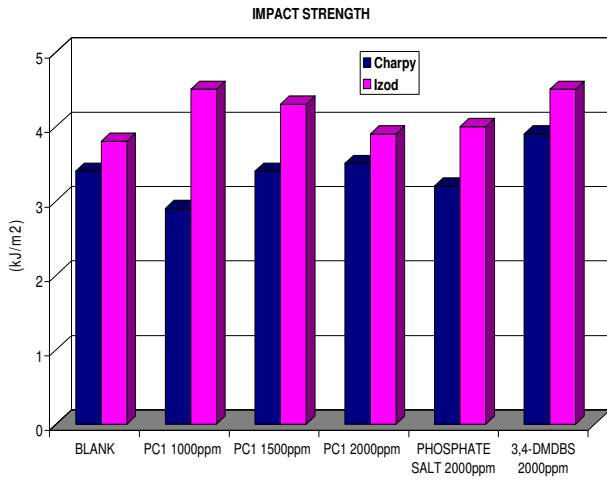


Figure 9. Impact strength at RT in Homo PP -notched

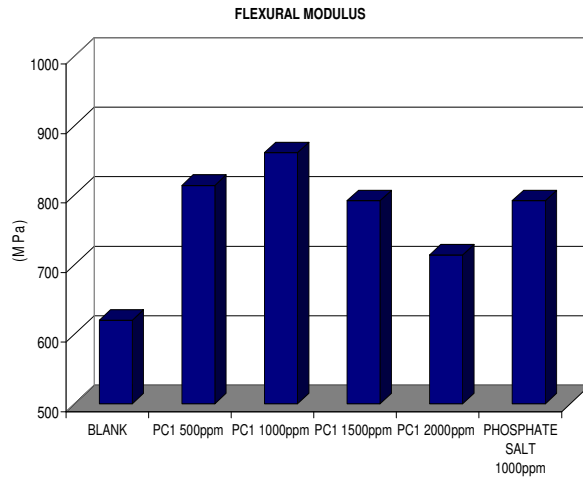


Figure 10. Flexural modulus in Block Copolymer

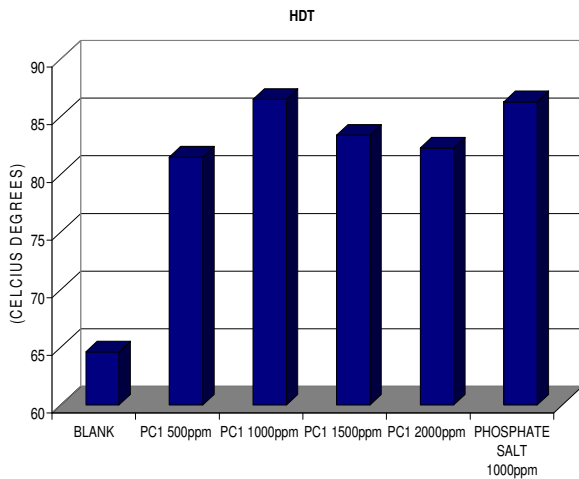


Figure 11. HDT in Block Copolymer

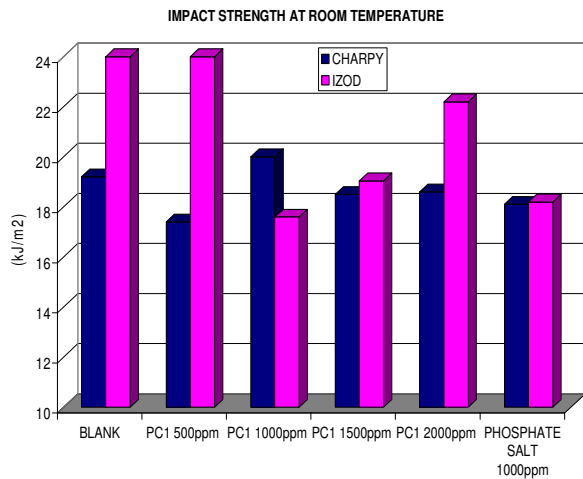


Figure 12. Impact strength at RT in Block PP -notched

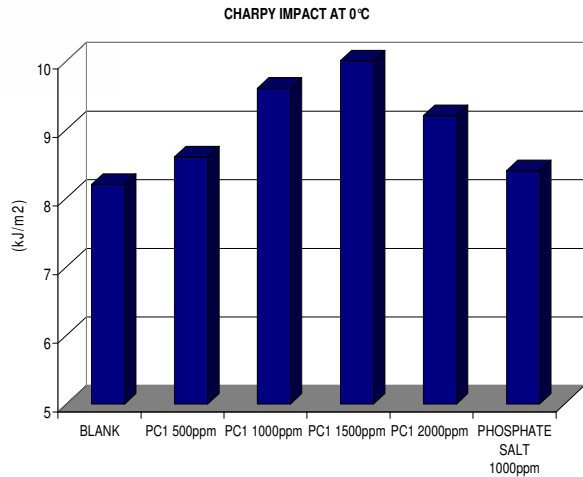


Figure 13. Charpy impact str. at 0°C in Block PP -notched

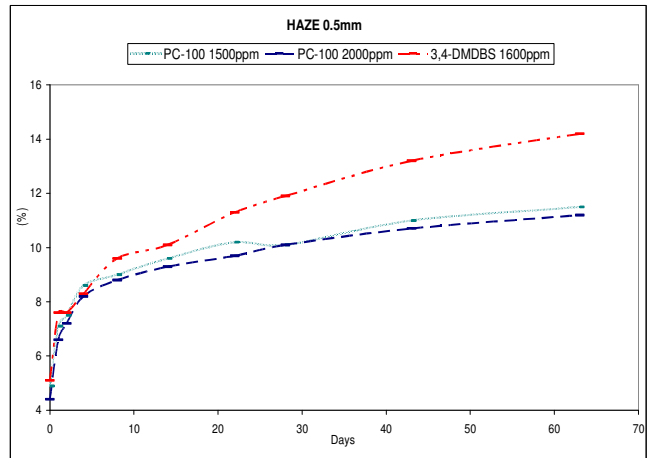


Figure 14. Long-term Haze 0.5mm plaques RACO

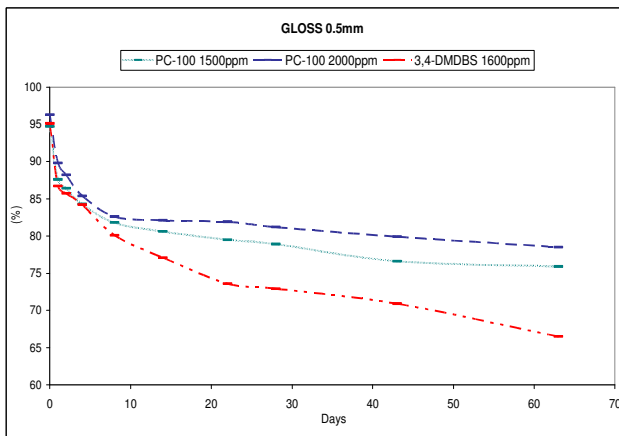


Figure 15. Long-term Gloss 0.5mm plaques RACO

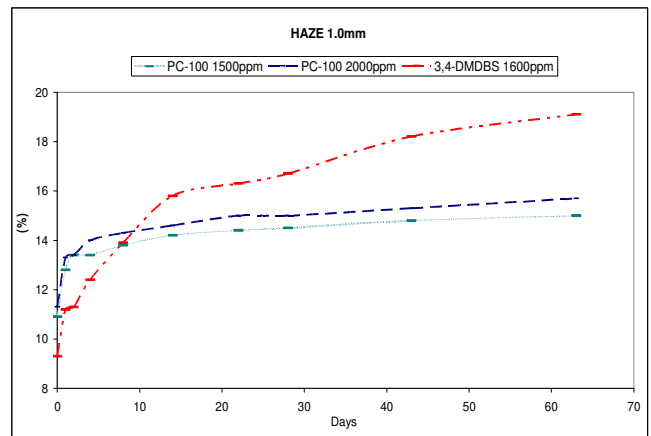


Figure 16. Long-term Haze 1.0mm plaques RACO

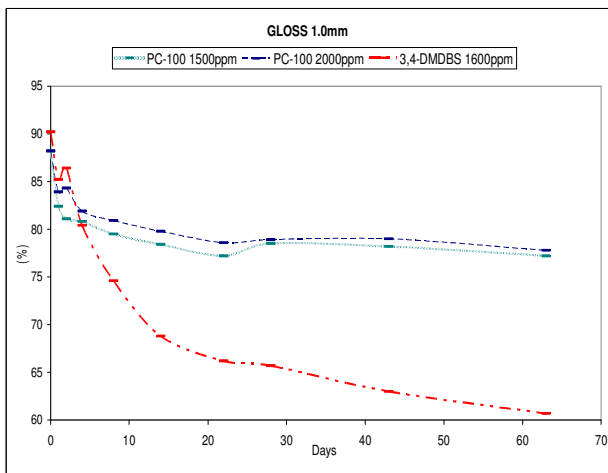


Figure 17. Long-term Gloss 1mm plaques RACO

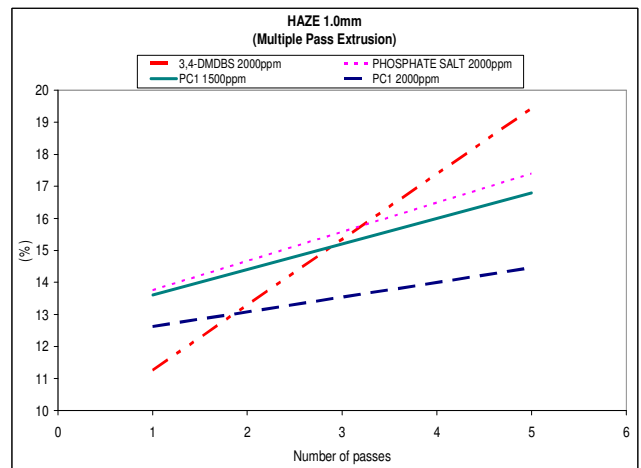


Figure 18. Trend line of haze measurements in MPE.

