Pyrolysis Carbon Fillers in Rubber

Given the recent growth of the pyrolysis derived carbon sector, ARTIS has focussed efforts on developing the tools necessary to fully understand and evaluate this new class of rubber filler. Market perceptions of such fillers are often negative; based on a lack of understanding and previous dealings with poor quality recyclate that do not represent some of the more refined products currently on offer today. To demonstrate the credentials of pyrolysis derived carbon black (often referred to as pCB), ARTIS recently conducted a global crosscheck programme, offering an independent assessment of their composition and in-rubber performance in relation to conventional carbon blacks. The key findings of this programme are outlined below.

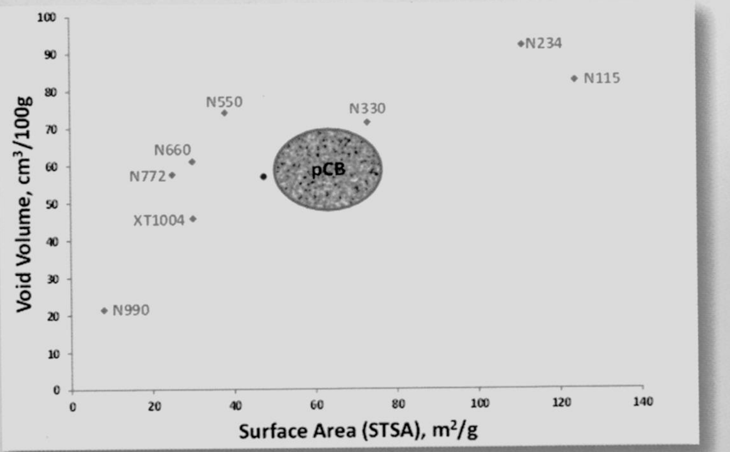

Figure 1: Colloidal map showing structure versus surface area.

Colloidal Properties: Structure levels and surface area are two key indicators of the reinforcing potential of a filler. Figure 1 shows that whole tyre derived pCB falls in the colloidal space between N550→N330 carbon blacks (carcass and tread grades). This may not be surprising given that a whole tyre feedstock will contain a blend of carcass and tread grade carbon blacks. Traditional carbon blacks of such colloidal properties (N500 to N300 series) find usage in a wide range of applications, indicating the potential commercial viability of pCB. However, using these typical colloidal properties as an indicator of performance may prove misleading if pCB is considered as a conventional carbon black.

Figure 1: Colloidal map showing structure versus surface area.

Cleanliness: Although colloidal properties were broadly similar, the pCB samples covered a wide range in transmission values (2 to 99%), highlighting significant variances in cleanliness. A number of the pCB samples had improved transmission values compared to the low surface area furnace carbon blacks; typically, low surface area furnace carbon blacks have relatively low transmission values due to their limited heat history during production.

Composition: fillers generated from pyrolysis processes are known to contain the original carbon black, carbonaceous deposits and inorganic rubber compounding ingredients. The pCB samples studied had ash contents ranging from 14 to 38wt%, the vast majority of which was accounted for by silica filler and zinc oxide. These variances in ash content are a reflection of the feedstock used at each location.

Surface Activity: Interrogation of TGA (thermogravimetric analysis) data highlighted all pCB samples to have significantly different surface activity compared to conventional carbon blacks, with earlier onset of oxidation associated with the presence of amorphous carbonaceous residues on the pCB surfaces. Such residues are formed by condensation of polymer decomposition products during the pyrolysis process. The reduced surface activity was later verified via DMA (dynamic mechanical analysis) testing.

Dispersion: Following compounding within a generic SBR formulation (containing 60phr carbon filler) the dispersion level achieved with each material was assessed. It is clear that some of the more refined pCB samples had dispersion levels approaching those of the conventional carbon blacks, Figure 2. Some of the pCB samples evaluated had very poor dispersion, having a negative impact on the physical properties and appearance of cured specimens; process optimisations are deemed essential in these cases.

In-Rubber Properties: Based on the findings of this study, current pCB materials can be considered as semi-reinforcing fillers and could find use in applications currently occupied by N600 to N700 series carbon blacks, see Figure 3. This is in contradiction to the performance predicted from the colloidal measurements, which suggest performance should be in the region of N500-N300 series carbon backs. The results clearly indicate that care should be taken when considering the colloidal properties of pCB and simply regarding them as a drop-in replacement for carbon blacks of similar colloidal properties is not appropriate. In-rubber properties were also demonstrated to be insensitive to the ash content of the pCB samples, negating concerns over slight variances in feedstock having an significant impact on performance.

Challenges: The data generated suggests that both surface area and structure levels are being overestimated by conventional techniques. It is suggested that the fusing of aggregates by the deposition of carbonaceous residues during the pyrolysis process leads to internal porosity that is accessible by the gaseous media utilised to determine both surface area and void volume. Such internal porosity is not accessible to the rubber matrix, leading to the apparent over-estimation of the colloidal properties. The outcome of this is that new testing regimes are necessary to characterise and control the properties of these pCB fillers. The poor quality of some of the pCB materials currently on the market highlights the urgent need for classification of pCB fillers. This will allow differentiation between the poor quality and refined products, offering potential customer's reassurances and the ability to make informed choices regarding filler selection.

Figure 2: Refined pCB performance reference N772.

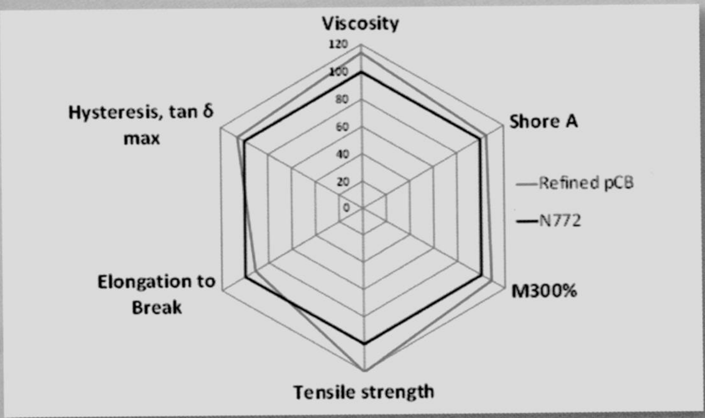

Figure 3: Refined pCB performance reference N772.

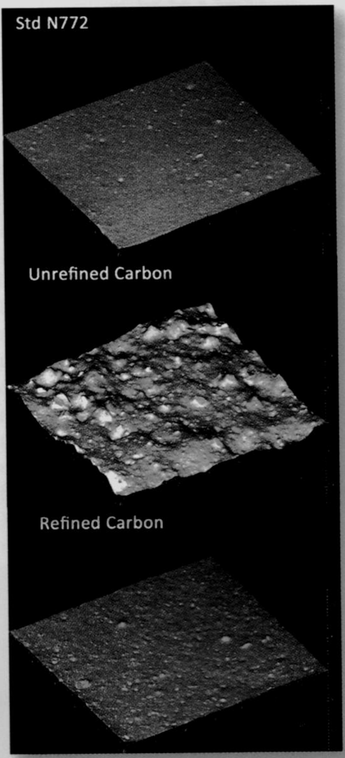

Figure 2: Surface roughness maps highlighting the dispersability of pCB.

In conclusion, pyrolysis of end of life tyres can generate valuable carbon based fillers, if the processes involved have been properly optimised. Although it has been demonstrated that refined pCB has in-rubber performance akin to N772 or N660 carbon blacks, classifying them as such should be strongly opposed given their significantly different surface activity and composition. Perhaps the biggest challenge facing pCB producers is the relatively low volumes of the material being generated, hindering potential validations in high volume/ lower cost rubber applications.