Deutsche Kautschuk-Tagung 2006

3. bis 6. Juli 2006, Nürnberg

German Rubber Conference 2006

July 3-6, 2006, Nuremberg

Kurzfassungen
Summaries

Niedrigere Material- und Verarbeitungskosten durch Einsatz von CBpES, einem neuen verstärkenden schwarzen Füllstoff
Lower Material and Handling Costs with New CBpES Black Reinforcing Filler

J. H. Fader (Sp), CBp Carbon Industries Inc., Bratislava (SK); J. Baaij, Elastomer Research Testing B.V., Deventer (NL); W. K. Dierkes, University of Twente, Enschede (NL); A. Moorefield, Cooper-Standard (USA)

Abstract

Testing of a new reinforcing black filler (**CbpES**) manufactured on production equipment from End-Of-Life tyres in Europe is presented. The results in SBR and EPDM prove the ability for meeting European mandates for recycled content.

Attempts to commercialise pyrolysis of scrap rubber and other carbonaceous materials such as plastics and automotive shredder residue have not been successful because the quality of the heterogeneous pyro-char was not commercially competitive. Ongoing developments integrating state-of-the-art thermal and mineral processing technologies have consistently produced an upgraded pyrolysed carbon black (**CBp**) that has competitive reinforcing properties to virgin carbon black and for blending in various rubber compounds.

The North American market demand for an upgraded pyro-char with reinforcing characteristics similar to N-700 commercial carbon blacks for industrial rubber goods (excluding tyres) is at least 50,000 tons per year when discounted by 20 %. (American Chemical Society paper 114). Similar market potential is expected within the EU.

Also presented is the ability to produce another grade of black reinforcing filler (**CBp-18**) as representative of the ability to economically recycle automotive shredder residue (ASR) for reuse in rubber and asphalt or bitumen modification. This paper will present available technology to comply with the EU 2006 mandate for End-Of-Life Vehicle recycling.

Introduction

As early as 1973 a major research study was made by the Firestone Tire Company for the U.S. Bureau of Mines, „Destructive Distillation (pyrolysis) of Scrap Tires“[6]. This project showed that scrap tires could provide a recoverable source of hydrocarbons (gas and oil) for fuel or chemical feedstocks and a blended carbon rich char which could act as a reinforcing filler to substitute for some carbon blacks when reduced to very small particles. Figure 1 shows how the pyrolyzed product yields were affected with changes in temperatures.

TEMP C	GAS%	OIL%	CHAR%
389	6	42	52
600	10	50	40
700	15	47	38
800	31	40	29

Fig. 1: Pyrolysis Temperature and Product Yields

Ever since, pyrolysis has been considered as a potential for recycling scrap tires. A 1983 study for the U.S. Department of Energy identified 31 tire pyrolysis plants throughout the world that were in some stage of concept or operation. (Dodds et al [8]). Many of these focused on the oil yield as the principal economic factor stimulated by the escalating crude oil prices. When this „oil crisis“ abated all of these projects eventually were discontinued.

However, there were several processes in this early report that also considered upgrading the pyro-char into a black reinforcing filler with some carbon black properties for added project value. Most notable were the 1975 Goodyear/Tosco and the 1977 Intenco pyrolysis and 1980 Firestone ventures. All of these integrated pyro-char post-treatment in their plants and established markets for the by-products. If these early pyrolysis operations had the benefits of the present environmental and market situations their economic conditions and factors would definitely be more favorable.

More recent research by Christian Roy at the University of Laval showed that the pyro-carbon properties can be improved by a vacuum pyrolysis technology that helped to clean the carbon particle from heavy hydrocarbon coatings.

See Figure 2 below.

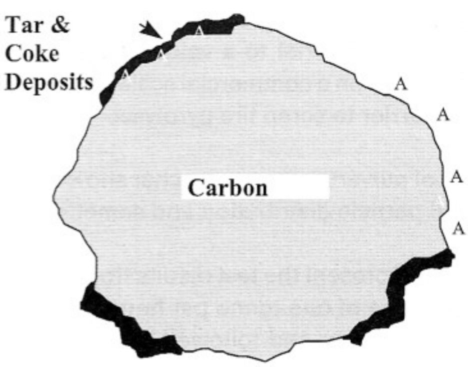

Fig. 2: Pyro-carbon particle surface coating

Other projects developed with ABB and Metso modern mineral processing technologies were applied to decrease and classify the grit particle sizes and agglomerates. See Figure 3.

PILOT PLANT PYRO-CHAR ANALYSIS

Ultimate Analysis	Passenger	Off-Road
Carbon (%)	81.5	86.6
Hydrogen (%)	0.1	0.6
Nitrogen (%)	0.2	0.3
Sulfur (%)	2.8	3.0
Mineral /Ash(%)	14.9	8.1
Iodine Number	130	108
DBP	91	103

Fig. 3: Source Metso (Carbon Black World 2002)

In a co-operative test with USCAR Vehicle Recycling Partnership extensive tests were made by Cooper-Standard to evaluate the CBp material in actual rubber compound formulations. See Figure 4.

Project: Cooper-Standard Evaluation of CBp Pyrolyzed Carbon Black in an EPDM Body Seal Compound

	Control	CBp	CBp
4'ML @ 100°C	**51**	**46**	**37**
Scorch @ 138°C	**3.5**	**4.2**	**5.3**
Cost (based on Control Cost)			
	1.00	**0.997**	**0.99**
Recyclate	**0**	**45**	**95**
(replacing equal parts of N650)			
Original Properties			
Duro	**65**	**63**	**56**
Tensile	**8.8**	**7.7**	**7.3**
Tensile Loss (%)	**0.0**	**13**	**17**
Elongation	**357**	**366**	**420**
Elong Increase (%)	**0.0**	**3**	**18**
100% Modulus	**3.6**	**2.6**	**2.1**
Modulus Loss (%)	**0.0**	**28**	**42**
Tear Die C	**28**	**28**	**29**
Max Cure Rate			
(MDR slope)	**8.0**	**6.9**	**5.7**

Fig. 4: Source ACS Paper 114

However, the ability to upgrade the pyro-char from a non-marketable raw material to a value-added carbon black property product on a commercial scale has been the main economic barrier to scrap tire pyrolysis.

Early tests of pulverized raw pyro-char show always showed bimodal particle distribution and sometimes trimodal.

This paper will present the test results from a combination of repeated runs of one tonne per hour production pyrolysis of scrap rubber and followed by 2 tonnes per hour pyro-carbon CBp proprietary upgrading.

Pyrolysis and CBp Carbon Upgrading Post Treatment

Pyrolysis tests were conducted at the Csongrad, Hungary pyrolysis plant site using CBp Carbon Industries proprietary processing methodology. The heterogeneous pyro-carbon particles surface areas were practically stripped of the degrading hydrocarbon and the hard agglomerates separated from the soft cluster agglomerates. This proprietary technology creates a new black reinforcing filler, pyrolysed carbon black (CBp) that can be substituted for conventional carbon blacks (CBc) as functional fillers.

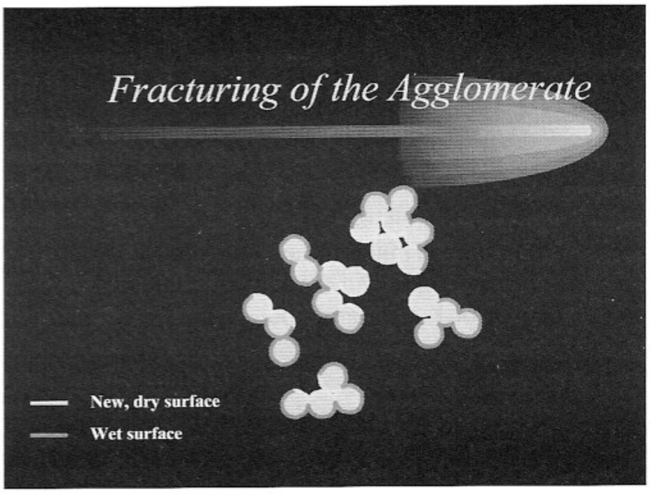

Fig. 5: Increasing dry surface areas

Fillers are, in general, solid substances or agglomerates that are imbedded or dispersed in polymers to reduce costs or improve performance. Distinguishes can be made between non-functional fillers which are mainly used to reduce costs and functional fillers that improve or generate new properties in the polymer composites and intermediate grades. Large particles, or agglomerates of particles serve as stress concentrators and can reduce the mechanical properties. The coarse particles in the particles sizes mix, has a considerable influence on the properties. See Figure 5.

Carbon black is the predominant functional filler used in commercial rubber parts manufacturing, including tyres and industrial rubber goods, such as belts, hoses, mats, etc..

A process was developed to „package" the CBpES fluffy black into an unusually high loaded masterbatch of EPDM and SBR polymer unvulcanized sheets. See Figure 6. This pre-dispersion allows for a clean and accurate method for delivery, handling and blending with existing rubber formulations. The tyre or rubber manufacturer receives the CBp black masterbatch using the same facilities as for receiving bales of rubber without carbon black with the advantages:

1. Mixing time saved because CBp is already pre-dispersed before using Banbury or roller mills
2. Saved electric power for mixing
3. Allows Banbury single stage mixing
4. Clean operations at customer's plant by eliminating or reducing the loss of airbourne carbon black dusting
5. Easy stocking of raw materials and clean storing
6. Easy quality control on incoming CBp products at customer's plant

	EPDM		SBR	
Compounds	05084-01 8	05084-028	05084-038	05084-048
	CBpES	N765	CBpES	N765
Keltan 5531A	200	200		
SBR 1502			100	100
CBpES	**300**		**250**	
SRF- N765		300		250
Sunthene *4240*			100	100
Sunpar2280	40	40		
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
S'cureTBB5-grs-2mm	1	1	1	1
Sulphur	1.8	1.8	1.8	1.8
Total phr lab	548.8	548.8	458.8	458.8

Tensile strength [MPa)	**8.6**	7.8	**3.7**	3.4
Elongation [%)	**375**	145	**275**	45
Mod 25% [MPa)	**1.2**	2.2	**1.6**	2.6
Mod 50% [MPa)	**1.9**	4.1	**2.4**	3.6
Mod 100% [MPa)	**3.3**	5.1	**3.2**	
Mod 200% [MPa)	**5.7**		**3.6**	
Mod 300% [MPa)	**7.6**			
Tear Strength (kN/m)	**30.5**	18.4	**24.2**	15.2
Compression Set (%)	**32**	31	**58**	61

Fig. 6: Source: Elastomer Research Testing B.V.

Summary

There are ongoing tests to demonstrate the blending compatibility for using a new reinforcing black CBp as a functional filler or extender. This CBp product can be produced in several grades between a functional reinforcing filler or as a cost saving extender filler.

By using end-of-life tyres and/or automotive shredder residue (ASR) as the primary pyrolysis feedstock the raw material costs are not subject to fluctuations of the crude oil market. Instead the costs of imported oil are diverted by using the CBp alternative energy products.