Kinetics of Formation and Degradation of Elastomer Matrix with New Generation Non ASTM Carbon Black

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Abstract: *With the advent of new generation car with IC engine, hybrid engine and electric car, the elastomeric part in the automobiles demand a very stringent and varied service requirement. The specific duties which the new generation vehicles are demanding leads to a challenge for the present day polymer-filler interaction with normal ASTM black. The morphology of ASTM blacks seems too inadequate for many dynamic applications in extreme conditions. The present article is an attempt to create a series of black which originated from ASTM grade but the morphology is suitably modified to provide better extrusion rate with increased dimensional stability. These blacks also have higher activation energy for rubber-filler interaction with better degradation kinetics.*

Keywords: automotive elastomers, polymer-filler interaction, ASTM black morphology, dynamic application challenges, rubber degradation kinetics

1. Introduction

Carbon black world has moved a step forward towards being application specific with precise special characteristics. The morphology, physio chemical properties, cleanliness and processability in different fields of application has drawn the interest of compounders according to their requirement. New age reactors and upgraded technology for production of speciality carbon black grades is commercially viable now a day. Carbon black as well as different rubber speciality chemicals has given a new life to rubber researchers which was looking saturated in the field of tyres from long time.

Though their are different interesting research is going on the field of rubbers synthesis, processing and regeneration of new resource from rubber waste, impact of speciality rubber chemicals and carbon black on rubber properties (reinforcing effect) has not lost its popularity to the researchers. EPDM rubber being highly weather resistant used in different applications of automotive parts like weather-stripping, transmission belts, seals etc (2). Chung et al. (1) in their patent used carbon black of different morphology to bring gloss and good surface finish in extruded profiles of EPDM rubber using paraffinic oil and sulphur curing system. Carbon black with high structure and low surface area resulted high gloss in the compounds as desired. Z. H. Li, J. Zhang, S. J. Chen in their paper (3) concluded that reinforcement of carbon black on EPDM rubber composite takes place due to surface energy which makes physical reinforcement as well as the dispersion in the matrix brings conductivity to the network. Free sulphur present in the system takes part in the curing and has certain impact on the activation kinetics. Akrochem in their technical bulletin (4) has shown the impact of different speciality carbon black produced in comparison to ASTM grades in terms of non tyre carbon black compounding with EPDM rubber at high loading. In this work, with Himadri's new developed grades of carbon black (RG 223 and RG 225) processed with EPDM based sulphur curing system and studied the activation and degradation kinetics from the cure curve obtained from MDR (alpha technologies). The target was to meet customer demands with better dimensional stability, better screen life with better extrudability, less product defects, less retention of strain energy, comparable mechanical properties and better product life.

2. Materials & Experiments

Materials - EPDM rubber (Keltan 5470Q) was sourced from Arlanxeo Netherlands B.V., Paraffin oil (HP Elasto 215) from Hindusthan Petroleum. Zinc Oxide and Stearic acid flakes were sourced from Merck Specialities (P) Ltd and Oster Chemicals (P) Ltd. Sulphur, TMTD, MBTS were supplied by a distributor of NOCIL India Ltd. Sample of three different carbon black grades, N550, RG 223, RG 225 were produced in Himadri Speciality Chemical Limited and other two were commercially available rubber speciality carbon black grades originated from Europe and USA were procured from market.

Mixing - The ingredients were weighted to scale for mixing in two wing internal mixer (Bainite 1.6 L lab scale mixer) as per below formulation.

Ingredients	PHR
EPDM (Keltan 5470Q)	100
Carbon Black	130
Paraffin Oil	70
Zinc Oxide	5
Stearic Acid	1
MBTS	0.5
TMTD	1
Sulphur	1.5

Two stage mixing process was performed : Stage I (master) - 330 sec, 60 rpm and Stage II (final) - 200 Sec, 40 rpm in the internal mixer followed by mixing in two roll mill. EPDM rubber was added first in the mixer and after 30 sec. the chemicals were added. Carbon black 130 PHR was added in two stages (50 PHR with chemicals and 80 PHR with Oil) for better mixing. The mixing temperature was recorded ~ 150-160°C for the master and ~110 - 120°C for the final.

Maturation time of 16 hrs was given to the master batch before final mixing.

1) Curing - Curing characteristics was tested in moving die rheometer (MDR2000, alpha technologies following ASTM D5289 at different temperature (150°, 160° and 170°C) for understanding the kinetics of activation (5) (6) (7) and deactivation of cross linking of the vulcanizates by using the test results of Maximum Torque (MH), Minimum Torque (ML), Scorch Ts2, T90, cure rate etc. The optimum cure time (Tc90) was obtained for curing of these compounds in Hydraulic Press (Radha Mohan Engineering Works) at 160°C. Specimens for tensile test, compression set and De Mattia flex-fatigue testing was moulded. After curing the cured specimens were kept in room temperature for 16 hrs for conditioning.

2) Mechanical Properties testing - Tensile test was performed as per ASTM D412 standard, in Instron 3365 UTM using Blue Hill 2 software, at room temperature as well as after aging condition of upto 72 hrs at 125°C for understanding degradation kinetics using Multicell Aging Oven (Zwick Roell.).

3) Compression Set – Compression set was tested as per ASTM D 395 (test method B). 12.5 mm specimens were compressed with 9.5 mm spacer thickness and kept at 125°C for 70 Hrs. The specimens were then released and kept at room temperature for 30 mins and then the measurements were taken with micrometer (mitutoyo).

4) Rebound Resilience- Rebound reliance of the sample were tested in Dunlop Tripsometer (8) at 45° incident angle. Test Specimen of 8 mm square and 4 mm thick was put in the sample station. % Rebound was calculated as per ASTM D7121.

5) De Mattia Flexing – Flex-fatigue was tested in De-Mattia flexing apparatus as per ASTM D430. The initiation of crack and growth rate was observed with no of cycles of run at flexing frequency of 300 cpm.

3. Results

Study of MDR test results - Activation energy for vulcanization:

Table 1: Test Results of MDR - Curing Characteristics

Grade	Temp. (°C)	Delta Torque (MH-ML) (dNm)	Ts2 (min)	T50 (min)	T90 (min)
N 550	150	22.89	2.67	5.50	20.52
	160	24.77	1.79	3.80	12.48
	170	23.14	1.03	2.12	7.13
RG 225	150	23.51	3.09	6.20	22.61
	160	23.21	2.02	3.91	13.40
	170	22.91	1.16	2.26	7.27
RG 223	150	22.85	2.60	5.60	21.11
	160	23.26	1.78	3.62	12.78
	170	22.47	1.02	2.08	7.03
Comp. 1	150	24.33	2.63	5.37	22.04
	160	23.87	1.71	3.33	12.92
	170	23.64	1.01	2.00	7.21
Comp. 2	150	23.21	2.38	5.43	22.23
	160	23.87	1.54	3.47	12.92
	170	22.9	0.92	2.06	8.10

The activation energy (was calculated based on the activation part (T50) of the curing curve. Considering the reaction is a 1ˢᵗ order reaction, below equation was used to calculate the rate constant (K):

$$\ln K = 0.693/T50$$

Where, T50 is the time for 50% vulcanization.

The calculated rate constant was used for calculating activation energy of the reaction using Arrhenius equation as below:

$$K = A\, e^{\frac{Ea}{RT}}$$
$$\ln K = \ln A + Ea/RT \quad \Longrightarrow$$

Where, A is Arrhenius constant, R is Universal Gas constant and T is the Temperature of the reaction and Ea is the activation energy of the reaction.

The activation energy was obtained from the slope of the graph ln K and 1/T.

Values reported in below table:

Table 2: Calculation of Activation Energy of Vulcanization

Grade	ln K	1/T x (10³) (K⁻¹)	Eact. (Kcal/mol)
N 550	-6.17	6.67	
	-5.80	2.31	19.7
	-5.21	2.26	
RG 225	-6.29	2.36	
	-5.82	2.31	18.8
	-5.28	2.26	
RG 223	-6.18	2.36	
	-5.75	2.31	18.5
	-5.19	2.26	
EU. Comp.	-6.14	2.36	
	-5.66	2.31	18.4
	-5.15	2.26	
US Comp.	-6.15	2.36	
	-5.71	2.31	18.1
	-5.18	2.26	

Activation energy for different compounds are depicted as graphs -
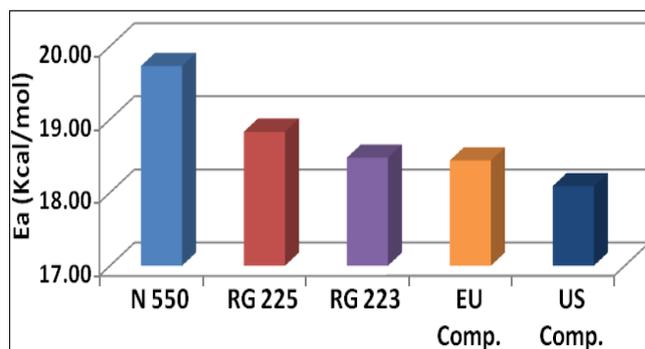

Figure 1: Activation energy for vulcanization

1) Study of Mechanical Property Testing – study of Degradation Kinetics of vulcanizate:

Table 3: Modulus at 100% elongation of unaged and aged samples

Modulus at 100%			
Grade	Unaged	24 Hrs/125°C	72 Hrs/125°C
N 550	6.04	12.74	14.81
RG 223	6.26	12.77	16.1
RG 225	6.47	13.26	16.33
EU Comp. 1	5.87	12.82	15.87
US Comp. 2	6.35	13.25	17.01

Table 4: Tensile Strength of unaged and aged samples

Tensile Strength			
Grade	Unaged	24 Hrs/125°C	72 Hrs/125°C
N 550	14.41	17.72	18.31
RG 223	15.2	18.63	19.85
RG 225	15.26	17.2	20.19
EU Comp.	13.34	16.98	16.71
US Comp.	14.93	19.22	19.27

Table 5: % Elongation at break of unaged and aged samples

Elongation at break			
Grade	Unaged	24 Hrs/125°C	72 Hrs/125°C
N 550	270.44	153.05	130.07
RG 223	279.67	152.31	133.11
RG 225	253.41	154.23	127.36
EU Comp.	271.24	158.22	104.83
US Comp.	263.07	162.75	115.95

Table 6: Fractional Stress Energy

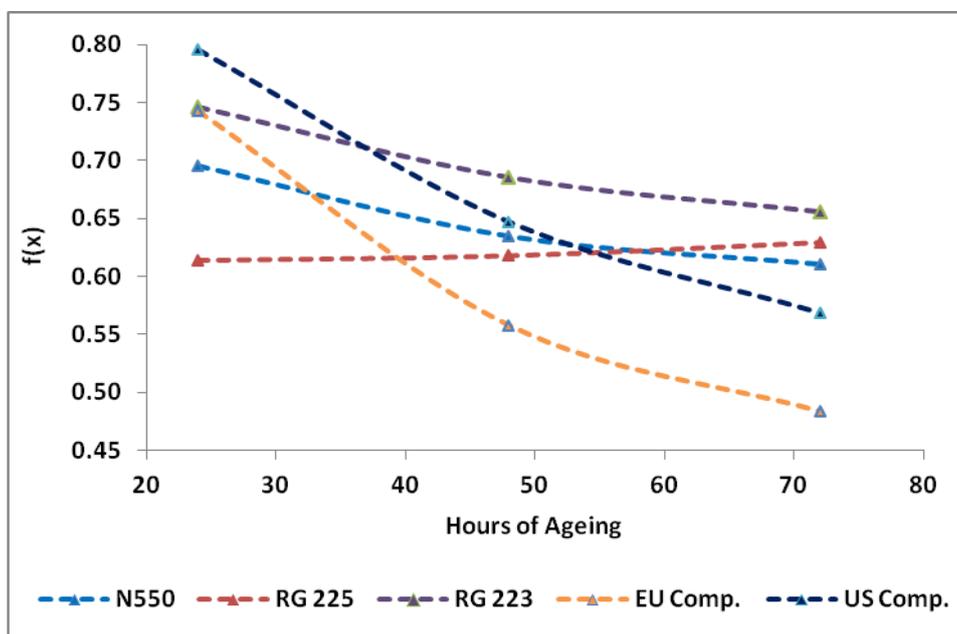| $f(x) =$	(tensile strength * elongation@break) aged sample		
	(tensile strength * elongation@break) unaged sample		
	24 Hrs	48 Hrs	72 Hrs
N550	0.70	0.64	0.61
RG 225	0.61	0.62	0.63
RG 223	0.75	0.69	0.66
EU Comp.	0.74	0.56	0.48
US Comp.	0.80	0.65	0.57

Figure 2: Degradation Kinetics after Ageing

Study of De-mattia flex Testing – Determination of fatigue of the Vulcanizate:

Table 7: De Mattia flex test results

Stages of Fatigue	N 550		RG 223		RG 225	
	Crack Growth	No of Cycles	Crack Growth	No of Cycles	Crack Growth	No of Cycles
Initiation of Crack	3	308	3.5	1550	2.5	2851
Crack Propagation	6.2	318	7.2	1567	6.7	2885
	14.5	330	12.5	1585	11.8	2917
	19.2	339	19.25	1602	17.8	2942
	23.3	348	22.5	1609	23.5	2965
Termination	25	359	25	1620	25	2990

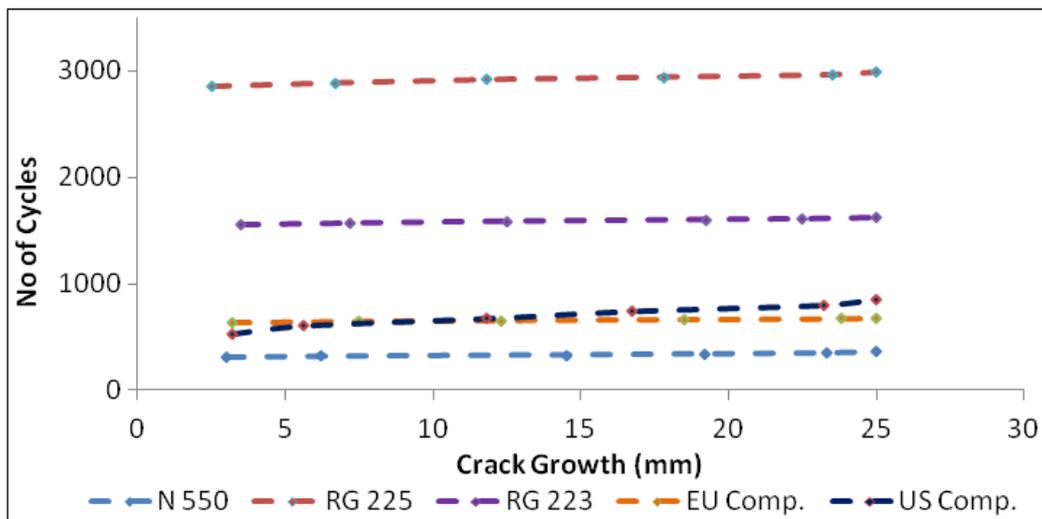| Stages of Fatigue	EU Comp.		US Comp.	
	Crack Growth	No of Cycles	Crack Growth	No of Cycles
Initiation of Crack	3.2	630	3.2	532
Crack Propagation	7.5	642	5.6	605
	12.3	652	11.8	672
	18.5	661	16.75	737
	23.8	669	23.2	792
Termination	25	675	25	845

Figure 3: Flex crack growth rate of vulcanizates

Compression Test results – Determination of Dimensional Stability of Vulcanizate:

Table 8: Test results of compression set at 72 hrs, 125°C

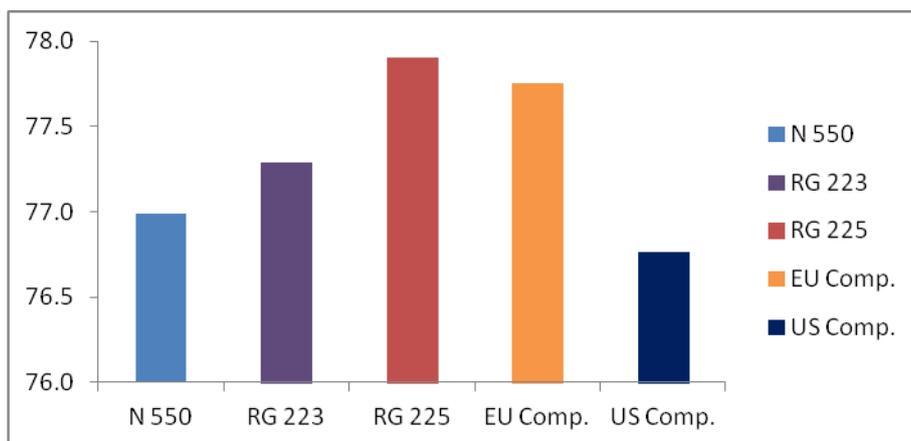| Grade	Compression Set (125°C/72 Hrs)
N 550	77.0
RG 223	77.3
RG 225	77.9
EU Comp.	77.8
US Comp.	76.8

Figure 4: Compression set test results at 72 hrs, 125°C

Test results of Rebound Resilience: Understanding resilience of vulcanizate:

Table 9: Test results of compression set at 45° angle

Grade	Rebound Resilience (45°)
N 550	21.8
RG 223	24.5
RG 225	25.9
EU Comp.	25.4
US Comp.	24.1

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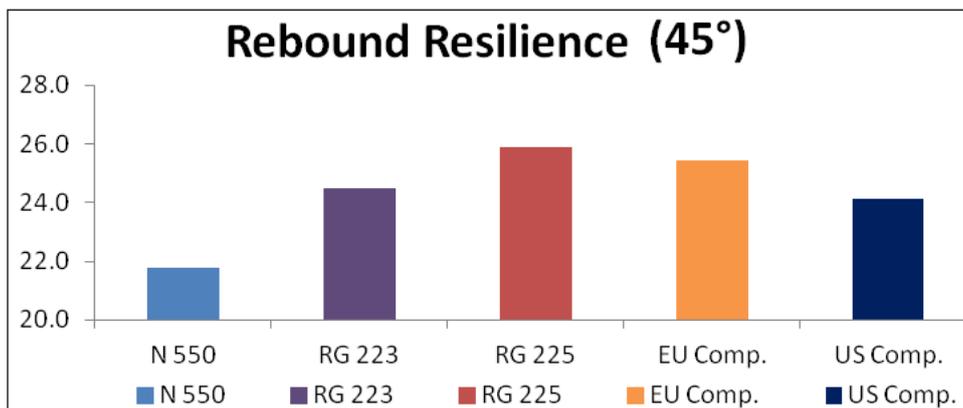
Figure 5: Rebound resilience test results

4. Discussion

Rate of reaction for formation of filler-polymer network along with vulcanization and devulcanization reaction were depicted in the rheograph (9). It reveals that RG 223 and RG 225 having more scorch safety than normal N550 and other competitor samples. (Table 1, Table 2, Figure 1). The modulus was higher than N550 and other blacks indicating better reinforcement (Table 3). This is also supported by higher tensile strength (Table 4) at equivalent elongation at break (Table 5).

When the rubber compounds are subjected to thermal stress at 125°C with varied duration (Table 6 and Figure 2), it was clear that RG 223 maintain the initial drop and RG 225 in fact increases its duration of degradation indicating some molecular rearrangement between thermal breakdown and reformation of residual deactivated bond.

Flexing at room temperature and ambient laboratory conditions, indicates better flexing property than N550 and any other blacks (Table 7, Figure 3). In case of compression set RG 223 and RG 225 shows comparable set value with other blacks (Table 8, Figure 4).

5. Conclusion

By changing the reactor geometry, the morphology of near equivalent ASTM grade, the new generation black shows good properties to extruded items like weather strip and under bonnet applications (transmission belts, seals, gaskets, moulded parts) and high temperature hose. The new blacks like RG 223 and RG 225 will increase the life of above rubber goods.

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