International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org ||Volume 7 Issue 7 Ver V || July 2018 || PP 08-16

Curing Characteristics and Kinetics of Natural Rubber – Nano Calcium Carbonate Composites.

Dr.Mausumi Saha
Raja Peary Mohan CollegeUttarpara, Hooghly

Abstract:*The effect of nano sized precipitated calcium carbonate on the kinetics of the vulcanization of natural rubber (NR) with a vulcanizing agent (sulfur) accelerated by N-oxydiethyl benzthiazyl sulfenamide (BSM) has been studied. Nano sized precipitated calcium carbonate filler can be suitably incorporated in a rubber matrix such as in natural rubber to make several composites.The vulcanization kinetics was determined by oscillating disc rheometry (ODR) and the kinetic parameters were determined by the model equations. Many kinetic models have been developed to describe vulcanization behavior. Generally, these models fall into two categories according to their fundamental ideas, namely mechanistic kinetic models and the phenomenological or empirical kinetic models The kinetic analysis suggests that the two-parameter auto catalytic model is the more appropriate one to elucidate the kinetics of the vulcanizing reaction of the present system. The autocatalytic reaction, the maximum rate of conversion will be other than zero due to involvement of product of reaction in the ongoing reaction. It is proved that all the models are temperature-dependent and fits the experimental data only at certain temperatures. These parameters support the nature of the experimental ODR curves (degree of conversion–time plots). The of nano precipitated calcium carbonate leads to a change in vulcanization reaction and has an effect on the kinetic parameters E, ln* K_0*, m and n, and consequently on the overall reactivity. In the present work, the effect of nano –Calcium carbonate addition to natural rubber on the cure characteristics.*

Keywords: *Vulcanization, Oscillating disc rheometry, Kinetics, Autocatalytic reaction*

Date of Submission: 10-07-2018 Date of acceptance: 24-07-2018

I. Introduction:-

Recently, a number of studies (1-4) have been Performed including nano particles in polymers. Due to larger interfacial area of Nano sized filler are better to their micron sized counterparts (5-7). The nano size filler particles are able to significantly greater number of sites in the polymer matrix to compared micron size filler particles(8). The inclusion of nano fillers improved mechanical, electrical, optical and other properties of polymer composite(9). Different type of polymers have been used for preparing polymer nano-composite such as natural rubber(NR), Epoxide-Natural rubber (ENR), Styrene-butadine rubber (SBR) etc. Latest studies have been shown that ppt. calcium carbonate, when presented in nano size form, possesses peculiar properties if it can be effectively dispersed within the polymer matrix (10,11). Since the interfacial interactions between the filler particles and the surroundings polymer strongly influence the properties of particulate filled composite. Nano-Calcium carbonate –composites show inferior physical properties compared to their micron sized counterparts (12). This paper studies with the effect of nano –Calcium carbonate addition to natural rubber on the cure characteristics

II. Experimental:

Filler-rubber composite preparation: -

Raw materials :- The formulation of the rubber compound is shown in table 1. ppt $CaCO_3$ 5,10,15,20,25,30,35phr (parts per hundred parts of rubber) were used. The amount of rubber and other ingredients were kept constant in all recipe. The sample were designated :- Gum compound (S_0)- composite with no filler, Composite S_1, S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , –composite with 5 ,10 , 15, 20, 25, 30, 35, phr ppt $CaCO_3$, respectively. The natural rubber (Mooney viscosity, $ML_{1+4}72$ at 100^0C) was obtained from Kerala rubber Board , India. Zinc oxide (99%), Stearic acid , BSM, IPPD, Sulfur were obtained from local market.

Mixing of the ingredients: - All mixes were prepared using a Brabender machine (Plastograph Electronical Torque Rheometer type 815606, Germany) according to ASTM D-3192, working at 70^0C and a rotor speed of 60 rpm, 5 min for cold mastication, and another 15 min for mixing of the ingredients except sulfur. Finally, sulfur was mixed on a laboratory size two roll mill (30 cm x 15cm) following ASTM D-3185-88.

Cure Characteristics: -
From the matured un-vulcanized stocks, samples were taken to evaluate cure characteristics using a Monsanto ODR 100 instrument at 140^0, 150^0 and 160^0C with a micro die and 3^0 arc of oscillation.

III. Results and discussion

ppt CaCO3 was mixed with natural rubber (cis-1, 4-polyisoprene). The purpose was to increase dispersion ability and compatibility of ppt $CaCO_3$ (filler) in the mix composite. This paper reports the results of a critical study to understand its vulcanization characteristics from kinetic parameters evaluated by ODR technique and suitable mathematical models.

Rheometric characteristics
The vulcanization characteristics of gum (without filler) and filler loaded NR composites are shown in Table – 2.

Minimum torque:
The minimum torque (M_L) indicates stock viscosity. It is important to understand flow behavior of the un-vulcanized rubber compound during processing. The results of the experimental compounds (Table 2) show that the change is insignificant.

Maximum torque :
Table- 2 shows maximum torque data. The maximum torque value of filler loading compound are higher than that of gum except 5 phr filler loading compound. So filler loading compounds show higher cross linking compared to gum compound.

Difference of Torque Values ($M_H – M_L$):-
The torque difference shows a similar trend with maximum torque (Table -2). This is approved to higher filler elastomeric interactions due to filler loading. The increment of ΔM values may suggest that ppt $CaCO_3$ also act as a cross linking agent in the matrices (Fig. 1) .

Scorch time (t_{2s}) and optimum time (t_{90}) : The cure characteristics of the NR- ppt $CaCO_3$ composites is shown in table -2. Values of t_{2s} and t_{90} are decreased with increasing ppt $CaCO_3$ contain 5phr to 20 phr also 30 phr and increased 25 phr 35 phr (Fig. 2 & 3). This is due to a poor interfacial interaction between rubber and ppt $CaCO_3$ which confirmed the formation of filler agglomerates of the filled compound (13).

CRI increases with ppt $CaCO_3$ addition 5phr to 20 phr and 30 phr in the composite. CRI also decreases 25 phr and 35 phr respectively in the composite. It is support increased the activation of the cure reaction upto 5 phr to 20 phr and 30 phr in the composite.

The effect of temperature on the curative system: The torque difference values of all composite are increased in all the experimental temperature which measured of the dynamic shear modules. It expects the effective elastic and viscoelastic characteristics of filler dispersion in composite material. All the filler loading composite except 35 phr composite the scorch time t_{2s} and cure time t_{90} are decreased in all experimental temperature due to effect of filler surface area. The smaller particle size , the larger surface area available for reaction. This will accelerate the process and shorten the cure time.

Vulcanization kinetics:

The vulcanization of rubber is a complex chemical process that involves a number of species as illustrated below. The reaction starts with the formation of an accelerator-activator complex that then proceeds to pick-up sulfur, which naturally occurs as an S_8 ring, to form the activated sulfurating species A_x. The sulfurating species are polysulfidic, where x can vary from 1 to more than 20. An activated sulfurating species then undergoes decomposition and reacts with the allylic carbon in the rubber to form B_x, which is another polysulfidic species that is terminated with rubber on one end. The species B_x then undergoes decomposition to form the radical species B^*_x that then reacts with an allylic carbon on a second rubber chain to form the crosslink Vu_x.

Sulfur vulcanization reaction is an autocatalysed reaction in which kinetic order is greater than one. It gives sigmoidal rate profile.In this paper some mathematical model have been used.

Borchardt and Daniel model (14)

The general rate equation and has the form $\frac{d\alpha}{dt} = K(1-\alpha)^n$

Where n is the reaction order ,K the specific rate constant at temperature T, and α the degree of conversion for cure- meter study. This form of the kinetic equation works for many simple , single stage reaction. But It is not enough when applied to more complex reactions such as auto catalyzed, chemical and polymer crystallization reaction.

Ŝestak- Berggen model (15)

The most popular form of auto catalyzed reaction is known as the Sestak- Berggen model equation.

$$\frac{d\alpha}{dt} = K(T)\alpha^{m}(1-\alpha)^{n}$$

Where m and n are reaction order constant.

The degree of conversion (α) in curing reaction is defined as follows :-

$$\alpha = \frac{M_t - M_0}{M_h - M_0}$$

Where M_0, M_t and M_∞ are torque at time zero, at time t and at the end of the curing reaction.

The above nth order reaction model (Borchardt and Daniel) considers that all the reacting species are converted in beginning of the reaction. The reaction rate is maximum at the initial stage. But in the autocatalytic reaction, the maximum rate of conversion will be other than zero due to involvement of product of reaction in the ongoing reaction. It is proved that all the models are temperature-dependent and fits the experimental data only at certain temperatures (16).

Plots of the degree of conversion (α) versus time of conversion(t) :-

Plots of α vs. t of ppt $CaCO_3$/NR composite at three different temperatures obtained from the rheometer curves are shown in Figures 4(a, b, c, d, e, f, g, and h). From the plots ,it is shown that at higher temperature all composites are faster kinetics behavior than that at lower temperature . The time required at different temperature for 80% conversion (α) is shown in Table 3.

Arrhenius equation can be expressed as follows: $K = K_0 e^{\frac{-E_a}{RT}}$ where K_0 is a pre-exponential factor, E_a, the activation energy and R the universal gas constant. By using Arrhenius relationship , we determined the activation energy E_a and $\ln K_0$ from the slop and intercept of the line and the values are given in table 4. The average values of E for ppt NR–$CaCO_3$ composite system are plotted in Figure 8 as a function of filler content.

Plot of vulcanization rate (dα/dt) verses cure degree (α)

Plot of $\frac{d\alpha}{dt}$ versus α is presented in Figures 6 (a, b, c, d, e, f, g and h). The peak data for composite samples are shown in Table 5.

The peak points for all the composites obtained in the test occure at higher degree of cure (α value) as compaired with gum at all the temperature used. This may be due to better distribution of filler, which helps the formation of crosslink between nearest rubber chin. Table -5 also shows the maximum conversion was achived above α = 0.4 at all the measured temperatures which does not agree with the earlier studies (17-19)

IV. Conclusions :-

In natural rubber ppt $CaCo_3$ as a filler accelerated curing process and improved curing characteristics. The effect of nano Calcium Carbonate as a filler on the kinetics of vulcanization of Natural rubber (NR) has been studies by Oscillating disc rheometry (ODR).

From the degree of conversion(α) vs. time plots, n^{th} order kinetics model shows faster kinetics for all the composites at higher temperature. Kinetics analysis suggests that autocatalytic model is more appropriate and consistent to describe the kinetics of the present vulcanization reaction.

Acknowledgements

I would like to express my profound gratitude towards my Ex- supervisor Late Professor Bidyuit Baran Konar Department of Polymer Science & Technology, University of Calcutta. I thanks him for the inspiring and encouraging way to guide me to a deeper understanding of knowledge of work. Also I express my sincere gratitude to my research supervisor Prof. Samit Kumar Ray, Department of Polymer Science & Technology, University of Calcutta.

Reference

[1]. P.L. Teh, Z.A. Mohd Ishak, A.S. Hashim, J. Karger-Kocsis and U.S. Ishiaku, “Effects of epoxidized natural rubber as a compatibilizer in melt compounded natural rubber organoclay nanocomposites,” Euro. Poly. J., 40, 2004, pp. 2513-2521.

[2]. A.M. Shanmugharaj, J.H. Bae, K.Y. Lee, W.H. Noh, S.H. Lee and S.H. Ryu, “Physical and chemical characteristics of multiwalled carbon nanotubes functionalized with aminosilane and its influence on the properties of natural rubber composites,” Compo. Sci. & Tech., 67, 2007, pp. 1813–1822.

[3]. R.W. Siegel, S.K. Chang, B.J. Ash, J. Stone, P.M. Ajayan, R.W. Doremus, and L.S. Schadler, “Mechanical behavior of polymer and ceramic matrix nanocomposites,” Scripta mater., 44, 2001, pp. 2061–2064.

[4]. S.J. Park, S.Y. Jin, and S. Kaang, “Influence of thermal treatment of nano-scaled silica on interfacial adhesion properties of the silica/rubber compounding,” Mater. Sci. & Eng. A., 398, 2005, pp. 137–141.

[5]. P.B,Messersmith and E.P. Giannelis, (1994) Chem. Mater., 6, 1719-1725.

[6]. K.Yano., A.Usuki.,A. Okada., T. Kurauchi. and O. Kamigaito, (1993) J. Poly. Sci., Part A: Poly. Chem., 31, 2493-2498.

[7]. M.Sumita., T.Shizuma., K.Miyasaka. and K. Ishikawa. (1983) J. Macromol. Sci., Phys., B22, 601-609.

[8]. P.M.Ajayan, L.S. Schadler and P.V. Braun, “Nanocomposite Science and Technology,” WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.

[9]. C.H. Jung, J.H. Choi, Y.M. Lim, J.P. Jeun, P.H. Kang and Y.C. Nho, “Preparation and Characterization of Polypropylene Nanocomposites contaning Polystyrene-grafted Alumina Nanoparticles,” J. Ind. Eng. Chem., 12, 6, 2006, pp. 900-904.

[10]. K. Ogawa., T. Vogt., M. Ullmann., S. Johnson. and S.K. Friedlander., Journal of Aerosol Science 30 (1999) 495.

[11]. C. Saujanya., and S. Radhkrishnan., Polymer 42 (2001) 6723.

[12]. Li, X.H., Tjong, S.C., Meng, Y.Z. and Zhua, J. (2003) Poly. Phys., 41, 1806-1813.

[13]. S. Maged., Sobhy, D.E.El Nashar , and Nabila A. Maziad. 26 (2) 2003

[14]. M. Abdul Kader.,C. Nah, (2004) Polymer, 45, 2237-2247]

[15]. C. Ŝestak, and G. Berggren, (1971) Thermochim. Acta, 3, 1-9.

[16]. 16.A. Arrillaga.,A.M. Zaldua., R.M. Atxurra and A.S.Farid. (2007) Euro. Poly. J., 43, 4783-4799.]

[17]. R.Ding, and. A.I. Leonov, . (1996) J. of Appl. Poly. Sci., 61, 455-465.

[18]. A.Arrillaga., A.M. Zaldua., R.M. Atxurra.,A.S. Farid. (2007) Euro. Poly. J. 43, 4783- 4799.

[19]. M. Abdul kader, and C.Nah, (2004) Polymer, 45, 2237-2247.

Table- 1

Basic recipe of the mixes samples.

Ingredient	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Natural rubber (RMA-IX)	100	100	100	100	100	100	100	100
Zinc oxide	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
IPPD[a]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
BSM[b]	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PPt $CaCO_3$	0	5	10	15	20	25	30	35

a…..Isopropyl paraphenylenediamine

b…..N- Oxydiethyl benzthiazyl sulfonamide

Table -2 Vulcanization characteristics of NR- $CaCO_3$ composites

Porperties	$T_c(^0C)$	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
M_L	140	1.8	1.6	1.8	1.8	1.7	1.7	1.6	1.9
	150	1.7	1.6	1.8	1.8	1.8	1.8	1.7	1.7
	160	1.7	1.7	1.7	1.8	1.7	1.6	1.6	1.8
M_H	140	6.6	6.0	6.9	6.9	6.7	7.2	6.8	7.6
	150	6.8	6.3	7.6	7.0	7.7	7.6	7.5	7.9
	160	6.8	6.7	7.4	7.6	7.5	7.2	7.4	7.8
M_H- M_L	140	5	4.5	5.1	5.1	5.	5.5	5.2	5.7
	150	5	4.7	5.8	5.2	5.9	5.8	5.8	6.2
	160	4.9	5	5.7	5.8	5.8	5.6	5.8	6.1
t_{S2}	140	12.75	12.5	12.50	12.00	10.75	11.25	9.00	13.50
	150	7	5.6	6.50	6.50	6.25	5.25	5.50	7.75
	160	4.25	4.0	4.25	4.25	3.75	3.75	3.00	4.75
t_{90}	140	21.82	20.47	18.00	17.10	15.07	17.5	13.73	20.25
	150	11.25	11.70	10.57	9.9	10.75	9.22	8.32	11.92
	160	6.75	5.85	6.75	6.07	5.85	5.85	5.40	6.75
CRI (%)	140	10.73	13.38	18.18	19.61	23.15	12.73	19.12	11.69
	150	23.53	16.81	28.01	31.75	26.67	22.69	38.91	15.58
	160	40.00	54.05	40.00	54.94	47.62	47.62	41.67	45.04

Table -3

80% conversion (α =0.8),time required at different temperature:-

	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Time at 140^0C, min.	5.24	4.62	4.37	4.5	3.62	4.25	3.5	5.5
Time at 150^0C, min.	2.54	2.62	2.62	2.5	2.75	2.04	1.87	3.25
Time at 160^0C, min.	2.21	1.37	1.75	1.625	1.56	1.15	1.37	1.19

Table-4

Kinetic parameters of NR-$CaCo_3$ composites following nth order cure reaction obtained from ODR test. Borchardt and Daniel model constant

Sample	Temp in ^{0}C	K	n	lnK_0	E_a (K.cal.mol^{-1})
S_0	140	0.3451	0.7507	31.7920	26.9767
	150	0.7806	0.6937		
	160	1.5363	0.6967		
S_1	140	.524925	0.7882	35.1014	29.3439
	150	1.30369	0.7418		
	160	2.66046	0.8753		
S_2	140	0.7172	0.8016	22.47183	18.6967
	150	1.40284	0.9892		
	160	2.0057	0.8864		
S_3	140	0.583681	0.6907	28.97393	24.2677
	150	1.056012	0.8176		
	160	2.256466	0.9436		
S_4	140	0.702156	0.7004	23.25151	19.4213
	150	1.077453	0.7677		
	160	2.078196	0.7914		
S_5	140	0.725931	0.7592	23.7826	19.80538
	150	2.13297	0.7808		
	160	2.50002	0.8296		
S_6	140	0.66664	0.6655	25.12254	20.9408
	150	1.3543	0.7509		
	160	2.1149	0.7906		
S_7	140	0.49718	0.8448	31.11093	26.0626

Table -5

Peak data for of NR-$CaCO_3$ composite sample

Sample	140^0C			150^0C			160^{0C}		
	Dα/dt at peak point	α at peak point	Time at peak point (min.)	Dα/dt at peak point	α at peak point	Time at peak point (min.)	Dα/dt at peak point	α at peak point	Time at peak point (min.)
S_0	0.16	0.52	2.5	0.4081	4.8	2.0	0.8979	4.6	1.0
S_1	0.2727	0.5454	3.5	0.5217	0.5435	1.5	1.12	0.480	1.0
S_2	0.3137	0.549	2.5	0.8276	0.550	2.25	0.7017	0.5965	1.4
S_3	0.3077	0.5769	3.5	0.5385	0.4746	1.75	0.7958	0.5517	1.25
S_4	0.3137	0.5098	2.0	0.4068	0.520	2.0	1.1034	0.480	1.375
S_5	0.2069	0.5581	2.25	0.5161	0.50	1.0	1.1111	0.520	0.65
S_6	0.3077	0.50	2.5	0.5517	0.5689	1.25	1.2414	0.480	0.875
S_7	0.2105	0.5088	3.5	0.5079	0.4921	2.25	1.0492	0.490	0.75

Table -6

Kinetics parameters (Sestak-Berggen model constant)

Sample	Temp (t_c) ^{0}C	Sestak –Berggen model constant					
		K	n	m	m+n	lnK_0	E_a (K.cal.mol^{-1})
S_0	140	0.7197	0.847	1.0943	1.9413	27.8009	23.0582
	150	1.6775	0.9142	1.0524	1.9666		
	160	2.5553	0.7296	0.918	1.6476		
S_1	140	0.7942	0.6025	0.963	1.5655	35.2218	29.0809
	150	2.1315	1.0111	0.9228	1.9339		
	160	3.9460	0.7619	1.0172	1.7791		
S_2	140	1.12275	0.8344	0.9553	1.7897	25.1928	20.6136

	150	1.9089	0.4304	1.1111	1.514		
	160	3.5349	0.8243	1.1009	1.9252		
S_3	140	0.78806	0.57	0.8167	1.3867	30.3347	25.0669
	150	1.9308	0.7871	1.0732	1.8603		
	160	3.1294	0.6188	1.0655	1.6843		
S_4	140	1.17688	0.9025	0.879	1.7815	24.6447	20.1053
	150	2.1267	0.9763	1.068	2.0443		
	160	3.5854	0.7838	1.0161	1.7999		
S_5	140	1.0238	0.8887	1.0358	1.9245	24.4827	20.0871
	150	1.8462	0.8081	0.9716	1.7797		
	160	3.1162	0.6348	0.841	1.4758		
S_6	140	1.2736	0.8334	0.9195	1.7529	23.2869	18.8879
	150	2.5704	0.8283	1.0177	1.8460		
	160	3.5938	0.8276	0.9931	1.8207		
S_7	140	0.9319	0.8989	1.1133	2.0122	32.1628	26.4526
	150	2.1817	0.8738	1.0915	1.9653		
	160	4.0174	0.9484	0.9651	1.9135		

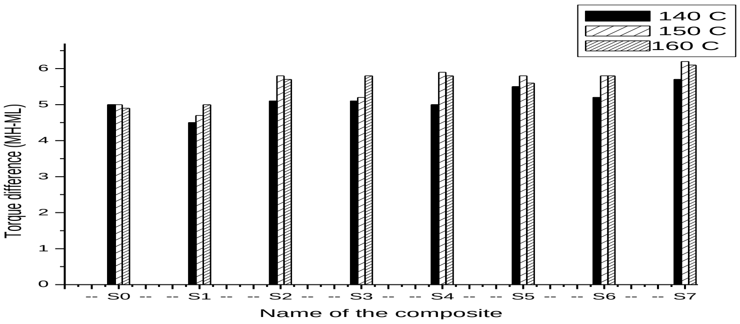


Fig. 1. Torque difference vs. composite

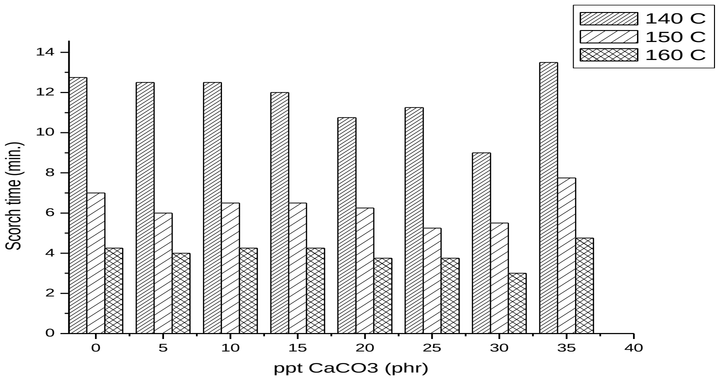


Fig. 2. Scorch time vs. composite

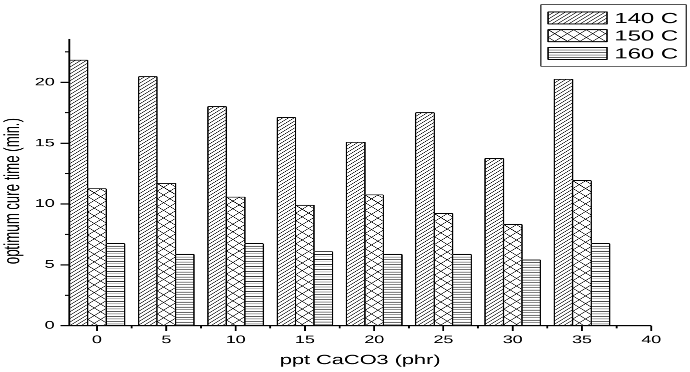
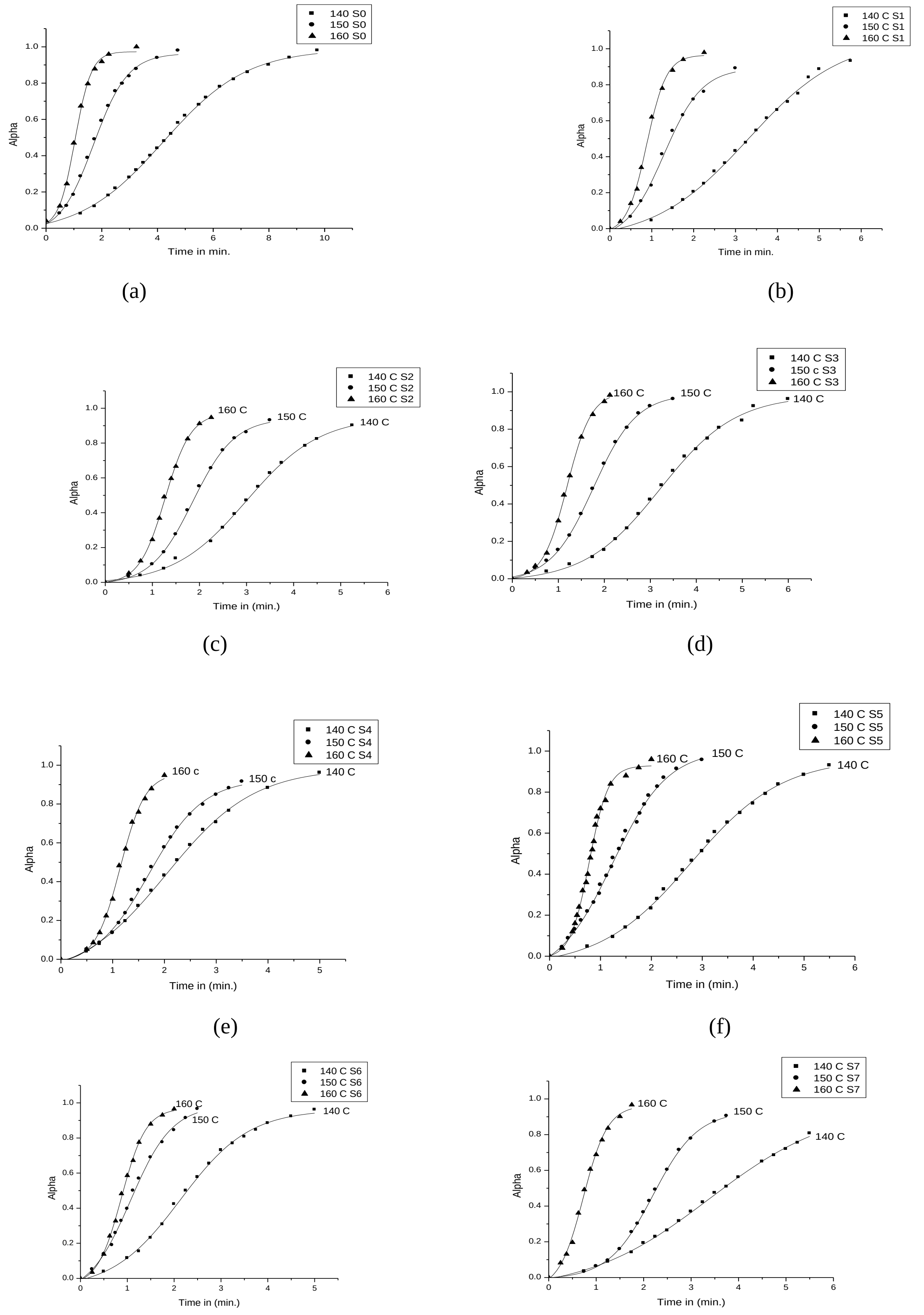


Fig. 3. optimum time vs. composite



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Fig. 4. Vulcanization kinetics curves: degree of conversion (α) vs. time (t) plots, for NR/ppt $CaCo_3$ composites at three different temperatures (140^0 C, 150^0 C and 160^0 C): (a) S_0, (b) S_1, (c) S_2, (d) S_3, (e) S_4, (f) S_5, (g) S_6, (h) $S_{7.}$

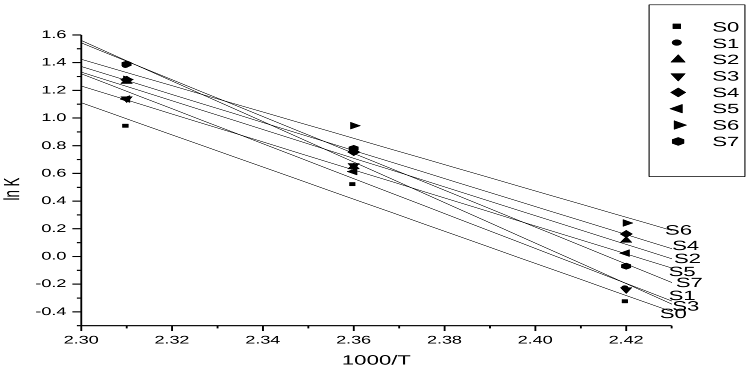
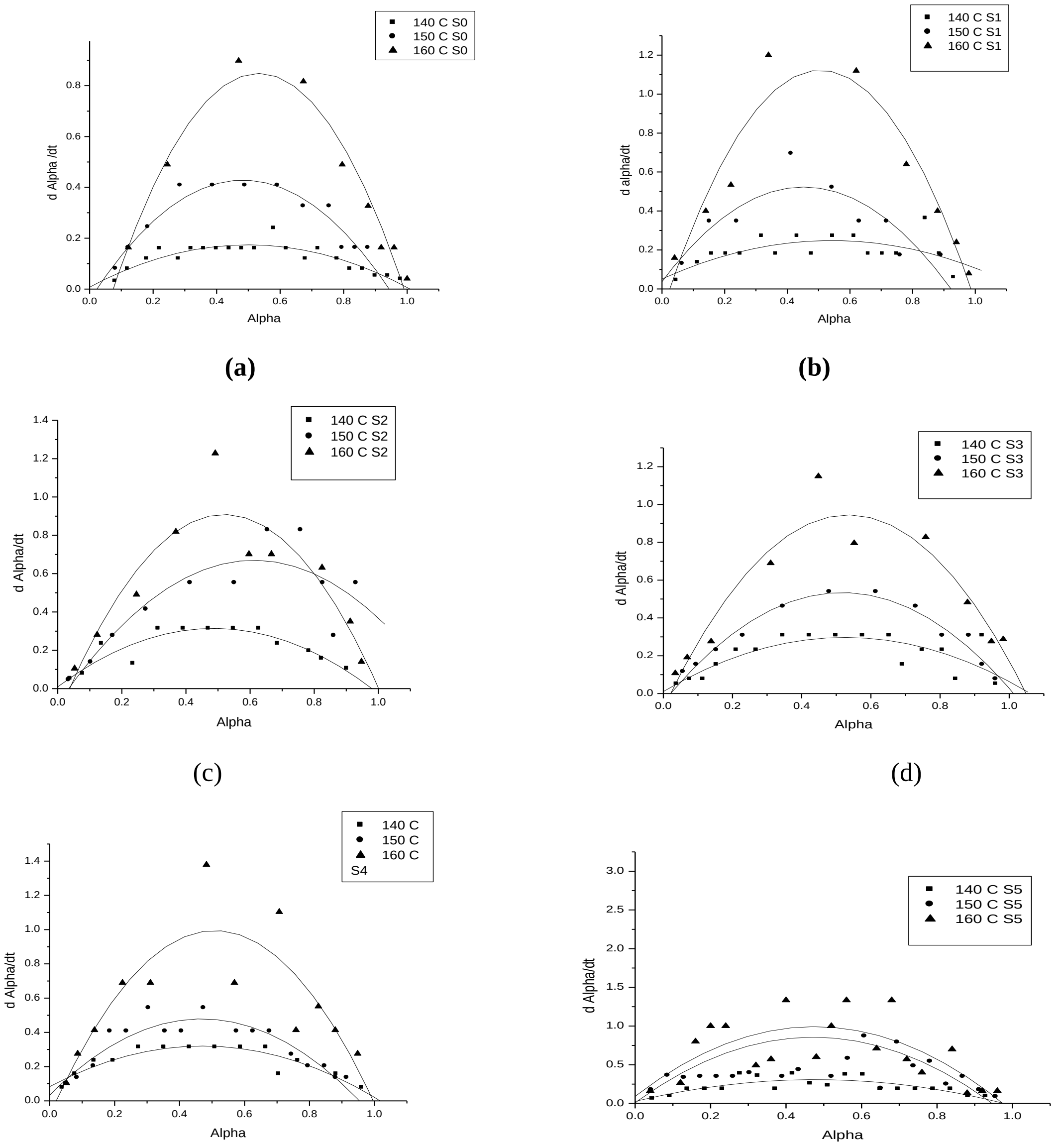


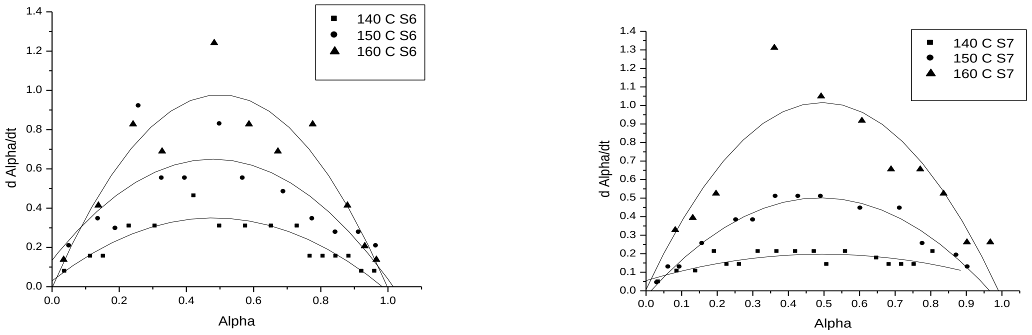
Fig. 5 . ln K vs. 1000/T plots of the composites (Borchardt and Daniel model, nth order cure reaction).



(a) **(b)**

(c) (d)

(e) **(f)**



(g) **(h)**

Fig. 6. Valcanization rate (dα/dt) vs. cure degree (α) plots at three different temperatures: (a) S_0 , (b) S_1 , (c) S_2 , (d) S_3 , (e) S_4 , (f) S_5 , (g) S_6 and (h) S_7 .

Dr.Mausumi Saha "Curing Characteristics and Kinetics of Natural Rubber – Nano Calcium Carbonate Composites. "International Journal of Engineering Science Invention (IJESI), vol. 07, no. 07, 2018, pp 08-16