



## Research article

## Poly(acrylonitrile-co-butadiene) as polymeric crosslinking accelerator for sulphur network formation



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## ARTICLE INFO

## Keywords:

Materials science  
Materials chemistry  
Crosslinking accelerator  
Sulphur network  
Solid state NMR  
Curing kinetics  
Activation energy  
Acrylonitrile butadiene  
Polybutadiene  
Low-temperature  
Crystallization

## ABSTRACT

The major controlling factors that determine the various mechanical properties of an elastomer system are type of chemical crosslinking and crosslink density of the polymer network. In this study, a catalytic amount of acrylonitrile butadiene copolymer (NBR) was used as a co-accelerator for the curing of polybutadiene (BR) elastomer. After the addition of this copolymer along with other conventional sulphur ingredients in polybutadiene compounds, a clear and distinct effect on the curing and other physical characteristics was noticed. The crosslinking density of BR was increased, as evidenced by rheometric properties, solid-state NMR and swelling studies. The vulcanization kinetics study revealed a substantial lowering of the activation energy of the sulphur crosslinking process when acrylonitrile butadiene copolymer was used in the formulation. The compounds were also prepared in the presence of carbon black and silica, and it was found that in the carbon black filled system the catalytic effect of the NBR was eminent. The effect was not only reflected in the mechanical performance but also the low-temperature crystallization behavior of BR systems was altered.

## 1. Introduction

The introduction of an ingredient commonly referred to as an accelerator, is highly appreciated for the rubber vulcanization reaction, which helps to improve both the rate and state of the crosslinking process [1, 2]. Indeed, vulcanization without accelerator is not commercially suitable, although the chemistry regarding un-accelerated vulcanization has gained much interest in scientific research. After a long time of discovery of vulcanization, Oenslager [3] demonstrated the effect of aniline as an accelerator on sulphur vulcanization. After that, thiocarbanilide [4] was introduced as an accelerator, which is a reaction product of aniline and carbon disulfide and comparatively less toxic than aniline. Then guanidine came into the market as an accelerator. Furthermore, dithiocarbamate [2], the reaction product of carbon disulfide and aliphatic amine was then commercialized as an accelerator, which is still useful due to its ability to improve both the rate and state of vulcanization. However, scorch (premature vulcanization) is also a problem for an ultrafast

accelerator. Therefore, a new type of accelerator, namely delayed-action accelerator, was introduced by the development of 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzothiazole di-sulfide (MBTS) [5]. Subsequently, benzothiazolesulfenamide was successfully commercialized [6], which exhibits a delayed-action and enhanced rate of vulcanization as well. The use of two accelerators (a mixture of two different accelerators) is also well-known to obtain better scorch resistance, an improved rate and state (degree) of crosslinking synergistically [7]. For this combined system, accelerators can be further classified into two different categories according to their functions; a) primary accelerator and b) secondary accelerator. Primary accelerators are used to get longer scorch time and improved rate of vulcanization simultaneously. Thiazoles and sulfenamides, both are considered as a primary accelerator. On the other hand, secondary accelerators are used in a small proportion and act as a booster for primary accelerators, which also improve the crosslink density of the rubber compound. Guanidines, thiurams, dithiocarbamates are typically used as secondary accelerators or booster. As far as environmental issues

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<https://doi.org/10.1016/j.heliyon.2020.e04659>

Received 16 March 2020; Received in revised form 2 June 2020; Accepted 4 August 2020

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are concerned, the usage of secondary accelerators should be reduced, as they all are derived from secondary amines. During vulcanization, those accelerators dissociate to generate secondary amines, which further react with the nitrogen oxides present in the environment and produce carcinogenic N-nitrosamines and related substances [8, 9, 10, 11]. Due to several rules and regulations [12] by different countries, nowadays there is an urgent need to use safe and environment-friendly accelerator systems.

Several results [13, 14, 15, 16, 17, 18, 19, 20] have been reported based on new types of accelerators or combinations of accelerators. Viridi et al. demonstrated the performance of nitrosamine safe thiuram disulfide as an accelerator. This product is derived from the amine containing a long-branched alkyl chain, which prevents the formation of N-nitrosamines [21]. Debnath et al. studied the effect of synthesized safe thiuram disulfide (TD, which is non-carcinogenic) and MBTS on natural rubber (NR) and found superior mechanical properties and aging characteristics in synthesized TD-MBTS system compare to the conventional TMTD-MBTS system [22]. Basu et al. showed the cure synergism between different dithiocarbamates (derived from safe amines) and thiazole group of accelerators in NR vulcanizate. Finally, it is concluded that dibenzylidithiocarbamate-dibenzothiazyl disulfide (ZBEC-MBTS) showed the highest activity in this respect [23]. Thomas et al. observed the effect of binary accelerator based on 1-phenyl-2,4-dithiobiuret (DTB) and sulfenamide in natural rubber compounds and described how DTB improved the vulcanization behavior in both conventional and efficient vulcanization system [24].

It is believed that in the case of sulphur vulcanization zinc oxide acts as an accelerator-activator. It forms an activated complex in presence of sulphur and organic accelerator. In butyl rubber system, a very small amount of chloroprene rubber along with ZnO is used as co-curing agent [25]. In this case, *in situ* developed zinc chloride is acting as active curing agent. Very similarly, in our present work, a small amount of nitrile rubber was used in sulphur cured BR system. It can be easily envisaged that a zinc nitrile complex [26] can be developed *in situ* during vulcanizing condition that can further assist the sulphur vulcanization of BR [26]. Therefore, addition of small amount of NBR could lead to an improvement in the rate of vulcanization and other physico-mechanical properties of the compound as well. In this study, NBR is being used for the first time as a secondary accelerator or booster instead of conventional secondary accelerators and the effect of this catalytic amount of NBR on the kinetics of vulcanization and related physico-mechanical properties are evaluated.

## 2. Experimental

### 2.1. Materials

Polybutadiene rubber (BR, Buna CB24, with Mooney viscosity  $ML_{1+4}$  at 100 °C 44 MU, density  $\sim 0.91$  gm/cc) and acrylonitrile butadiene rubber (NBR, Krynac 4975 F, with  $48.5 \pm 1.5$  acrylonitrile content, Mooney viscosity  $ML_{1+4}$  at 100 °C-75 MU and density  $\sim 1.01$  gm/cc) were provided by Lanxess (Leverkusen, Germany). Zinc oxide (purity  $\sim 99.5$  %) was obtained from Acros Organics. Stearic acid (general

purpose grade) was purchased from Fisher Scientific. Sulphur (purity  $\sim 99.5$  %) was obtained from Acros Organics. N-tert-Butyl-2-benzothiazolesulfenamide (TBBS) was obtained from Lanxess. Precipitated silica (Ultrasil-VN3) was supplied by Evonik Industries (Essen, Germany). Orion Engineered Carbons (Köln, Germany) provided carbon black (Corax-N330).

### 2.2. Fabrication of the composites

Elastomer and the other ingredients were mixed in a laboratory two roll mill (Polymix 110L, size:  $203 \times 102$  mm<sup>2</sup>, Servitech GmbH, Wustermark, Germany) with a friction ratio of 1:1.2 at 50 °C for 15 min. The formulations of all the compounds are given in Table 1. At first, BR was masticated in two-roll mill for 1 min, and then a small piece (a specified amount) of NBR was added onto the BR and mixed for several minutes. After that, zinc oxide, stearic acid, TBBS, and sulphur were added one by one and mixed for a few minutes. The compound thus obtained was subjected to the curing study. A mass of  $\sim 5.5$  g was taken from the compounded sample and placed in a moving die rheometer (Scarabaeus SIS-V50) for 1 h at 160 °C, with a frequency of 1.67 Hz and the torque was measured with respect to time. From this torque-time curve, the optimum curing time ( $t_{c,90}$ ) was obtained. The samples were then cured by using a compression molding machine (Fontijne TP400, Delft, Netherlands) at 160 °C to their respective curing time, to produce a vulcanized rubber compound of dimension  $110 \times 100 \times 2$  mm<sup>3</sup>. Then the cured samples were kept at room temperature for 24 h before doing any analysis.

## 3. Characterization

### 3.1. Vulcanization characteristics

Rheometric analysis of all the samples was done with a moving die rheometer (Scarabaeus SIS-V50) at 160 °C for 1 h and at a frequency of 1.67 Hz. To study the kinetics of vulcanization, the measurement was done by the rheometer at four different temperatures; 150 °C, 160 °C, 170 °C, 180 °C for 60 min. Vulcanization plays an important role to obtain optimum properties from the rubber vulcanizate. There is a significant influence of vulcanization or curing temperature on the properties of the rubber composites like crosslink density, type of crosslink formation like monosulfidic, disulfidic or polysulfidic bridges between two rubber chains. Therefore, in this work, the activation energy analogous to the vulcanization or more precisely was studied to understand the kinetics of vulcanization [27] reaction.

According to the literature, several mathematical models and techniques were introduced to study the kinetics of vulcanization [28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38]. Some differential equations related to time and temperature were used to study the kinetics of vulcanization [39]. Some of the researchers utilized the Han model, which is applicable for the compound showing reversion during vulcanization. It means that the Han model [40] is more significant in the case of natural rubber (NR) based compound, but it cannot be used in other rubber system where reversion curing patterns is not present. A phenomenological approach

Table 1. Formulation of all compounds\*.

Sample name	BR	NBR	ZnO	Stearic acid	TBBS	Sulphur	Carbon black	Silica
BR	100	-	5	2	1.7	1.7	-	-
BR-NC	100	2.5, 5, 10	5	2	1.7	1.7	-	-
BR-NC-CB	100	2.5	5	2	1.7	1.7	40	-
BR-NC-Silica	100	2.5	5	2	1.7	1.7	-	40
BR-CB	100	-	5	2	1.7	1.7	40	-
BR-Silica	100	-	5	2	1.7	1.7	-	40

\* All the ingredients were taken in (weight) parts per hundred parts of rubber (phr). In compounds with BR-NC in their names, NBR was considered as an additive.

based on the experimental data was adopted by several researchers. Ding and Leonov [41] used the kinetic approach to obtain information about all the stages of vulcanization, which is more sophisticated for the analysis of the rheometric curve [42].

### 3.2. Autocatalytic model

The data obtained from the rheometer will be used in this study. The extent of crosslinking at time  $t$  can be expressed as

$$\alpha = \frac{M_t - M_0}{M_e - M_0} \quad (1)$$

where  $M_t$ ,  $M_0$  and  $M_e$  are the torque values at a time  $t$ , at time zero and the time when crosslinking ends. The vulcanization kinetics of rubber is studied under isothermal condition, this can be expressed in two different ways. One is the  $n^{\text{th}}$  order kinetics, and the other one is the autocatalytic model. The  $n^{\text{th}}$ -order kinetic model can be utilized for the overall curing process and can be expressed as

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad (2)$$

where  $k$  is the rate constant, and  $n$  is the order of the reaction. According to the autocatalytic model, the reaction rate will be maximum at any time after the beginning of the reaction. This model has been utilized in this study and can be expressed as

$$\frac{d\alpha}{dt} = k(T) \alpha^m (1 - \alpha)^n \quad (3)$$

where  $k$  is the rate constant,  $m$  and  $n$  are the order of reactions; all of them are temperature dependent parameter. The kinetic parameters  $k$ ,  $m$ ,  $n$  are extracted from experimental data and the values are shown later (in Table 3). The rate constant  $k$  has a direct relation with the activation energy which could be expressed by the Arrhenius equation [39] as follows:

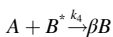
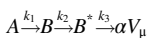
$$k = A \cdot \exp(-E_a/RT) \quad (4)$$

$$\text{or, } \ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

From the slope of the  $\ln k$  vs.  $1/T$  curve, the activation energy ( $E_a$ ) would be calculated.

### 3.3. Ding-Leonov model

Ding and Leonov [41] proposed a kinetic approach and the related reactions are as follows:



and the mass balance equation is –

$$A_0 = A + B + B^* + \frac{V_\mu}{\alpha} + \frac{D}{\gamma} \quad (7)$$

here  $A$  is the active complex formed by the reaction of sulphur, activator, and accelerator,  $B$  represents crosslink precursor,  $B^*$  is the active form of  $B$ , which might be a polymeric radical,  $D$  represents the inactive side products.  $V_\mu$  is the crosslink. The constant  $k_1$  reveals the rate of conversion from the curing agent to the crosslink precursor. The temperature-dependent rate constant  $k_2$  represents the rate of cure. A higher value of  $k_2$  indicates the faster reaction rate which corresponds to an improved rate of cure.  $k_3$  and  $k_4$  are the reaction rate constants for the formation of crosslinks from  $B^*$  and for the formation of the precursor from  $A + B^*$  respectively.  $k_5$  and  $k_6$  are the reaction rate constants where inactive side groups are formed. Indeed,  $k_6$  is related to the reversion process in the over-cure region and exhibits the degradation of the crosslinked rubber.  $\alpha$ ,  $\beta$ ,  $\gamma$  are the stoichiometric parameters. Now the solution of Eq<sup>n</sup> (6) and (7) is expressed as,

$$V_\mu = \frac{A_0 k_2 [\exp(-k_2 t) - \exp(-k_6 t)]}{(1 + \Psi)(k_6 - k_2)}, \quad \Psi = \frac{k_5}{k_3} \quad (8)$$

where,  $t$  is the cure time after the induction period, i.e., the difference between cure time  $t'$  and induction time,  $t_i$  ( $t = t' - t_i$ ).  $\Psi$  is the ratio between the rate of inactive side group formation and the rate of effective crosslink formation.

### 3.4. Fourier transform infrared (FTIR) spectroscopy

FTIR analysis of the cured samples was performed with a Bruker, Tensor 27 spectrometer, which was equipped with a diamond ATR (Attenuated total reflection) cell. Each spectrum was recorded in the wavenumber range of 4000 to 400  $\text{cm}^{-1}$  under a resolution of 4  $\text{cm}^{-1}$ .

### 3.5. Measurement of crosslink density

#### 3.5.1. Swelling method

A small piece of the sample of specific weight ( $\sim 0.5$  g) was immersed in toluene and kept for 72 h. After that, the sample was taken out from the toluene and the excess solvent was wiped off from the surface using a filter paper. Then the swollen weight of the sample was taken and the sample was dried in an air oven at 70 °C until a constant weight was reached. After that, the weight of the dried sample was taken. The crosslink density of the sample was calculated from the Flory-Rehner equation [43] which is as follows:

$$v = - \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s \left( V_r^{\frac{1}{3}} - 0.5 V_r \right)} \quad (9)$$

$$\text{where, } V_r = \frac{\frac{\text{Weight of dry rubber}}{\text{Density of rubber}}}{\frac{\text{Weight of dry rubber}}{\text{Density of rubber}} + \frac{\text{Weight of absorbed solvent}}{\text{Density of solvent}}} \quad (10)$$

It is important to mention that the uncertainties [44] in this experimental approach, mainly caused by the assumed theory of rubber elasticity that does not take the effect of entanglements into the account [45].

#### 3.5.2. Low field NMR method

A low field Bruker minispec mq 20 spectrometer was used to perform  $^1\text{H}$  double-quantum (DQ) NMR experiments. It was functioning at 0.5 T with 90° pulses of 3.1  $\mu\text{s}$  length and a dead time of 12  $\mu\text{s}$ . The temperature of the experiments was set to 80 °C, after ensuring that the structural results do not depend upon temperature on further heating. The experiments and raw data analysis were performed following the procedures outlined in previous works [46, 47] to obtain direct and quantitative

**Table 2.** Curing characteristics of the mixed rubber compound\*.

Sample name	$t_{s,2}$ (min)	$t_{c,90}$ (min)	$M_H$ (dN.m)	$M_L$ (dN.m)	$(R_{\infty} = M_H - M_L)$ (dN.m)
BR (0 NBR)	12.73	23.25	14.91	1.23	13.68
BR-NC (2.5 NBR)	11.13	19.89	15.29	1.19	14.10
5 NBR	11.00	19.64	14.99	1.15	13.84
10 NBR	8.99	16.11	14.71	1.03	13.56

\* All the compounds contain 2 phr stearic acid, 5 phr zinc oxide, 1.7 phr sulphur and 1.7 phr TBBS.  $t_{s,2}$  is the time required for a 2 unit rise of the torque from the minimum torque ( $M_L$ ), indicating the scorch time, and  $t_{c,90}$  is the optimum cure time, i.e., the time required to reach the 90 % of the maximum rheometric torque ( $R_{\infty}$ ).

information about the residual dipolar couplings distribution between protons in the rubber samples ( $D_{res}$ ) and the relative fraction of elastically active network chains. The correlation between  $D_{res}$  and the network structure (represented by the tensor order parameter of the polymer backbone  $S_b$ ) is given by [46, 48]:

$$S_b = D_{res} \frac{k}{D_{stat}} = \frac{3}{5} \cdot m \quad (11)$$

where  $D_{stat}/k$  is the effective static dipolar couplings (after averaging of intra-segmental motions), the factor 3/5 is derived from the assumption of Gaussian statistics, and  $m$  is the vector order parameter. The latter depends on the average number of segments between constraints ( $N_x$ ), i.e. crosslinks ( $N_c$ ) and entanglements ( $N_e$ ), being that dependence defined by the applied model of rubber elasticity [49]. Considering the Lang-Sommer model [48] and assuming that  $N_c \approx N_e$  (assumption valid for most of the technological valuable rubber compounds), it is possible to obtain the widely used simplified expression  $D_{res} \frac{k}{D_{stat}} \propto \frac{1}{N_c}$  [49] and to apply the defined relationship  $M_c = \frac{656 \text{ Hz}}{D_{res}} \frac{\text{kg}}{\text{mol}}$  for the cis-BR matrix [46]. Some particular details about the analysis procedure applied in this work will be described in the following sections.

Finally, the quantification of the actual non-coupled network defects fraction requires the analysis of swollen samples (in deuterated toluene) [50]. For this purpose, samples were swollen in excess of deuterated toluene in a flame sealed NMR tube for 24 h before being measured at 40 °C to minimize the evaporation of the solvent.

### 3.5.3. Mechanical and dynamic mechanical properties

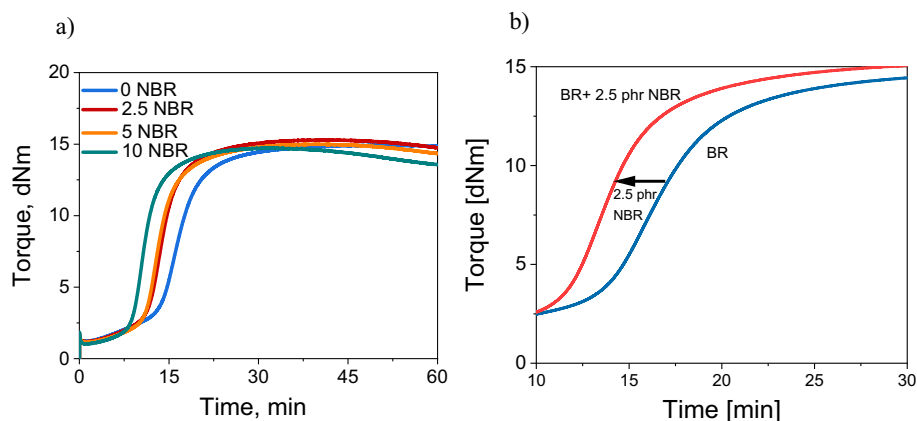
The tensile measurement was performed using a universal testing machine (Zwick 1456, Z010, Ulm, Germany) with DIN S2 dumbbell specimen with a cross-head speed of 200 mm/min (according to DIN 53504) and load cell of 1 kN at room temperature. Tensile strength, elongation at break, stress at different strains were obtained from the tensile stress-strain curve.

A dynamic mechanical thermal spectrometer (GABO Qualimeter, Eplexor 150N) was used to evaluate the dynamic mechanical properties

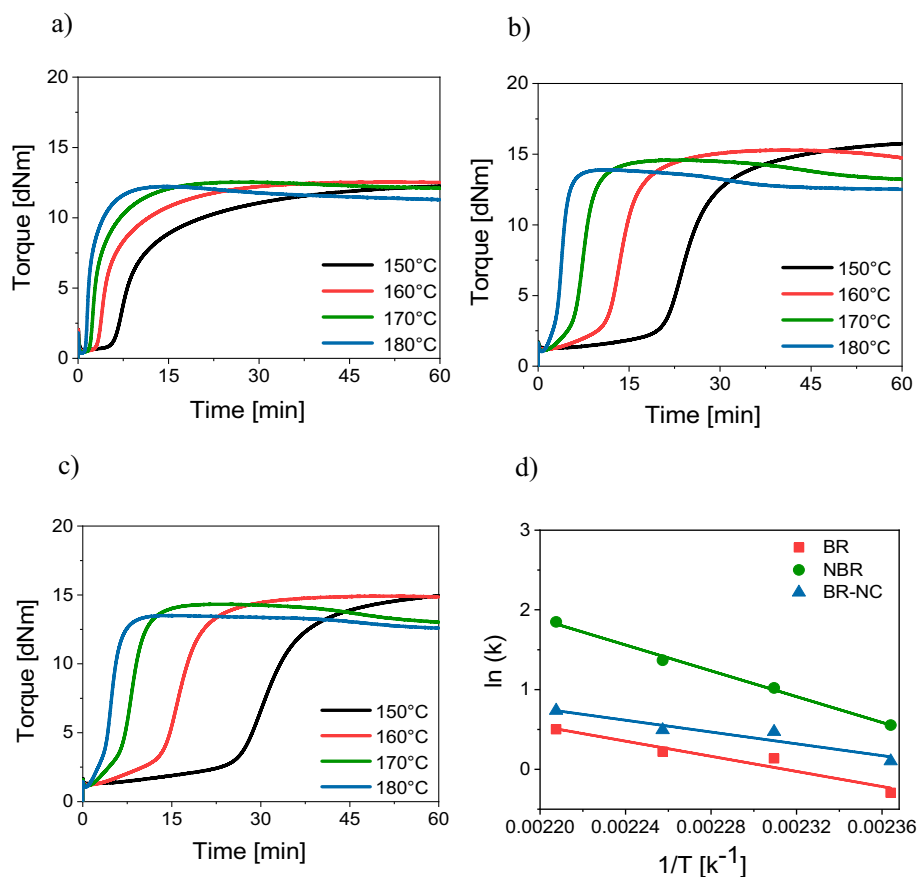
of all the samples of rectangular shape ( $30 \times 10 \times 2 \text{ mm}^3$ ) under tension mode. The measurements were carried out in a temperature range of  $-120$  to  $+100$  °C with a heating rate of 2 K/min at a frequency of 10 Hz under 0.5 % dynamic and 1 % static strain. Elastic modulus ( $E'$ ), viscous modulus ( $E''$ ), damping factor ( $\tan \delta$ ) were plotted as a function of temperature.

## 4. Results and discussion

From rheometric characterization, the parameters related with the curing characteristics like scorch time ( $t_{s,2}$ ), optimum cure time ( $t_{c,90}$ ), maximum torque ( $M_H$ ), minimum torque ( $M_L$ ), maximum rheometric torque ( $M_H - M_L$ ) are shown in Table 2, and the torque-time curve is given in Figure 1. It can be observed from Figure 1 that a small amount of nitrile butadiene copolymer (NBR) accelerated the vulcanization reaction of polybutadiene elastomer (BR). Here NBR resembled as a secondary accelerator (booster) or as a crosslinking agent. Probably, the functionality of NBR (due to the presence of polar -CN group) plays a role in the vulcanization process. It can be seen that due to addition of a small amount of NBR (2.5 phr–10 phr),  $t_{s,2}$  and  $t_{c,90}$  both are reduced significantly for all of the cases. Maximum rheometric torque could be found highest with the sample containing 2.5 phr NBR. Further increase of the NBR reduces the maximum rheometric torque indicating a non-compatible behavior of NBR with BR. Normally, sulfenamide accelerators are known as delayed-action accelerators as they provide delayed scorch. Sulfenamide takes more time to dissociate into smaller fragments and then to start the crosslinking reaction. Though TBBS (a sulfenamide) is used as a primary accelerator in this study, still a reduction in scorch time is observed in the sample containing a small amount of NBR. This can be explained to the higher reactivity of the nitrile group, which might react with the accelerator to form some basic complex, e.g., amine type. Furthermore, this amine acted as an ultra-accelerator or accelerator activator along with zinc oxide and stearic acid. Simultaneously, the zinc ion can also react with the nitrile group to form a zinc-nitrile complex [26] and this complex also takes part in the sulphur vulcanization reaction. This network formation with zinc and nitrile group could also



**Figure 1.** a) Rheometric curing curves of the polybutadiene rubber (BR) gum compound and BR-gum with a catalytic amount (2.5 phr) of nitrile rubber (BR-NC) at 160 °C, b) comparison the curing curve of BR and BR filled with 2.5 phr NBR. All of the samples contain standard sulphur curatives.



**Figure 2.** Rheocurves at four different temperatures of all gum compounds (a) NBR, (b) BR-NC, (c) BR and (d) Arrhenius plot ( $\ln k$  vs  $1/T$ ) for all the compounds. All the samples were compounded with common sulphur curatives.

contributes overall crosslinking density, however, at higher amount of NBR the maximum rheometric torque was not increased as expected. Therefore, the contribution of the zinc-nitrile (complex) towards the overall crosslinking degree could play a very marginal role.

The minimum torque ( $M_L$ ) represents the viscosity of the uncured compound. Sample containing a small amount of NBR shows a reduction in the  $M_L$  as compared to the 100 % BR sample. Most probably, due to the reaction between nitrile group with the accelerator at high temperatures, particularly, at the initial stage, a small reduction in viscosity was observed. Along with the improved rate of vulcanization, an increment in extent of crosslinking (state of vulcanization) is observed with the compounds containing 2.5 phr NBR. Further addition of NBR, the ultimate rheometric torque is also gradually decreasing. At higher amount of NBR, the matrix became an incompatible blend. Several reasons like viscosity

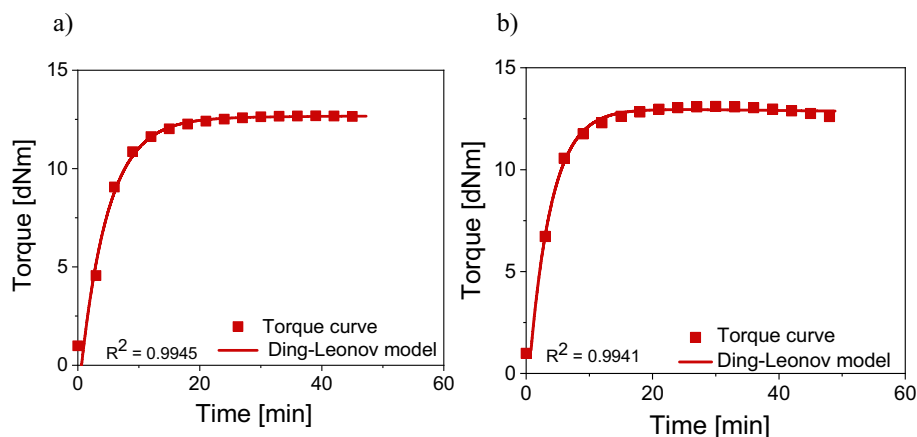
mismatch, cure rate mismatch, higher rubber ratio as compared with a given sulphur curative amount etc. could play a major role here for lowering the ultimate rheometric torque. Therefore, a further investigation with higher amount of NBR is beyond the scope of this study. So, presence of a catalytic concentration of NBR (2.5 phr only) might cause an additional crosslinking during vulcanization. For the same reason the stiffness of the compound also increased, which is reflected in the  $M_H$  value (which is commensurable with the elastic modulus of the compound).

From the curing study, the participation of NBR in the vulcanization reaction is noticed which is associated with the higher torque value as well as, the faster rate of the vulcanization reaction. As mentioned earlier, NBR might react with the present accelerator into the system to form an amine based complex. This amine provides ultra-accelerating

**Table 3.** Kinetic parameters and activation energy of the rubber compounds.

Sample name	T (°C)	k	m	n	$E_a$ (KJ/mol)
BR	150	0.7459	1.5248	1.4460	39.43
	160	1.1458	1.6140	1.3463	
	170	1.2491	1.4788	0.9792	
	180	1.6505	1.3535	0.9429	
NBR	150	1.7420	1.0298	2.8989	67.34
	160	2.7756	0.9274	2.9999	
	170	3.9284	0.8740	2.8489	
	180	6.3530	0.8630	2.6594	
BR-NC	150	1.1077	1.4434	1.7660	30.74
	160	1.6008	1.5757	1.4704	
	170	1.6381	1.4104	1.1026	
	180	2.0882	1.2589	0.8808	





**Figure 3.** Rheometer curve obtained for the gum rubber compound (a) BR, (b) BR-NC at 160 °C. The rectangular dots and the solid lines represent the experimental values and fitted Ding-Leonov model respectively.

**Table 4.** Values of rate constant  $k_2$  (obtained from Ding-Leonov model) and crosslinking densities (measured by swelling method) of gum rubber compounds.

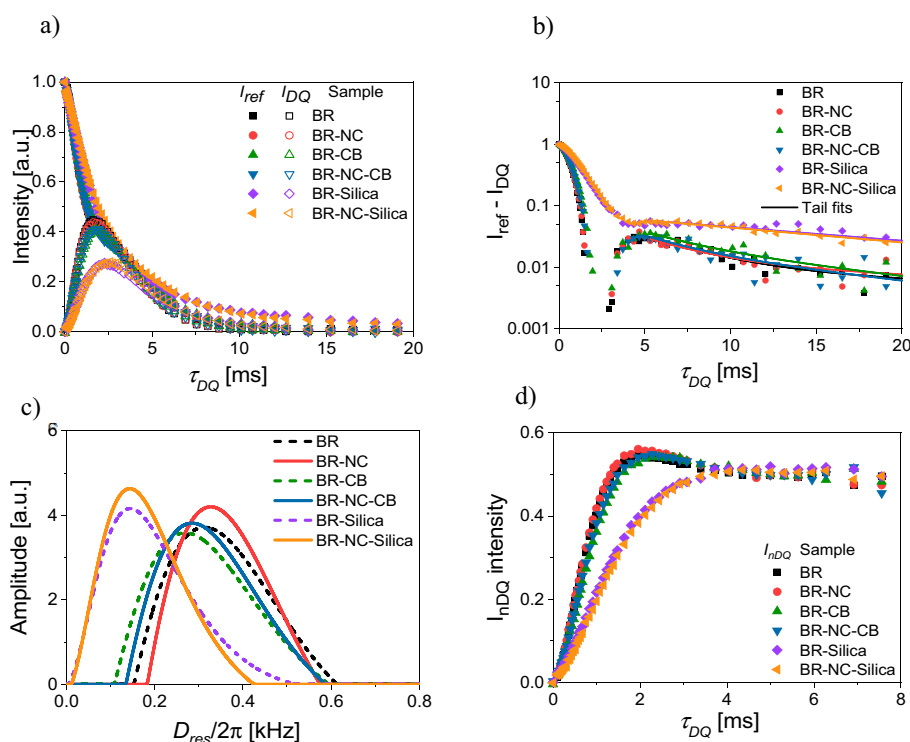
Sample name	$k_2$ ( $\text{min}^{-1}$ )	Crosslink density ( $\text{mol}/\text{cm}^3$ )
BR	0.2225	$4.66 \times 10^{-04}$
BR-NC	0.2857	$5.03 \times 10^{-04}$

activity along with zinc oxide and stearic acid. Simultaneously, NBR also acts as a ligand to form zinc-nitrile complex [26] by reaction with zinc ions. Generally, during crosslinking process an activated intermediate sulphurating zinc based complex is formed. This sulphurating agent creates an anchor between the rubber chains to make them crosslinked. Due to the formation of such zinc-nitrile complex [26], the state of vulcanization was also improved. To emphasize the phenomenon, the kinetics of the vulcanization was studied. The autocatalytic model is used to study the kinetics of vulcanization. The samples were cured at different temperatures, and the corresponding curing curves are shown in

**Figure 2.** Kinetic parameters (as described) for all three compounds are shown in Table 3.

In Figure 2, the activation energies of three different compounds were calculated from the  $\ln k$  vs.  $1/T$  plots, as shown in Table 3. It is noteworthy that a reaction becomes more spontaneous when the value of activation energy is lower at that particular condition. It can be clearly seen in Table 3 that the sample containing a small amount (2.5 phr) of NBR (BR-NC) has the lowest value of activation energy among all the compounds. This indicates that the vulcanization reaction becomes much more spontaneous in the presence of a small amount of NBR.

To further analyze the rheometric data obtained from the moving die rheometer, the Ding-Leonov model was used. Figure 3 shows that this model is well fitted with the experimental results with  $R^2$  value 0.9945 and 0.9941 for BR and BR-NC compound respectively. According to the Ding-Leonov model, a higher value of  $k_2$  indicates a faster rate of vulcanization. In Table 4, it is clearly seen that a higher value of  $k_2$  is obtained for the 2.5 phr NBR containing compound (BR-NC). This study



**Figure 4.** Data analysis of DQ-NMR measurements for the gum and filled rubber compounds. a) Raw DQ build-up ( $I_{DQ}$ ) and reference decay ( $I_{ref}$ ) intensity represented as a function of the double-quantum evolution time  $\tau_{DQ}$  procedure, b) Identification of the non-elastic and isotropically mobile defect fraction, c) Normalized DQ build-up curve obtained after removing the long-time relaxation effects (caused by the polymer dynamics), d) Dipolar couplings distributions obtained by Tikhonov regularization of  $I_{nDQ}$ .

**Table 5.** Network characterization results by means of DQ-NMR and equilibrium swelling experiments.

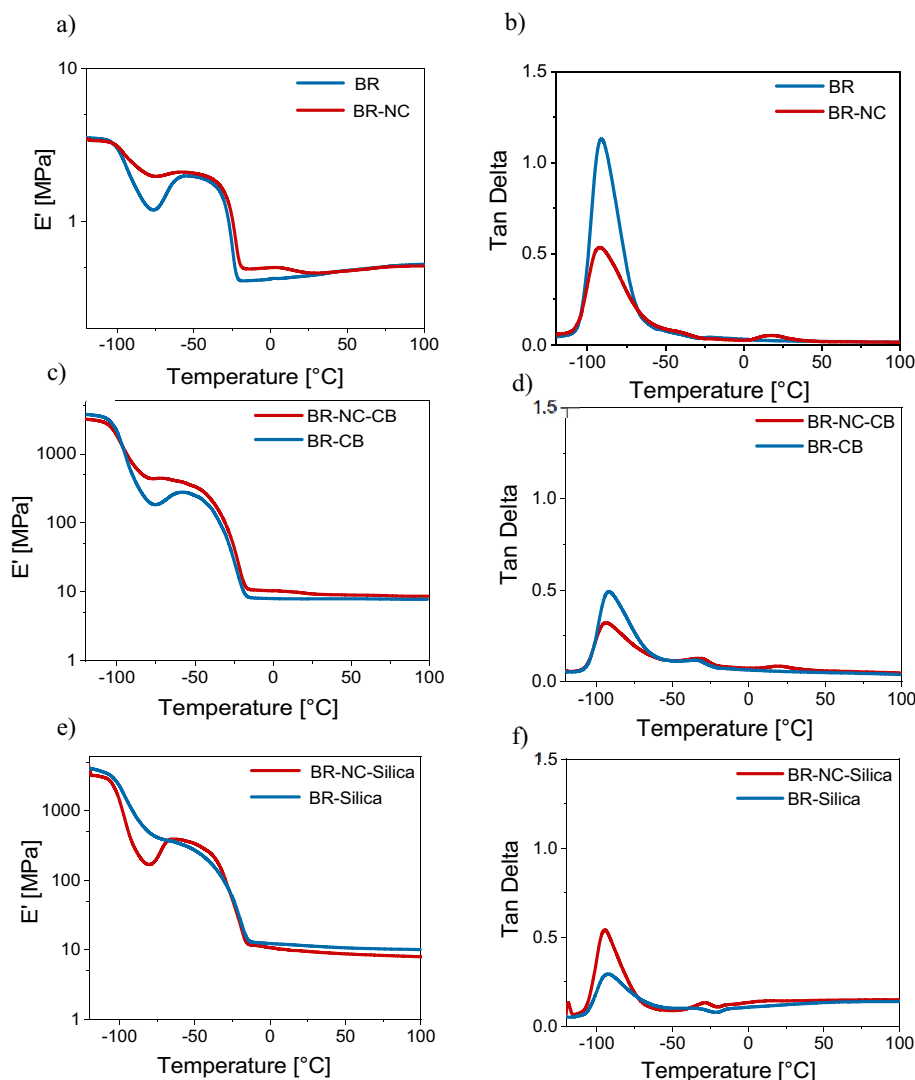
Sample name	% Defects (dry-state)	% Defects (swollen-state)	$D_{res}$ (Hz)	$\sigma/D_{res}$	$1/M_x$ (mol/kg)	$\nu_x \cdot 10^4$ (mol/cm <sup>3</sup> )	Q
BR	9	16	349	0.28	0.565	2.52	3.75
BR-NC	9	18	355	0.24	0.575	2.57	3.63
BR-CB	11	20	310	0.33	0.503	2.17	2.60
BR-NC-CB	10	19	323	0.29	0.523	2.27	2.55
BR-Silica	8	56	193	0.50	0.312	1.37	3.54
BR-NC-Silica	8	64	179	0.46	0.290	1.29	4.45

also confirms that an improved rate of vulcanization is observed in presence of a catalytic amount (2.5 phr) of NBR.

The crosslink density of the rubber compounds was obtained from the swelling experiment. The Flory-Rehner equation [43] was used to calculate the value of crosslink density. As discussed earlier, there is an increment in the maximum torque in case of 2.5 phr NBR containing compound (BR-NC). It is also an indication of raising the value of crosslink density. The results obtained from the curing study are in good correlation with the results obtained from the measurement of crosslink density. It can be seen from Table 4, the value of crosslink density of a 2.5 phr NBR containing compound (BR-NC) is comparatively higher than the compound with 100 % BR. Although, the degree of improvement is not so significant in this aspect. In this study, NBR is used as an accelerator. So, the objective is to achieve a higher rate of vulcanization without affecting

other properties adversely. Here in this case, a significant improvement in rate of vulcanization is noticed. But due to a very small amount of NBR present into the system, But the presence of a minute amount (2.5 phr) NBR results a marginal improvement in other desired properties (e.g., crosslink densities) which is quite obvious. Furthermore, we can interpret the result in such a way that a small percentage of NBR is not only accelerating the rate of vulcanization but also helps to improve the state of vulcanization (network density/degree of crosslinking).

In all above-mentioned studies, only gum compound was included to get insight to the reaction which is responsible for such behavior. From the previous results, a significant improvement in vulcanization characteristics is clearly noticed in presence of a catalytic amount (2.5 phr) of NBR. In this stage, compound filled with carbon black and silica are introduced into the context. To investigate the effect of filler using <sup>1</sup>H DQ



**Figure 5.** Dynamic mechanical properties of cross-linked BR, BR containing small amount of polyacrylonitrile butadiene copolymer (BR-NC) and their composites comprised with carbon black and silica. a) Storage modulus vs. temperature and b) loss tangent vs. temperature for gum rubbers (without any filler); c) storage modulus vs. temperature and d) loss tangent vs. temperature for carbon black filled systems; e) storage modulus vs. temperature and f) loss tangent vs. temperature for silica filled systems.

NMR technique, carbon black and silica filled compounds are considered along with gum compound.

A more in-depth and detailed characterization of rubber network structures was made by performing  $^1\text{H}$  DQ NMR experiments based on the improved [51, 52] pulse sequence of Baum and Pines [53]. The experiment provides two different sets of data as a function of the DQ evolution time,  $\tau_{\text{DQ}}$ : (i) a double-quantum (DQ) build-up curve ( $I_{\text{DQ}}$ ) dominated by dipolar-coupled network segments and (ii) a reference intensity decay curve ( $I_{\text{ref}}$ ) which codify, beyond other additional structural information, the long-time intensity from the uncoupled (isotropically mobile) network defects, e.g. sol fraction, loops and dangling chain ends (Figure 4a). The latter is characterized by a slower long-tail relaxation compared with the faster decay of the dipolar coupled network segments. This difference is amplified by plotting  $I_{\text{ref}} - I_{\text{DQ}}$  (see Figure 4b), and thus the behavior from the non-couple network defects ( $I_{\text{def}}$ ) can be identified and by fitting the long-time data range.

For the studied compounds, the use of two additive exponential functions provides the best fit of the observed long tails, within the exception of those compound filled with silica, where a single exponential function is used for defining  $I_{\text{def}}$ . Using these signal functions, the sum of the total refocused signal is obtained ( $I_{\Sigma\text{MQ}} = I_{\text{DQ}} + I_{\text{ref}} - I_{\text{def}}$ ) and it can be used to remove the temperature-dependent long-time relaxation effects (caused by polymer dynamics) by a point-by-point normalization procedure:  $I_{\text{ndQ}} = \frac{I_{\text{DQ}}}{I_{\Sigma\text{MQ}}}$ . The so-obtained normalized DQ build-up curve (which achieves a plateau value at 0.5 if  $I_{\text{def}}$  is properly defined, see Figure 4c) can be analyzed by using a Fast Tikhonov Regularization (ftikreg) procedure [54] in order to obtain the residual dipolar coupling ( $D_{\text{res}}$ ) distribution between protons for each rubber compound (see Figure 4d). The analysis of these distributions provides the quantification of the distribution-averaged value ( $D_{\text{res}}$ ) and the overall relative distribution width, which is reported as the standard deviation normalized by the average value ( $\sigma/D_{\text{res}}$ ). Table 5 summarizes the different parameters that define the network structure obtained by DQ-NMR measurements.

The Addition of NBR seems to slightly, but systematically, increase the crosslink density (i.e., the molecular weight between constraints seems to be slightly reduced) for the BR compound except those that contain silica. Additionally, the spatial distribution of crosslinks (i.e., the molecular weight distribution between constraints provided by the distribution width) is slightly but systematically, narrower in those compounds containing 2.5 phr of NBR (BR-NC) when they are compared with the BR counterparts without NBR (including the filled composites). This is an important result because of two main reasons:

- i) The incorporation of NBR copolymer as an accelerator has a negligible effect on the NMR signal. According to some previous work [55], the NBR matrix has a much broader  $D_{\text{res}}$  distribution ( $\sigma/D_{\text{res}}^{\text{NBR}} \sim 0.9$ ) than BR compound. However, its incorporation in a quite low amount in the studied samples avoids any interference in the obtained NMR results.
- ii) The reduction in the distribution width provoked by the addition of NBR has to be unambiguously related to an improved and more homogeneous spatial distribution of crosslinks formed in the BR matrix during the vulcanization process.

Finally, it is essential to point out that the addition of fillers has a strong effect on the crosslinking reaction, provoking the reduction in the crosslink density and increasing their distribution width as compared with the unfilled counterparts. The most important effect (by a factor 2) is observed with the addition of silica, being more modest the effect of carbon black on the network structure.

It is crucial to take into account that equilibrium swelling results show the same effect of NBR on the crosslink density when unfilled, CB-filled, and silica-filled compounds are compared individually. It demonstrates the reliability of the results that shows the influence of NBR in the

vulcanization process and the consequent effect on the BR network structure.

Nevertheless, the equilibrium swelling results show a completely different scenario than the NMR results when the effect of fillers on the rubber crosslink density is analyzed. In this case, the equilibrium degree of swelling  $Q$  ( $Q = 1/V_r$ ) is strongly underestimated in the filled compounds because the swelling behavior of these samples is strongly affected by the filler-rubber interface. Fillers act as macro crosslinks and they drastically reduce the swelling capacity of the samples [56], and consequently, an apparent increase of rubber crosslink density in filled compounds could be incorrectly supposed according to the measured degree of swelling (see Table 5). It means that an equilibrium swelling experiment is not the right approach to analyze the crosslink density of filled samples. DQ-NMR measurements overcome these experimental problems, providing the actual crosslink density of rubber matrices in filled compounds without the interference of filler effects.

Finally, it should be noticed that rubber networks are not perfect and they contain elastically inactive defects such as dangling chain ends and unentangled loops, which are attached to the rubber network and therefore un-extractable, and also free (uncrosslinked) rubber chains that is commonly associated to the sol-content of the network. Thanks to recent studies, these network defects (including the non-extractable fraction) are accessible by DQ-NMR spectroscopy [45, 46, 49, 54] because they show slower relaxation processes as compared to the faster decay of the network segments. According to the non-coupled network defects fraction obtained from Figure 4b (e.g. the y-intercept value from the  $I_{\text{def}}$  fitting function) and summarized in Table 5 (e.g., % defects (dry-state)), all the studied samples have similar content (between 8 to 11 %) of these elastically inactive rubber segments. However, a large dependency of the fraction of non-coupled network defects on network density and temperature was noticed [47]. It is noteworthy that the latter one is associated with the terminal relaxation of large and branched structures which is being slow in the millisecond range during DQ experiment (resembling to a slow mechanical relaxation processes in case of an ineffective networks). So, due to the effect of entanglements, the defect fraction might be mostly underrated.

This problem can only be addressed by increasing the measurement temperature, but the main inconvenience for applying this approach is the degradation of the rubber matrix. For that reason, the most reliable quantification of the actual fraction of non-coupling network defects is obtained for swollen rubber samples [50], because an increasing solvent content results in the disentanglement of network defects from network chains, hastening their terminal dynamics and allowing isotropic motion on the experimental time scale. For that reason, the measured fraction of non-coupled network defects in swollen-state (see Table 5) is much higher (by a factor 2) than in the dry state. This effect is especially significant in those compounds filled with silica, revealing that about 55–65 % of the rubber segments act as non-elastic network defects, as opposed to both unfilled and CB-filled samples where this percentage is about 15–20 %. This is a crucial structural information that should be taken into account for a better understanding of the mechanical and viscoelastic properties of these rubber samples [57].

The storage modulus ( $E'$ ) and the  $\tan \delta$  were plotted over a wide range of temperatures for different gum and filled rubber compounds, which is shown in Figure 5. It could be observed that after glass transition, the storage modulus of NBR catalyzed sample (BR-NC) is a bit higher, and at a higher temperature, it is merged with pure BR. The higher crosslinking state of the NBR catalyzed compound might be the reason for such behavior.

The temperature dependence of the storage modulus is completely different for BR compound from BR-NC compound, which can be found in Figure 5a. An abrupt reduction in storage modulus ( $E'$ ) value followed by a further increment from  $-75^\circ\text{C}$  is noticed for pure BR compound at very low temperature (around  $-100^\circ\text{C}$ ). This phenomenon is known as the cold crystallization of polybutadiene rubber (BR) and, surprisingly, such behavior is rarely observed in BR-NC compound.

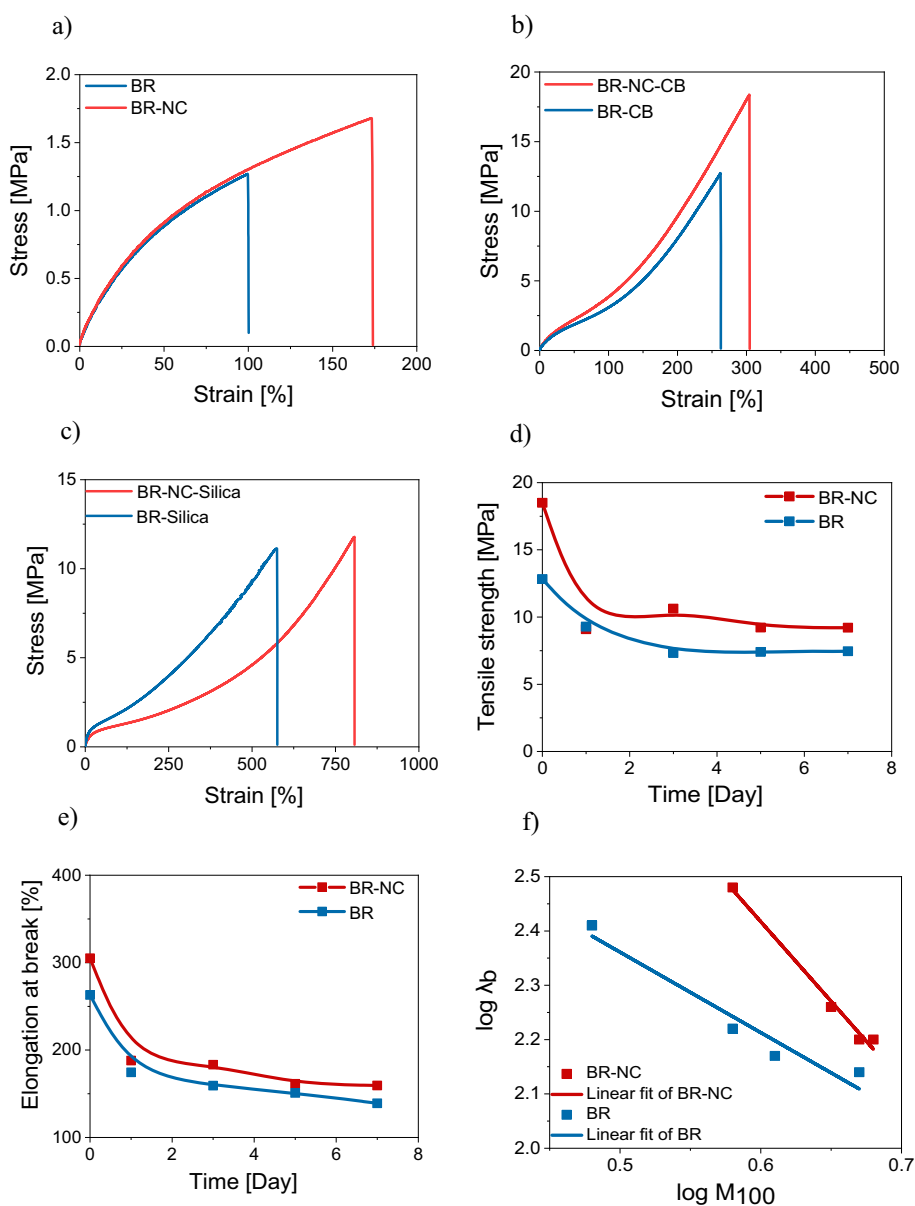


In the beginning,  $E'$  value decreases due to the melting of crystallites with increasing temperature. After that, there is a sudden increment in  $E'$  value, which is observed at around  $-75$  °C and it could be attributed in terms of cold crystallization of BR. In further view at that low-temperature range, the rubber chains might be dynamically activated to form new crystallites with rising temperature, which leads to an increment in  $E'$  value.

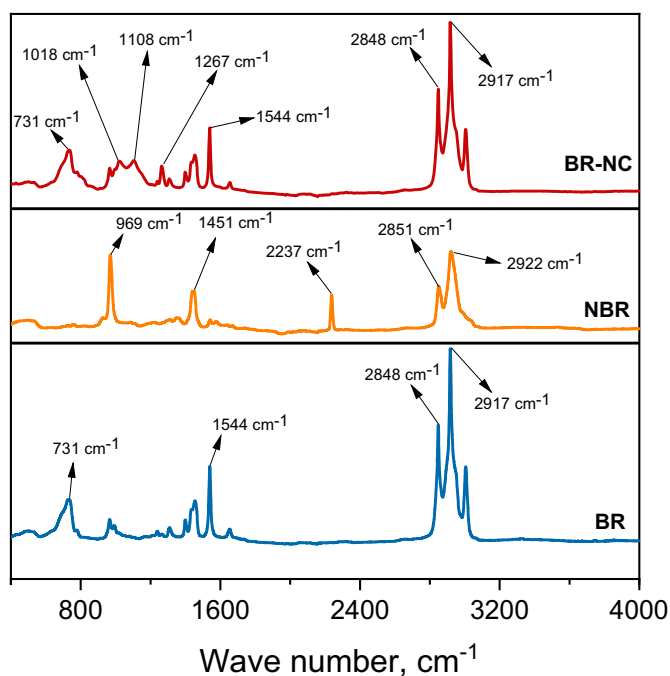
Additionally, as a result, the reduction of  $E'$  value is caused by the remelting of the newly formed crystallites with a further rise in temperature. At a certain heating point the glass-phase is converting to a rubbery phase, but such kind of effect is not so prominent in the case of the BR-NC compound. This might be due to the additional crosslink formation in presence of NBR, which restricts the orientation of the rubber chain and prevent the formation of new crystallites at low temperature region. Furthermore, the participation of the nitrile group in the zinc-nitrile complex formation [26] could lead to additional macro-crosslinking network, which can also inhibit the crystal formation. In pure BR compound, due to the availability of the free elastomer chains, cold crystallization phenomenon is perceived in a distinct way. But with the

utilization of a small amount of NBR (2.5 phr) into the composition leads to a different behavior. It helps to form some additional crosslinks by a chemical reaction (which is mentioned earlier). Due to that most of the free elastomer chains are engaged during crosslinking reaction, which prevents the formation of new crystallites. Cold crystallization behavior is hardly ever observed for the BR-NC compounds, which leads to a negligible impact on the  $E'$  value at that particular low temperature region. In this study, we did not focus deeply into this phenomenon. A detailed study is required to reveal the mechanistic pathways for this peculiar behavior of BR. Loss tangent curves show that the dynamic glass transition temperature at 10 Hz of BR is  $-91$  °C. BR compound containing a small amount (2.5 phr) of NBR shows only one  $T_g$ , which corresponds to the  $T_g$  of a pure BR compound. As the amount of NBR is minimal, the presence of NBR is not reflected in the result as a separate loss tangent peak.

It is interesting to note that a strong reduction of the  $\tan \delta$  value could be observed indicating an increment of the crosslink density of the BR matrix in presence of NBR. The effect of filler on this system was also studied. A slight increase of the storage modulus in the rubbery plateau



**Figure 6.** Stress-strain curve of a) gum, b) carbon black filled, and c) silica filled BR and BR-NC compound, d) Tensile strength, (e) elongation at break vs time of aging (at 80 °C), f) Ahagon plot of the crosslinked rubber compounds.



**Figure 7.** FTIR spectra of BR, NBR, and NBR catalyzed BR samples in ATR mode. All the rubber samples were sulphur vulcanized.

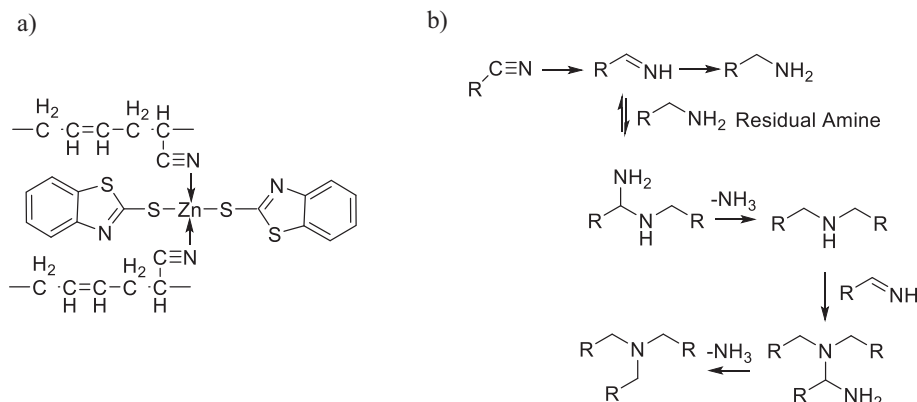
region can be found when the BR is filled with carbon black (CB) and a small amount (2.5 phr) of NBR (BR–NC–CB).

As the amount of NBR is minimal, its contribution to storage modulus could be neglected. However, in the presence of silica, the effect cannot be seen. In this case, a lowering of the storage modulus could be observed when BR is formulated with a small amount (2.5 phr) of NBR (BR–NC–Silica). The catalytic activity of NBR on the sulphur crosslinking reaction is valid only for the gum and carbon black filled compound but not for the silica filled compound. The formation of zinc-nitrile complex [26] helps to produce more active sulphurating agent, which promotes the sulphur crosslinking reaction in a significant way. However, in case of silica filled BR compound with a small amount (2.5 phr) of NBR (BR–NC–silica), the nitrile groups of NBR might interact with the silanol groups of silica which hinders the formation of zinc-nitrile complex [26]. As a result the overall sulphur vulcanization reaction is adversely affected. In this study, along with elastic modulus at rubbery region,  $\tan \delta$  peak height is increased in the silica filled compound (BR–NC–silica) which indicates an adverse effect on the crosslink density.

The addition of a catalytic amount of NBR to BR (BR-NC) influences the tensile properties of the compound as well, particularly, the ultimate elongation at break values. The elongation at break reaches  $\sim 173\%$ ,

where the values for pure BR is  $\sim 100\%$ . Moreover, the tensile strength of the BR-NC is found to be  $\sim 1.68$  MPa, whereas the value of pure BR compound is only  $\sim 1.25$  MPa (Figure 6a). The lower tensile strength and elongation at break values are characteristic features of pure BR due to its nonpolar nature and inability to undergo strain-induced crystallization like natural rubber. It can be imagined that the participation of the nitrile group (BR-NC) can modify the sulphur network by the formation of more poly-sulfidic linkages [58]. This could be the reason that a high elongation at break and tensile strength of the composites is obtained due to the formation of more poly-sulfidic linkages in the presence of a catalytic amount of NBR into the system. In this present study, the high amount of accelerator and a low amount of sulphur were used, and all of the samples contain an equal amount of sulphur. In this regard, a change in mechanistic pathways of sulphur vulcanization could offer higher number of poly-sulfidic linkages rather than mono- or di-sulfidic linkages. It results in a higher elongation with improved tensile strength. Another possible explanation for higher elongation at break is the homogeneous and narrower distribution of the crosslinked chain length when NBR is added to the compounds. However, it could be possible to prove and elaborate the fact with some more additional experiments like the quantitative estimation of di-sulfidic and poly-sulfidic linkages by special swelling experiment and subsequent measurement by NMR technique. But the idea is beyond the scope of this study.

After the addition of reinforcing carbon black to the BR-NC compounds, it is found that the tensile strength is improved as compared with pure BR (Figure 6b). Small particle size of carbon black leads to a large surface area. The chemical reaction in presence of NBR is further facilitated due to the large available surface area. This reflects on the tensile properties of the compound which enhanced for BR-NC compound over pure BR compound. However, inferior tensile properties were realized when the compounds filled with silica without a coupling agent. To study the effect of a small amount (2.5 phr) of NBR on silica filled BR compound, the silane coupling agent is not used. Otherwise, the effect might not be realized due to the silanization reaction. Composites containing un-silanized silica generally show a marching modulus in the vulcanization curve due to the adsorption of other chemical ingredients by hydrophilic silica surface. This kind of behavior is also observed in this study. Even, modulus at 300 % elongation is found to be lower as compared with pure BR compound and almost no change in tensile strength is noticed (Figure 6c). The presence of silanol group hinders the active participation of nitrile group towards sulphurating complex formation during sulphur crosslinking reaction. Simultaneously, a deterioration of network density is noticed. It could be concluded from the previous results that NBR is well-suited as a secondary accelerator for sulphur vulcanization. Not only it accelerates the vulcanization reaction but also it provides improved mechanical properties of the samples. To study the thermal stability of the composite containing a small percentage (2.5 phr) of NBR, aging experiment was carried out.



**Figure 8.** a) Schematic representation of zinc-nitrile complex, b) network formation by nitrile group by residual amine route.

For that experiment, the samples were placed inside an air-aging oven at 80 °C for different time (1, 3, 5, 7 days). After that, aged samples were subjected to tensile measurement. Figures 6d and 6e show a significant reduction in tensile strength and elongation at break (% EB) for both the compound without and with NBR (BR and BR-NC) at 80 °C after 1 day heat aging experiment. However, after 3 days, there is an increment in tensile strength and a slight improvement in % EB for the NBR containing compound is noticed. This might be due to the additional crosslinking in presence of a small amount (2.5 phr) of NBR. This effect is more prominent after 3 days (80 °C) heat aging. This behavior is not observed for the pure BR compound and there is almost no change in tensile strength even up to 7 days and a sharp reduction in % EB is noticed with increasing aging time. There is a slight reduction in tensile strength in case of NBR containing compound with 5 days aging time. After that the properties are retained up to 7 days. However, in absence of NBR, properties are found to be not stable.

Three different types of chemical aging can be identified by plotting  $\log \lambda_b$  vs  $\log M_{100}$ , which is known as the Ahagon plot [59]. The aforementioned parameters are associated with the following phenomenological equation  $\lambda_b = A^*(M_{100})^{-0.75}$ , where  $\lambda_b$  is % elongation at break (strain value at break) and  $M_{100}$  is the stress value at 100 % strain. The mechanism of aging reveals; Type-1: aerobic or anaerobic at a lower temperature, Type-2: anaerobic at a higher temperature, and Type-3: aerobic at a higher temperature. In Type-1 aging, typically reduction in  $\lambda_b$  and increment in  $M_{100}$  are observed, which is nothing but an indication of improved state of vulcanization. It indicates an increment in crosslink density, which is quite relevant to this work.

Figure 6f represents  $\log \lambda_b$  vs  $\log M_{100}$  curve for both the composite, which exhibits the tendency of Type-1 aging. So it could be concluded that Type-1 aging is noticed for this study where a reduction in  $\lambda_b$  and an increment in  $M_{100}$  is observed. This corresponds to an improved crosslink density of the compound in presence of a catalytic amount of NBR.

FTIR analysis was performed to gain more knowledge about the formation of different rubber bound complexes. In Figure 7, the IR spectra obtained from three different compounds are shown. Two sharp peaks can be observed at 2848  $\text{cm}^{-1}$  and 2917  $\text{cm}^{-1}$  for both BR and BR-NC compounds, which were appeared due to the C–H stretching of the  $\text{CH}_2$  groups. Another characteristic peak at 2237  $\text{cm}^{-1}$  was assigned for the NBR compound, which is due to the presence of –CN groups in NBR. Surprisingly, in the case of BR-NC compound (BR compound, with 2.5 phr of NBR), the peak at 2237  $\text{cm}^{-1}$  is disappeared, and in-addition three new peaks were appeared at 1018, 1108, and 1267  $\text{cm}^{-1}$ . As the NBR used here only 2.5 phr, due to dilution effect the peak may be disappeared. Moreover, it is a clear indication that –CN group of NBR was involved in a chemical reaction, which could form new complexes with zinc ion. A plausible chemical reaction or intermediate involved with nitrile group is shown in Figure 8. During vulcanization reaction, amines are produced which are free to further react resulting tertiary amine type product which can be interlinked with rubber chains.

This reaction can be referred as catalytic coupling reaction [60]. Due to the formation of tertiary amine structure, a peak at 1267  $\text{cm}^{-1}$  appeared for C–N stretching. As far as the zinc-nitrile complex is concerned, the active sulphurating agent formed during the vulcanization reaction might further involved in the reaction with the nitrile group of NBR to form a zinc-nitrile complex [26]. As a ligand it donates the electron pair to the zinc present in the complex structure and accelerate entire process. This might be the reason for a new peak appeared at 1018  $\text{cm}^{-1}$ . Another peak at 1108  $\text{cm}^{-1}$  could be assigned to the C–H in-plane bend vibration of the newly formed complex.

## 5. Conclusions

The main goal of the present work is to study the catalytic role of nitrile functionalities as an accelerating agent in sulphur vulcanization of diene rubber-like BR in terms of vulcanization characteristics without

affecting the other properties (i.e., mechanical properties, dynamic mechanical properties) of the rubber composites. The type of chemical reactions involved and also the nature of the formed complex are discussed based on different experimental findings. The acceleration in the sulphur vulcanization reaction due to participation of nitrile group of NBR is investigated and the crosslinking kinetics concerning the activation energy are studied based on various available mathematical models. The formation of carcinogenic N-nitrosamines during vulcanization reaction in the presence of conventional secondary accelerators is a major issue from the environmental point of view. The utilization of NBR as a secondary accelerator could be a possible way to avoid the formation of carcinogenic N-nitrosamines. Consequently, the network structure of vulcanized rubber compounds also has been modified in presence of NBR by increasing the average crosslinking density and improving the homogeneity in the spatial distribution of crosslinks during the vulcanization process. Finally, this humble approach to use NBR as an active accelerating agent to vulcanize other diene rubber may pave a new way in rubber research to understand and utilize the concept in different technological applications.

## Declarations

### Author contribution statement

Sakrit Hait: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Juan L. Valentín: Analyzed and interpreted the data; Wrote the paper.

Antonio G. Jiménez, Pilar B. Ortega, Anik K. Ghosh: Performed the experiments.

Klaus W. Stöckelhuber, Gert Heinrich: Analyzed and interpreted the data.

Sven Wießner: Contributed reagents, materials, analysis tools or data.

Amit Das: Conceived and designed the experiments; Analyzed and interpreted the data.

### Funding statement

This work was partially funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - within the Research Training Group RTG 2430 "Interactive Fiber Elastomer Composites".

### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

## Acknowledgements

The authors are thankful to Rene Jurk and Holger Scheibner for technical help and measuring the mechanical properties.

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