



## Mechanical degradation of elastomers in the presence of silica and inhibitors using a new design of mechano reactor

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### ABSTRACT

A newly designed mechanochemical reactor has been home built and used to investigate mechanical degradation of SBR rubber and SBR/SiO<sub>2</sub> blends under N<sub>2</sub> and O<sub>2</sub> atmosphere and in the presence of aromatic amines (DTPD) and tetramethyl piperidine (HALS) radical inhibitors. Continuous on line determination of torque, temperature and O<sub>2</sub> uptake have been made together with solution viscosity and mechano-radical yields at definite time intervals. The fraction of mechanical energy resulting in chemical effects is determined to be less than 0.01%. Chain scission and crosslinking are found to be major mechanochemical reactions with crosslinking acquiring importance with increasing the processing time. According to the results of COGEF type DFT UB3LYP 6-311++G (d,p) relaxed scan computations, the favoured chain scissions sites are predicted to be the ones leading to allylic (prominent) and benzylic radicals. The kinetics of mechano-radicals formation is coherent with torque and viscosity decay kinetics being expressed by the equation  $[R^*](\text{mol/kg}) = -0.0775 \times 10^{-2}t^2 + 0.6755 \times 10^{-2}t$ .

The mechano-radical yield is greater than expected from the chain scission yield; furthermore, oxygen and radical inhibitors have minor effects on torque and viscosity decay kinetics in the first part of the process where chain scissions are dominant, whilst they do inhibit crosslinking. It is inferred from these results that a significant part of permanent chain scissions takes place via caged-radical disproportionation and that only scavengeable mechano-radicals escaping cage reactions are responsible for the initiation of crosslinking.

From free radical chemistry analysis supported by DFT calculations it is inferred that H abstraction and 1-3 double bond addition by chain scission allyl radicals can be major paths for crosslinking initiation, the addition mechanism acquiring importance with increasing reaction time. The oxygen uptake is approximately linear with process time and consequently does not fit the formation and decay kinetics of scavengeable mechano-radicals; it is suggested that the contribution by other mechanisms involving mechanical excitation coupled with thermal activation may be important. The addition of SiO<sub>2</sub> filler causes an increase of total absorbed mechanical energy and a decrease of the equilibrium molecular weight limit (enhanced chain scissions). In contrast, the scavengeable mechano-radicals yield is found to be less than 50% of that determined in the absence of SiO<sub>2</sub>. These observations are related to the mechanical degradation of bound rubber in conditions of enhanced cage effect and build up of frictional energy by silica-rubber Van der Waals interaction.

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### 1. Introduction

Understanding the mechanism of polymer mechanical degradation in processing conditions, normal function and laboratory experiments is an essential prerequisite for improving material

properties and lifetime prediction [1]. A mechanochemical process is a multistage phenomenon involving at least three main steps: a) mechano-activation, b) mechano-cracking; c) macroscopic cleavage. The first step corresponds to modification of bond lengths and bond angles coupled with conformational changes (unfolding) of chains with a consequent increase of potential energy. This mechano-excited state precedes the second stage where chemical reaction, often mediated by mechano-radicals from bond cleavages, takes place. The third stage is just the evolution of the molecular damage to a macroscopic level causing a structural reorganization of polymeric material and related effects on mechanical properties.

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Chain scissions generally occur near the midpoint where frictional forces between monomer units accumulate [2–6]. This selectivity is a peculiar difference with respect to peroxide induced degradation which is essentially a random process [7]. When a coiled polymer is submitted to elongational strain the chain first begins to elongate by uncoiling than scission occurs when the energy bond limit is achieved. The stretching force is zero at ends and maximum at the centre with a proposed Gaussian [8–10] distribution within the middle 15% of the chain. The probability for chain scission increases with increasing molecular weight as a consequence of strain accumulation at critical sites which implies that the forces reach their maximum where all of the small contribution from monomer units of the two halves work together [6,8–10]. It is now generally accepted that the chain scission mechanism is based on homolytic bond cleavage with formation of neutral free radicals intermediates [11–13], however a proposal of heterolytic bond scission in polar solvents has also been made [14]. The relationship between average molecular weight and shear stress has been analysed within the framework of several models. According Nguyen and Khaush, the equilibrium molecular weight limit for degradation follows a  $1/M$  relationship with increasing shear stress [3,4,6,15], whilst, according to Smith and Chou,  $1/M^2$  dependence should apply [16]. In the stretched polymer chain bond cleavage occurs when thermal fluctuations overcome the bond length limit, so mechanical energy cooperates with vibrational (thermal) energy for bond cleavage by decreasing the activation energy. This cooperation is effective only if stress energy is applied in a time lower than the bond vibration period ( $<10^{-10}$  s). Within this framework the theoretical model TABS (Thermally Activated Bond Scission) has been developed [6,17] which strictly pertains ultrasound induced polymer degradation but it is likely to be generally valid for all types of mechanochemical reactions. The TABS model is embodied in the equation:

$$k_0 \propto \exp \left[ -U_0/(kT) + (\alpha/l)\beta N^2/8 \right]$$

where  $k_0$  is the specific rate of chain scission,  $U_0$  is the minimum potential energy in the Morse bond stretching equation,  $\beta$  is proportional to strain rate,  $N$  is the number of monomers units,  $\alpha$  is the stretched bond length and  $l$  is the monomer length. A variant of the model which embodies the concept of mechanical bond cleavage as a thermally activated process is that of Zhurkov where the activation energy for bond rupture in an Arrhenius type equation is expressed by the difference ( $E_A - \alpha\sigma$ ) where  $E_A$  is the thermal activation energy,  $\sigma$  is the tensile strength  $\alpha$  is a proportionality constant for dimensional homogeneity [13]. Mechano-activation not only affects the chemical structure of the polymer by chain scission and/or crosslinking but also enhances sensitivity toward chemical reactions so that it can be used to initiate chemical processes of practical use (reactive processing) [2]. Recently interest for mechano-chemistry research was prompted by the discovery of mechanically sensitive chemical groups (mechano-phores) which enable specific reaction pathways to be activated which are not allowed by other initiation methods [18,19]. This framework of fundamental and practical interests does justify the increasing number of studies devoted to mechano-chemistry and carried out sometime with the help of very sophisticated experimental and theoretical methods [2,6]. In this work, unexploited aspects of the mechanism of mechano-chemical degradation of styrene-co-butadiene (SBR) rubber are investigated under anaerobic and oxygen atmosphere in the presence and absence of radical inhibitors by addressing the attention to specific features of the mechanism as the determination of the energy fraction going into chemical effects, the mechano-radicals yield and its material balance with chain scissions, the ability of radicals scavengers to

interfere with chain scission and crosslinking yields, the effect of silica filler in SBR/silica blends. The results are analyzed within the framework of free radical chemistry knowledge supported by kinetic and activation parameters available from literature in order to arrive at new insights of chain scission and crosslinking mechanisms. A significant achievement of this work is also the development of a new design homemade mechano-reactor suited to fit the experimental needs of the investigation [20].

## 2. Experimental

### 2.1. The mechano-chemical reactor

A technical description of the mechanochemical reactor is given in the scheme and picture shown in Figs. 1 and 2.

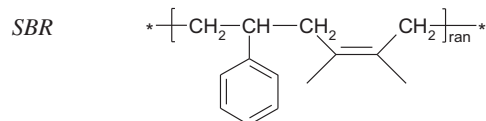
The apparatus is powered with an ICME electric motor (0.5hp, 0.37 kW, 50 Hz, 230 V, 3.2 A, rotation speed 105 rpm). The 22 cm<sup>3</sup> processing chamber consists of a fixed and a rotating plate both bearing uniformly distributed interpenetrating pins of 9 mm length; the fixed grinder plate is connected to a Tekkal BM 4500 torsionmeter for on line torque measurements; the data from the torsionmeter are transferred to the acquisition system via an A/D converter. For gas (N<sub>2</sub>, O<sub>2</sub>) admission at the start of the reaction and the on-line oxygen uptake measurement, the processing chamber is connected via a vacuum rack to a gas volumetric apparatus using silicone oil as manometric fluid. Temperature control during processing is made by a water circulation through coils embedded within the walls of the processing chamber; a thermocouple located at less than 0.1 mm from the interior of the processing chamber is used for continuous temperature monitoring.

The temperature in the processing chamber, after an initial (<10 min) transitory change of 2 °C is kept constant at 25.5 °C for the entire course of the reaction (inset in Fig. 1).

### 2.2. Materials

The following materials were used as received:

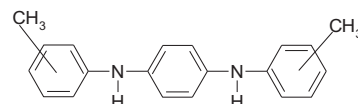
- Styrene-co-butadiene copolymer SBR-1500 (76.5% butadiene, 23.5% styrene, 20% vinyl double bond);



SBR was purified from trace amounts of a phenolic additive by Soxhlet extraction with a 70/30 ethanol/toluene solvent.

- Precipitated silica Zeosil 1165 with total surface area within 160–170 m<sup>2</sup>/g.

As radical inhibitors in mechanochemical experiments, N,N'-ditolylparaphenylenediamine (DTPD) and the HALS Tinuvin 770 were used. SBR samples containing about 1% of DTPD or T770 were prepared by vacuum evaporation of SBR samples swollen with calculated volumes of the additives in tetrahydrofuran



N,N'-ditolylparaphenylenediamine (DTPD)

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