



Role of strain induced crystallization and oxidative crosslinking in fracture properties of rubbers



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ABSTRACT

Tensile properties and crack propagation properties, especially critical strain energy release rate in mode I, G_{IC} , have been used to investigate fracture properties of elastomers and their relationships with microstructure. These investigations were mainly based on a series of comparisons: first, the behaviour of polychloroprene rubber (CR), undergoing stress hardening due to strain induced crystallization (SIC) and oxidative crosslinking (OCL) was compared with that of chlorinated polyethylene (CPE), which undergoes SIC but not OCL, and with a polyurethane based on hydroxyl terminated polybutadiene (PU) which undergoes OCL but not SIC. Comparisons were also made on CR between fracture behaviour at ambient temperature, where SIC occurs and at 100 °C where there is no SIC. Finally, oxidative crosslinking was used to vary in a continuous way the crosslink density in CR and PU, in order to evaluate the role of crosslinking in fracture behaviour.

The results reveal the strong contribution of SIC to fracture strength. Crosslinking, even at low conversion, inhibits SIC which explains the sharp decrease of CR toughness in the early period of exposure to oxidation. When SIC has disappeared, it is possible to appreciate the effect of crosslinking on fracture behaviour. This effect, as evaluated from the density of deformation energy at rupture in tension or from G_{IC} value, is almost negligible while the sample modulus increases regularly as a consequence of crosslinking. It appears that the toughness remains almost constant because it is under the influence of two contradictory phenomena: the negative effect of a reduction of ultimate elongation and the positive effect of a modulus increase. Such behaviour can be explained in terms of heterogeneous distribution of the lengths of elastically active chains. After long exposure, the sample behaviour becomes brittle, very high modulus values indicate that the samples approach, presumably in a heterogeneous way, the glassy state.

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1. Introduction

This article deals with fracture properties of chlorinated elastomers, their relationships with structure, and the consequences of their oxidative ageing on these properties. There is a relatively abundant literature on the effect of crosslink density on fracture properties of elastomers. These studies have been performed essentially on network families of well controlled architecture such as crosslinked polydimethyl siloxanes [1,2] or polyurethane elastomers [3], in which all the additives susceptible to modify the

mechanical behaviour, especially fillers, were avoided. A peculiar attention has been paid to the quasi equilibrium properties which could be deduced from the network theory and the theory of entropic elasticity applied to quasi ideal networks in which the length distribution of elastically active chains (EAC) would be unimodal. In such cases, a key characteristic is the number of chains crossing a unit area in unloaded state [4]; according to Lake [5], there is a simple relationship with the molar mass M_c of EACs:

$$G_{IC0} = K.M_c^{1/2} \quad (1)$$

where G_{IC0} is the threshold tear strength that characterizes fracture free of viscoelastic or strain induced crystallization (SIC) effects. K is mainly related to the rupture energy of a single chain. This kind of

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relationship has been experimentally checked by various authors [6–8], but counter-examples have also been found. For instance Yanyo observed that in polydimethyl siloxane networks, the fracture behaviour depends also on the length distribution of EACs [9]. This was confirmed by Mark and co-workers [1,2] who studied a series of polydimethyl siloxane networks based on long chains to which variable quantities of short chains were added. It appeared that the modulus increases regularly with the average crosslink density. In contrast, the ultimate elongation does not vary with the crosslink density except at high concentrations of short chains, showing that in a wide interval of crosslink densities, for a bimodal network, the fracture behaviour remains controlled by the extension of long chains. In such systems, indeed, the fracture energy increases regularly with crosslink density as long as ultimate elongation remains constant.

“Equilibrium” fracture properties are interesting from a theoretical point of view but they do not correspond to the real use conditions of rubbers. Under such conditions, viscoelastic effects cannot be ignored. Persson [10] proposed a simple equation to represent the contribution of viscoelasticity to toughness:

$$G_{IC} = G_{IC0}[1 + \varphi(T, v)] \quad (2)$$

where G_{IC0} is the “equilibrium” G_{IC} value and $\varphi(T, v)$ is a function of temperature T and crack velocity v expressing the contribution of dissipative, viscoelastic processes to fracture energy. This approach has been used recently in a study of fracture properties of polyurethane elastomers by Cristiano et al. [3]. The fracture behaviour depends not only on crosslink density but also on the type of crosslinks [11].

Some elastomers, e.g. natural rubber at elongations higher than c.a. 200%, undergo strain induced crystallization (SIC) [12–17], because they have a regular chain structure and, due to entropic effects linked to chain orientation, their melting point tends to become higher than the test temperature. Crystallization at the crack tip increases the crack propagation energy significantly. In other words, SIC improves the fracture strength substantially [12].

The technological interest of SIC has resulted in a large number of studies which were recently reviewed by Huneau [17] who concluded that there is an optimum crosslink density of the order of 0.13 mol/kg to obtain the highest SIC effect. At low crosslink densities, crosslinks favour chain orientation upon tensile loading because they prevent loss of orientation by chain relaxation. At high crosslink density, crosslinks appear as defects limiting crystallinity.

For the family of unsaturated elastomers, oxidative crosslinking is often the major mode of atmospheric thermal ageing because in these polymers, macro-radical addition to double bonds is an important propagation process for radical oxidation. Indeed, intermolecular addition, responsible for crosslinking, coexists with intramolecular addition, responsible for cycle formation and eventually with other processes such as chain scission, but in several cases, among which the polychloroprene (CR) and polyurethane (PU) studied here, crosslinking predominates. It seemed to us interesting to study its consequences on fracture behaviour, which can bring valuable data, both in the domain of structure–property relationships and in the domain of rubber ageing.

The fracture properties of elastomers have already been studied from this point of view [18–24], including studies on polychloroprene [19,20], but unfortunately the measurements were made on thick samples. In these oxidation is diffusion controlled [25] in such a way that an aged sample tends to adopt a sandwich structure with an undegraded core and two degraded superficial layers. Indeed, the change in fracture properties of such samples is not easy to interpret. For this reason it seemed to us interesting to study the effect of oxidative ageing on samples either undergoing

crosslinking or not, and either displaying or not SIC. For the interpretation of oxidation mechanisms and kinetics, we used classical theories [26] [27] but powerful numerical tools are available for the resolution of kinetic schemes [28].

2. Materials and methods

2.1. Materials

The three elastomers considered in this study are polychloroprene (CR), chlorinated polyethylene (CPE) and polyurethane (PU). CR is a sulphur cured material. CPE is a peroxide cured material without any fillers and the PU is made of hydroxyl terminated polybutadiene (PBHT) cured by the diisocyanate derived from methylene dianiline (MDI) in stoichiometric ratio. It should be noted that none of these materials contain any stabilization additives nor reinforcing fillers. Initial molar mass between crosslinks, M_c has been evaluated from tensile modulus measurements using the classical rubber theory linking the molar mass between crosslinks and the rubber modulus [29]:

$$M_c = \frac{\rho \cdot RT \cdot (\lambda - \lambda^{-2})}{\sigma} \quad (3)$$

where ρ is density, R is the gas constant, T is temperature in K, λ is elongation and σ is stress.

These data are reported in Table 1. T_g was measured using Q200 DSC with a typical 10 °C/min scanning speed.

2.2. Ageing

Ageing was performed on 200 μm thick films in Memmert ovens with forced convection at 100, 120 and 140 \pm 2 °C. These temperatures have been chosen high enough to obtain significant changes in reasonably short times. Special care was taken on homogeneity of the degradation through sample thickness in order to avoid diffusion limited oxidation (DLO). This latter aspect has been studied previously for oxidation of CR [25] and PU-PB [30]. The films were cut from bulk samples, cooled by liquid nitrogen, with a Leica microtome.

2.3. Molecular modification

Chemical modifications such as double bond consumption and carbonyl formation have been followed by FTIR spectroscopy in transmission mode using thin films (about 10 microns). During exposure, FTIR analyses have been performed on a Perkin Elmer Spectrum 2 with a resolution of 4 cm^{-1} and double bond concentration has been assessed by using the peak at 1660 cm^{-1} (typical FTIR results are plot in Appendix 1). In order to convert the absorbance at 1660 cm^{-1} into a concentration value, the Beer–Lambert law has been used with a molar absorptivity equal to 25 l mol^{-1} cm^{-1} [30].

Table 1
Initial characteristics of rubbers used in this study.

Elastomer	Acronym	Modulus (MPa)	Density (g/cm^3)	M_c (kg/mol)	T_g (°C)
Polychloroprene	CR	1.89	1.40	5.50	–40
Chlorinated polyethylene	CPE	2.91	1.17	2.99	–21
Polyurethane	PU	3.78	0.90	1.77	–63

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