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Crosslinking, thermal properties and relaxation behaviour of polyisoprene under high-pressure

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ABSTRACT

The transient hot-wire method has been used to measure the thermal conductivity κ and heat capacity per unit volume ρc_p of untreated (virgin) and crosslinked *cis*-1,4-poly(isoprene) (PI) in the temperature range 160–513 K for pressures p up to 0.75 GPa. The results show that the crosslinking rate of the polymer chains becomes significant at ~513 K on isobaric heating at 0.5 GPa changing PI into an elastomeric state within 4 h without the use of crosslinking agents. The crosslinked PI and untreated PI have about the same $\kappa = 0.145\ \mathrm{Wm^{-1}\,K^{-1}}$ and $c_p = 1.81\ \mathrm{kJ\,kg^{-1}\,K^{-1}}$ at 295 K and 20 MPa, but different relaxation behaviours. Two relaxation processes, corresponding to the segmental and normal modes, could be observed in both PI and crosslinked PI but these have a larger distribution of relaxation times and become arrested at higher temperatures (~10 K) in the latter case. The arrest temperature for the segmental relaxation of untreated and crosslinked PI, for a relaxation time of ~1 s, are described well by the empirical relations: $T(p) = 209.4\,(1 + 4.02\,p)^{0.31}$ and $T(p) = 221.3\,(1 + 2.33\,p)^{0.40}$ (p in GPa and T in K), respectively, which thus also reflects the pressure variations of the glass transition temperatures.

1. Introduction

The name 'rubber' was first used by Joseph Priestley in 1770 to describe the material which could rub out lead pencil marks from a paper, but later it has become almost synonymous with an elastomer, i.e. a polymer which can be reversibly extended, in some cases several times its own length. A rubber material consists of many components, but the polymer itself is the most important in determining the properties and performance. In general, rubber materials contain a filler e.g. carbon, silica and clay or whiting. Moreover, a rubber, or elastomeric, material is normally produced using a vulcanization system, i.e. crosslinking agents, accelerators, activators and retarders of the crosslinking reaction. The composition of the vulcanization system will determine both the properties of the vulcanized material and the characteristics of the crosslinking process. All these main components of the rubber: polymer, filler and vulcanization system normally form the basis of a rubber material.

One of the most well-known polymers is poly(isoprene) PI. It is used commercially for cases requiring low water swell and high gum tensile strength. It is also used as reactive plasticizer. Its monomer, isoprene, is highly reactive, capable of polymerizing when heated or by use of catalysts. PI is amorphous under normal condition, but it crystallizes on stretching. It is the main constituent of the natural rubber obtained from the latex of *Hevea brasiliasis* (tree rubber). Natural rubber is a polymer of mainly *cis*-poly(isoprene) with a relative molecular mass in the range 100,000–1000,000. Almost all of the poly(isoprene) production is devoted to *cis*-1,4-poly(isoprene), i.e. the synthetic version of the major polymer in natural rubber.

The vulcanization of rubber, i.e. the process of crosslinking between polymer chains with the aid of sulfur, improves the rubbers' mechanical strength, elasticity, and reduces its sensitivity to changes in temperature [1]. The

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effects of crosslinking are most important and best understood for elastomers. The viscoelastic and heat resistance properties of polymers are dependent on the type of crosslink, e.g. sulfur or carbon–carbon, and on the degree of crosslinking. Increasing degree of crosslinking, raises the glass transition temperature of a polymer and the polymer becomes harder, which is due to the restrictions introduced by a crosslink on the molecular motions of the chain. The vulcanization process is normally accomplished by adding various amounts of sulfur and other chemicals that accelerates the crosslinking process to shorten the time and/or lowering the temperature needed for crosslinking. Dependent on the product other chemicals are added for reinforcement anti-degradants and processing aids. During the vulcanization process, it is common to apply slight pressure to shape samples as well as to improve their mechanical properties. Pressure may also affect the crosslinking rate, which can decrease or increase depending on the polymer [2].

As shown here for PI, it is possible to crosslink a liquid polymer to form an elastomeric state purely by high-pressure treatment, i.e. without the use of vulcanization chemicals. It has been shown previously that high-pressure crosslinking can be used to form, for example, poly(butadiene) and nitrile rubber [2, and references therein], and more recently that tetraethylene glycol dimethacrylate can be both polymerized and crosslinked under pressure [3]. Since the vulcanization system can be omitted, this is an environmentally friendly method. Moreover, the significantly higher sample density during the crosslinking process (typically 10–20%) can be important for obtaining improved properties. Especially in the case of polymer composites since the interaction between the components is enhanced. This work is aimed at establishing good conditions for crosslinking in PI at high-pressures for future use in composite synthesis and to determine its effect on thermal properties and relaxation behaviour.

The relaxation behaviour of polymers is complex and at least three distinctly different processes can commonly be observed, which are typically referred to as α-, normal and β-relaxation processes. The main, or most prominent, process is the α-process, which is associated with the segmental motions within the polymer chains. The arrest of these motions is responsible for the glass transition in polymers. The normal process, which is normally less pronounced than the α-process, is attributed to motions of the whole polymer chain, i.e. the polymer backbone. Since the process is associated with whole chain motions, the relaxation time is dependent on the molecular mass. It has been shown to move toward higher frequencies with decreasing molecular mass and, in fact, merges with the α-process for very low relative molecular masses, i.e. the relaxation times of the normal and segmental modes become identical. Moreover, the α- and the normal processes also tend to merge with increasing relaxation time or, equivalently, decreasing temperature at atmospheric pressure. The normal mode process occurs at lower probe frequencies than the α-process at constant temperature and pressure. Consequently, if the two processes are studied in isothermal or isobaric measurements using a constant probe frequency, then the normal process becomes arrested at slightly higher temperatures or lower pressures than the α-process. The third process which is often observed in polymers, the β-process, freezes-in at even lower temperatures or high-pressures. Although it is considered as a universal phenomenon a β-process was reported only recently to occur in PI [4]. However, since it is very weak, i.e. associated with very small changes in the heat capacity, it cannot be observed in studies using the hot-wire method and can therefore be ignored in the discussion here concerning the relaxation processes of PI.

The normal and segmental mode processes in PI (not crosslinked by vulcanization or high-pressure treatment) have been studied previously at atmospheric pressure [5–10], and high-pressure [11–14] for both molecular masses above and below the entanglement limit ($M_e = 5400$). Schönhals [8] has studied PI with relative molecular masses M in the range 1000–8000 using dielectric spectroscopy at atmospheric pressure, showing that the two processes tend to merge on cooling.

Elastomeric PI, i.e. PI that has been crosslinked by vulcanization has been studied by dielectric spectroscopy [15]. Donth et al. [15] followed the changing character of the relaxation processes with increasing degree of vulcanization. These results show that the relaxation process of the normal mode becomes broader, or its strength decreases upon vulcanization and new modes appear, which Donth et al. [15] referred to as “Rouse-like modes”. These appear in the frequency range in between the normal and segmental modes, which gives a very broad dielectric loss spectrum.

Heat capacity spectroscopy [16] has also been used to study natural rubber [17]. The results are interesting since the method is the frequency domain counterpart of the transient hot-wire method employed here. The results obtained using heat capacity spectroscopy at atmospheric pressure show only one relaxation process, which presumable means that the segmental and normal modes cannot be separated in these results.

In this study, the thermal properties of untreated PI and crosslinked PI have been measured at high-pressures, *in-situ*, using the hot-wire method. A preliminary report of the results has appeared previously [18].

2. Experimental

The sample of liquid *cis*-1,4-poly(isoprene) (98 mole% unsaturation) made from natural rubber, molecular formula $[CH_2CH{=}C(CH_3)CH_2]_n$ (CAS number 104389-31-3), with a number-average relative molecular mass of 38,000, was supplied by Sigma–Aldrich.

The transient hot-wire method was used to measure simultaneously the thermal conductivity κ and the heat capacity per unit volume ρc_p, where c_p is the isobaric specific heat capacity and ρ is the mass density. The method has previously been described in detail [19]. Briefly, the sensor was a nickel wire (0.1 mm in diameter) placed horizontally in a ring of constant radius within a Teflon cell. The hot-wire was surrounded by the medium under investigation (PI). To determine κ and ρc_p, the hot-wire probe embedded in the sample was heated by a 1.4 s