

## Test method

## Investigation of thermo-reversibility of polymer crosslinked by reversible covalent bonds through torque measurement



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## ABSTRACT

Brominated butyl rubber (BIIR) was crosslinked through an esterification reaction using the sodium salt of dicyclopentadiene dicarboxylic acid (DCPDCA) as crosslinking agent. The crosslinked BIIR could de-crosslink upon heating and re-crosslink upon cooling due to Diels-Alder type reversible de-dimerization/re-dimerization of dicyclopentadiene moieties in the rubber networks. Torque measurement of the crosslinked rubber was conducted at various temperatures using a typical curemeter to investigate the thermo-reversibility. It was revealed that proper temperature for thermal processing of the crosslinked BIIR would be around 174 °C, at which the crosslinked polymer exhibits good flowability and is not too high to induce unexpected side reactions. The torque measurement was also carried out to investigate the efficiency of antioxidant on retarding the loss of the thermo-reversibility of the crosslinked polymer during heating-cooling cycles. It was found that addition of antioxidant 2246 [2,2'-methylenebis(6-tert-butyl-4-methylphenol)] into BIIR could significantly improve the thermo-reversibility of DCPDCA crosslinked BIIR. Torque measurement provides a convenient and sensitive method to understand the thermal behavior of reversible covalent crosslinked polymer.

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## 1. Introduction

In recent years, thermo-reversible covalent crosslinked polymers have attracted increasing attention due to their unique property, namely, thermal re-processability with covalent bonding networks [1]. Such polymers are crosslinked through formation of covalent networks between polymer chains. Thermo-reversible Diels-Alder cycloaddition reactions have been used to generate covalent

networks of polymers in which de-crosslinking occurs based on the retro-Diels-Alder reaction. A typical thermo-reversible Diels-Alder reaction system is the reaction between furan and maleimide, the former acts as diene and the latter as dienophile in the Diels-Alder reaction and retro reaction [2–4]. No catalyst is required for the forward and reverse reactions. Therefore, polymers crosslinked by the reaction between furan and maleimide moieties have been widely investigated and applied as self-mending materials [3–5], dynamic polymers [6] and renewable polymer materials [7]. Another reversible Diels-Alder reaction system is cyclopentadiene (CPD). CPD dimerizes to form dicyclopentadiene (DCPD) via Diels-Alder addition and DCPD de-dimerizes upon heating ( $\geq 120$  °C) to form two CPD monomers via retro-Diels-Alder reaction. In this case, CPD serves as diene and also dienophile, hence only

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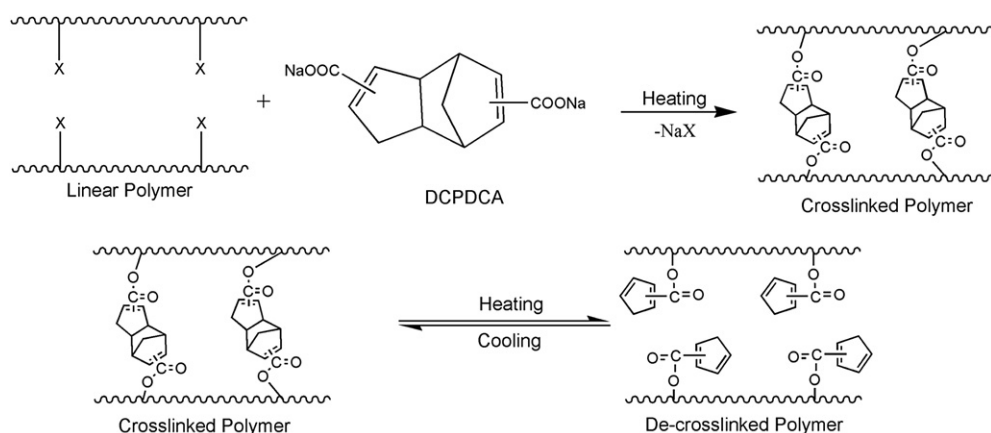
a single type of functional group (CPD) is required to generate thermo-reversible covalent bonding between polymer chains. Indeed, DCPD-based reversible crosslinked polymers have been investigated for quite a long period. In the 1970s, Kennedy et al prepared ethylene-propylene copolymer and polyisobutylene with pendant CPD moieties [8,9]. Both of these polymers showed thermo-reversible crosslinking behavior due to thermo-reversible dimerization of the side CPD groups. Following Kennedy's work, thermo-reversible crosslinked polyphosphazene [10] and many other reversible crosslinked polymeric elastomers were reported in the literature [11–15]. DCPD derivative was also employed in making thermally re-mendable polyester [5].

Since the crosslinking/de-crosslinking equilibrium is non-catalyst dependant and is controlled only by temperature, how to figure out a proper temperature or temperature range for de-crosslinking or thermally re-processing of a crosslinked polymer is a critical issue. In addition, for most thermo-reversible crosslinked polymers reported in the literature, the de-crosslinking temperature was between 100 °C and 200 °C. At such high temperatures some unexpected side reactions may take place at the unsaturated backbone and the functional moieties involved in the reversible crosslinking, resulting in formation of irreversible crosslinks during the heating stage. A very small amount of unexpected side reaction may generate permanent crosslinks, leading to significant loss of the thermo-reversibility. That is why only a limited number of thermo-re-processing cycles could be achieved for most reversible covalent crosslinked polymers reported in the literature [16]. Side reaction of C=C double bonds at high temperature is expected to be major reason causing the loss of reversibility after each heating and cooling cycle of a reversible crosslinked polymer. Generally, a stabilizer or antioxidant can be used to reduce the side reactions related to C=C double bonds. However, it remains a challenge to tell which kind of antioxidant is effective for a specific polymer system since the side reactions may occur to such a small extent that is hard to detect by traditional structure characterization methods such as nuclear magnetic

resonance (NMR) and Fourier transform infrared (FTIR) spectra. Therefore, there is need for a sensitive method to evaluate the efficiency of antioxidant applied.

Differential scanning calorimetry (DSC) was used by several researchers to study the thermo-reversibility of Diels-Alder polymers [17,18] and provided good signal of heat flow when the polymer contained a large amount of functional moieties. NMR and FTIR spectroscopy were also used to investigate the structure changes related to the thermo-reversible conversion of crosslinked polymers [19–21]. Dynamic mechanical analysis (DMA) was also carried out to test the thermal property of thermally re-mendable highly crosslinked polymeric materials [19,22,23]. All these methods provided useful results to confirm the reversibility of the crosslinked polymers. However, quantitative information on the loss of the reversibility of the crosslinked polymers during heating and cooling cycles is rarely available in the literature.

Rubber curemeters which provide information about torque increase during crosslinking of rubber have been extensively used for a long time to obtain the vulcanization curve of rubber compounds. This is actually an in-situ method to observe crosslinking of polymer at near zero shear rate. In-situ measurement could well reflect the dynamic behavior of polymers being crosslinked [24]. In the present study, torque measurement was performed using a typical rubber curemeter to investigate the crosslinking and de-crosslinking behavior of thermo-reversible crosslinked polymer. The torque change of a crosslinked rubber specimen during heating and cooling cycles was tested in-situ to compare the effect of antioxidant on the reversibility. Reversible crosslinked brominated butyl rubber (BIIR) was used as a model, which was crosslinked by sodium dicyclopentadiene dicarboxylate through esterification, as shown in Scheme 1. Such esterification crosslinking of halogenated polymer was intensively investigated previously [11–14]. The results presented in the current paper indicate that the torque measurement provides a simple, sensitive and reliable method to acquire information on the thermo-reversibility of crosslinked polymer and the efficiency of antioxidant to maintain reversibility.



**Scheme 1.** Esterification crosslinking of brominated butyl rubber by sodium dicyclopentadiene dicarboxylate and Diels-Alder mechanism of thermo-reversible conversion (X=Br).

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