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Effects of sodium and zinc neutralization on large deformation hysteresis of an ethylene methacrylic acid butyl acrylate copolymer

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ABSTRACT

The mechanical hysteresis and recovery behaviors of an elastomeric ethylene methacrylic acid butyl acrylate (EMAABA) copolymer, its sodium-neutralized ($EMAABA_{Na}$) and zinc-neutralized ($EMAABA_{Zn}$) counterparts are evaluated and compared under large strain loading conditions. Experiments at different rates, under cyclic loading conditions and in relaxation indicate two major hysteresis mechanisms: a characteristic viscoelastic mechanism operative at all strains and a microstructural evolution/breakdown mechanism incurred during large strains. Loading-unloading cycles show large rate-dependent hysteresis loops with significant recovery of strain upon unloading, revealing a highly dissipative yet resilient behavior. The microstructure breakdown mechanism occurs during the initial strain excursion as revealed by subsequent loading cycles showing a significantly more compliant behavior and dramatically reduced hysteresis loops. The neutralized materials are found to be significantly stiffer, stronger and more dissipative compared to the neat material while still retaining the same level of recovery. Therefore the neutralization of this material provides an excellent means to tune stiffness and dissipation while retaining resilience, providing mechanical performance properties attractive for abrasion, impact and puncture resistant applications.

1. Introduction

Ionomers are polymers possessing ionic functional groups pendant to the polymer backbone [1]. Ethylene methacrylic acid (EMAA) and ethylene methacrylic acid butyl acrylate (EMAABA) copolymers neutralized with sodium, magnesium, or zinc cations form a class of ionomers with an outstanding combination of mechanical properties, including stiffness, strength, toughness, resilience (i.e., recovery of strain upon unloading), abrasion resistance and puncture resistance [2,3]. These properties can be tuned by varying the relative amounts of amorphous domains, crystalline domains and ionic aggregates, with the resulting range in mechanical properties being remarkably broad [4–6]. This range in properties can be further broadened by changing the type and concentration of ionic aggregates, and their distribution along the polymer chain backbone [1,7].

Previous mechanical studies have investigated the dynamic mechanical properties [8], the yielding [7,9], and the large deformation and rate-dependent behaviors [10] of EMAA [7–9] and EMAABA [10]. However, a detailed characterization of the dissipative nature of these materials at large strain has not been conducted. Due to the use of these materials as cut-resistant coatings, puncture-resistant packagings and impact absorbing materials, the dissipation and resilience upon large strain deformation are governing behaviors for application. Thus, it is important to understand how neutralization affects the dissipation and recovery. In this paper, we study an ethylene methacrylic acid butyl acrylate copolymer (EMAABA) both in its neat (non-neutralized) and neutralized forms – here the homopolymer is neutralized with Sodium ($EMAABA_{Na}$) and Zinc ($EMAABA_{Zn}$). These three copolymers are studied in their elastomeric regime of behavior (at 25 °C) in large deformation uniaxial compression over a wide range of strain rates (from $10^{-4}\,s^{-1}$ to $9000\,s^{-1}$); results from monotonic loading tests, cyclic tests and relaxation tests are presented, as well as results from small strain dynamic mechanical analysis. The results are used to characterize the effects of neutralization on the dissipative character of the homopolymer.

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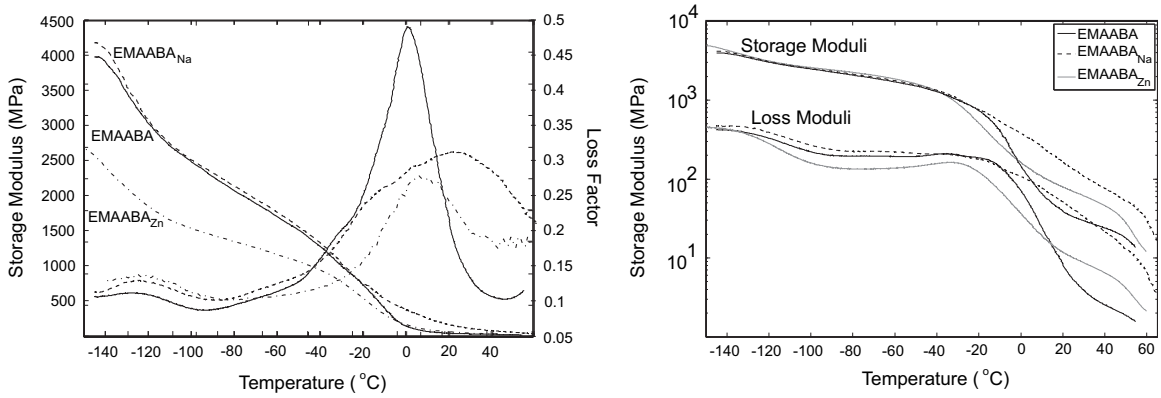

Fig. 1. Storage modulus (decreasing from left to right) and loss factor (increasing from left to right) vs. temperature for EMAABA (solid lines), EMAABA$_{Na}$ (dashed lines), and EMAABA$_{Zn}$ (dotted lines) at a frequency of 1 Hz (left). Storage and Loss moduli (logarithmic scale) vs. temperature for the three materials (right).

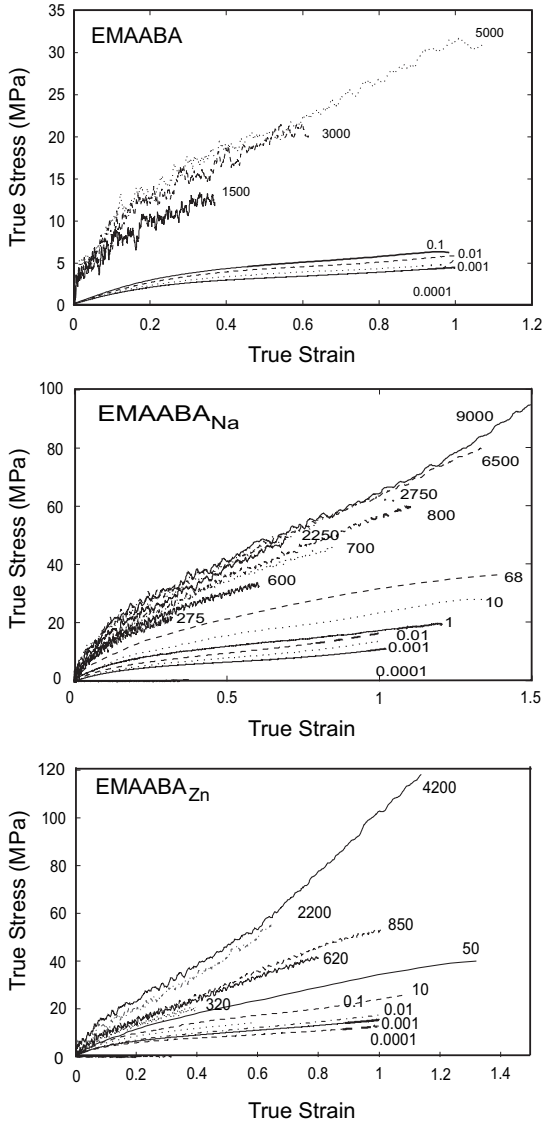

Fig. 2. Uniaxial compression true stress-true strain curves for EMAABA (top), EMAABA$_{Na}$ (center), and EMAABA$_{Zn}$ (bottom) at different strain rates.

2. Experimental protocol

2.1. Materials

The ethylene methacrylic acid butyl acrylate copolymer (EMAABA) used in this study contained 9% methacrylic acid (MAA) and 23% *n*-butyl acrylate (nBA). The EMAABA terpolymer was partially neutralized with sodium cations (53% of the acid groups neutralized with Na^+) and Zinc cations (53% of the acid groups neutralized with Zn^+) to produce ionomer forms of the polymer, herein referred to as EMAABA$_{Na}$ and EMAABA$_{Zn}$ respectively. These random copolymers with long chain branches were produced using a high pressure autoclave process. The nature of the branching in their polyethylene sections is assumed to be similar to what is found in polyethylene homopolymers [11,12] produced via similar processes. Both materials were provided by DuPont in compression molded plaques, approximately 150 mm × 150 mm × 3.15 mm. Compression specimens were punched from the plaques using special expulsion punches fabricated by the Dewes-Gumbs Die Co. For compression testing, circular punches were used, giving cylindrical samples approximately 6 mm in diameter for low-rate testing and 5 mm in diameter for high-rate testing.

2.2. Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) was performed on a TA Instruments Q800 dynamical mechanical analyzer. Specimens were cut from the 3.15 mm thick plaque, with a width approximately

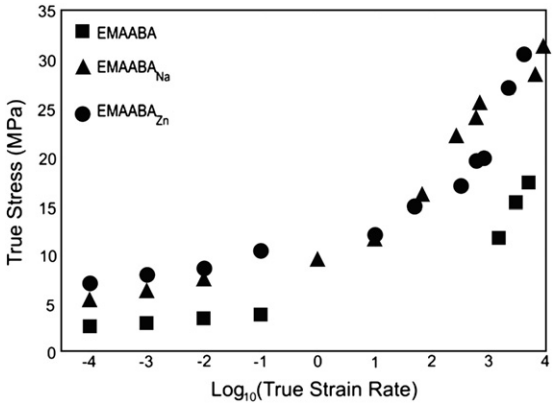

Fig. 3. True stress vs. log$_{10}$(true strain rate) for the materials at a true strain of 0.3.