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A molecular dynamics study on the surface welding and shape memory behaviors of Diels-Alder network

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ABSTRACT

As a notable example of the recently emerged covalent adaptable network (CAN) polymers, Diels-Alder (DA) networks could depolymerize at high temperature through the reversible DA reactions, which bestows interesting behaviors of thermosetting polymers, such as malleability, surface welding behavior, and recyclability. Recently, there are increasing research interests in combining CANs with shape memory polymers (SMPs) to enable the next generation reprogrammable and recyclable actuation materials. However, our macromolecular-level understanding of DA networks that are intended for SMP applications is still limited. In this paper, we established a molecular dynamics method to investigate the surface welding and shape memory behaviors of DA networks. The mechanical properties of fresh and fully welded networks are examined by uniaxial tension measurements. The results indicate that with sufficient welding time, the welded networks can fully recover the mechanical properties as those of fresh network. The glass transition temperature of welded network with varying weight fractions of epoxy monomers are studied, and the simulation results agree well with experiment results. In addition, the shape fixity and recovery simulations reveal ideal shape memory property of the DA networks. Parametric studies revealed that with a decreased end-to-end distance of polymer chains, the DA networks exhibit higher flexibility, which significantly influences their mechanical and shape memory properties.

1. Introduction

Traditional thermosetting polymers and their composites are extensively used as structural materials [1] due to the excellent mechanical properties, thermal stability, solvent/environmental resistance [2]. However, once set, the physical state and chemical structures of crosslinked networks cannot be modified, which leads to the difficulties of reforming and recycling. The recently emerged covalent adaptable networks (CANs) [3–5] provide exciting opportunities for thermosets reprocessing and recycling. After incorporating dynamic covalent bonds and applying a suitable stimulus, the networks could alternate their topology through reversible reactions, such as bond exchange reaction (BER) [6,7], Diels-Alder (DA) reaction [8,9], and radical addition fragmentation chain transfer (RAFT) reaction [10,11]. When the external stimulus is removed, the rate of reversible reactions is negligible, and CANs behave like traditional thermosets with excellent thermomechanical properties.

Among a variety of the reversible reactions that have been employed for CANs development, DA reactions have drawn significant interests due to their wide range of activation temperature by changing reactive groups in the networks. Furan and maleimide derivatives are among the most popular functional groups to create DA networks [12–14]. Upon heating, the retro-Diels-Alder reactions enable the network depolymerization with equilibrium shifting, which consequently leads to the macroscopic malleability, surface welding effect, and recycling behaviors of thermosets. For example, Chen et al. [15] developed DA networks which can be recycled multiple times at moderate temperature without any loss in mechanical properties. Liu and Chen [16] reported crosslinked polyamides with maleimide and furan pendent groups, which show thermally reversible crosslinking behavior by the reversible DA reactions.

In addition to the thermoset processing, efforts have been made in recent years to incorporate CANs with shape memory polymers (SMPs) applications, where a programmed polymeric materials can

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Table 1
Number of DGEBAEO-2 and DGEBAEO-6 monomers in three systems.

	$PHAE_{06}(50)$	$PHAE_{06}(75)$	$PHAE_{06}(100)$
DGEBAEO-2	40	20	0
DGEBAEO-6	40	60	80

recover their original shapes upon exposure to external stimuli [17–19]. For example, Zhang et al. [20] synthesized a thermally self-healing reversible DA network, which exhibits excellent triple shape memory effect even after being recycled multiple times. Fan et al. [21,22] developed furan-functionalized poly-

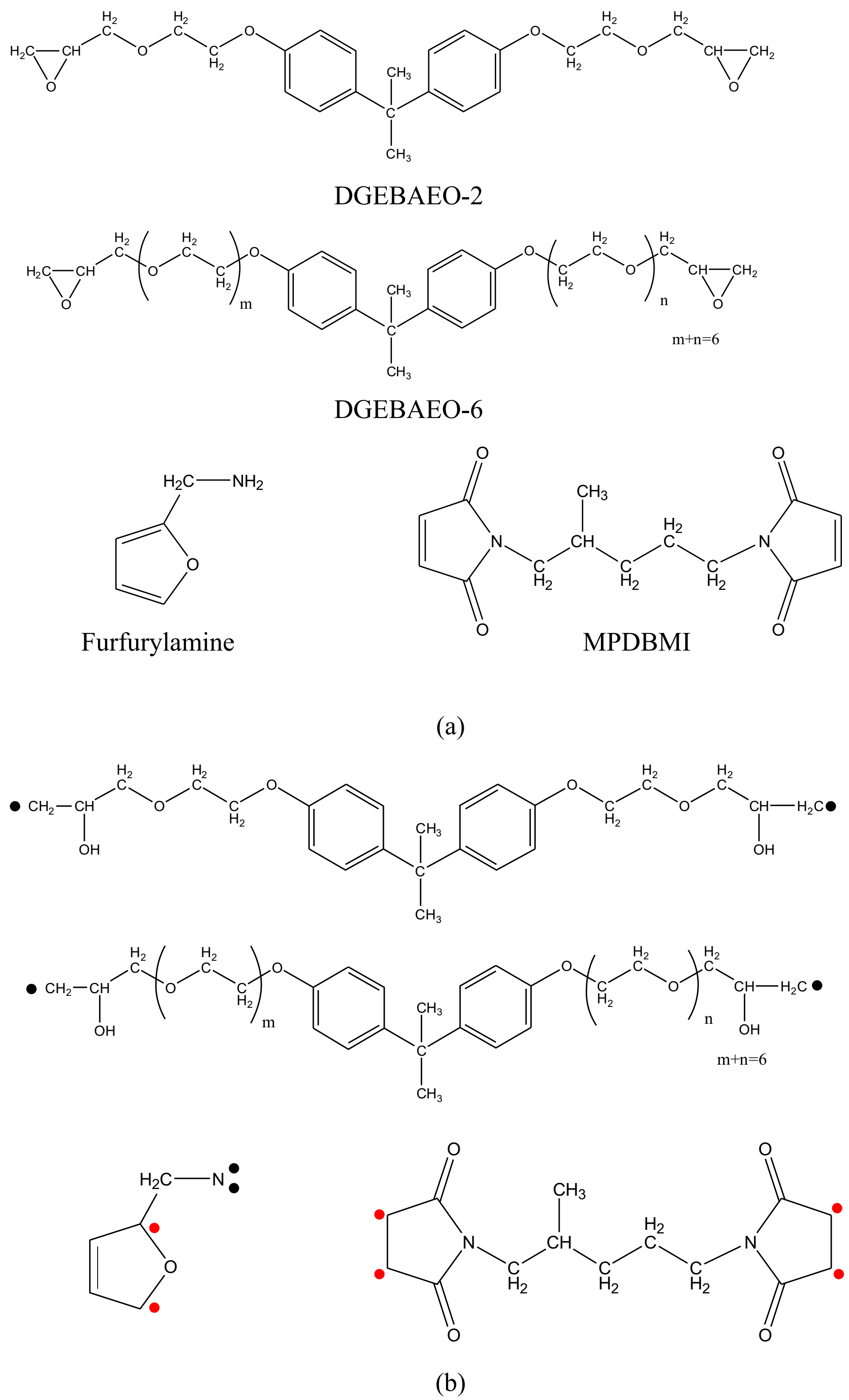

Fig. 1. (a) Chemical structures of DGEBAEO-2, DGEBAEO-6, fufurylamine and MPDBMI (b) activation of DGEBAEO-2, DGEBAEO-6, fufurylamine and MPDBMI ends for the reactions (black (•) and red (•) symbols show their activity toward the polymerization and DA reactions, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)