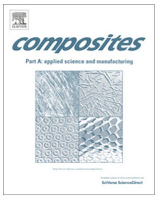
Composites: Part A 54 (2013) 20–27

Contents lists available at SciVerse ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa



Tensile properties of fumed silica filled polydimethylsiloxane networks

Yinglei Yue [a,c], Hui Zhang [a], Zhong Zhang [a,*], Yunfa Chen [b]

[a] National Center for Nanoscience and Technology, Beijing 100190, China
[b] Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 9 March 2013
Received in revised form 17 June 2013
Accepted 21 June 2013
Available online 29 June 2013

Keywords:
A. Polymer–matrix composites (PMCs)
A. Particle-reinforcement
B. Mechanical properties
B. Stress transfer

ABSTRACT

Tensile properties of fumed silica filled hydroxylated polydimethylsiloxane (PDMS) networks were investigated in the current work. Similar to unfilled bimodal networks, unimodal networks filled with concentrated fumed silica exhibit non-Gaussian effect and improved ultimate tensile properties. The concept of "hierarchical network" was proposed to depict the networks exhibiting non-Gaussian effect at sufficiently high strains. It was found that the reinforcing effect originates from both the effective volume effect from filler volume and polymer–filler interaction and the synergistic effect between network chains within the "hierarchical network". Experimental results showed that filler's dispersion, concentration, specific surface area and surface chemistry have a great influence on the tensile properties, which could be interpreted by analyzing the variation of both effective volume effect and synergistic effect.

1. Introduction

Polydimethylsiloxane (PDMS) rubber networks display a combination of very interesting properties such as extremely low glass transition temperature, high thermal and UV stability, low surface energy, excellent insulating properties, physiological inertness and biocompatibility [1,2]. They have potential applications in many fields such as elastomeric seals, adhesives, coatings, plastic surgery, etc. However, the poor mechanical properties significantly limit their application. In order to improve the mechanical properties, various fillers have been introduced, among which fumed silica is one of the most effective one. Moreover, PDMS network is a model network [3,4] to study reinforcing mechanisms, thanks to the controllable structure and the absence of self-reinforcing effect from, for example, strain-induced crystallization [5,6].

Networks are synthesized from single polymer chains by chemical crosslinking reaction. Therefore, the response of single polymer chain to external stress plays a fundamental role in the final mechanical properties of networks. Force spectroscopy for single polymer chains investigated by atomic force microscopy (AFM) showed that polymer chains exhibit Gaussian behavior from being taut to being straightened while exhibit non-Gaussian behavior when reaching their limited extensibility [7,8]. The former behavior was generally attributed to the conformational entropy loss caused by simple rotation of skeletal bonds and the later mainly to the enthalpic change due to the distortion of bond angles [9,10].

For unfilled networks, rearrangement and orientation of polymer chains proceed with increasing extension [11,12]. Part of network chains start to participate in transferring stress since they are stretched taut until disentanglement or rupture occurs (we name these chains as "transfer-chains"). Only Gaussian effect (or, linear behavior) is observed on the Mooney–Rivlin plots for unfilled unimodal networks (Fig. 1), suggesting that nearly all transfer-chains are in the Gaussian behavior regime before network breakup occurs thanks to the non-affine deformation [13]. It has been confirmed that the modulus of these networks decreases with chain length [14,15], increases with crosslinking functionality [15–17], and has nothing to do with dangling chains [18,19]. Compared with unfilled unimodal networks, unfilled bimodal networks show obvious non-Gaussian effect (non-linear upturn behavior) at sufficiently large strains and exhibit much improved ultimate tensile properties (refer to Fig. 1). The variance of modulus in the Gaussian regime can be attributed to the change of network structure and the non-Gaussian effect is unanimously attributed to the limited extensibility of short transfer-chains [13,20]. Mark and Tang [21] found that too many or too few short chains preclude the non-Gaussian effect and there exists an optimum mole ratio between short chains and long chains for bimodal networks to exhibit optimum ultimate tensile properties. Experiments [13,22,23] showed that "upturn strain" (i.e. the strain at the start of deviation from linearity on modulus plots, α_u) decreases with the mole ratio of short chains or with the increasing length difference between short chains and long chains. Research results [20,24] showed that trimodal networks can also exhibit non-Gaussian effect and improved ultimate tensile properties.

---

* Corresponding author. Tel./fax: +86 10 82545586.
E-mail address: zhong.zhang@nanoctr.cn (Z. Zhang).

1359-835X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesa.2013.06.016

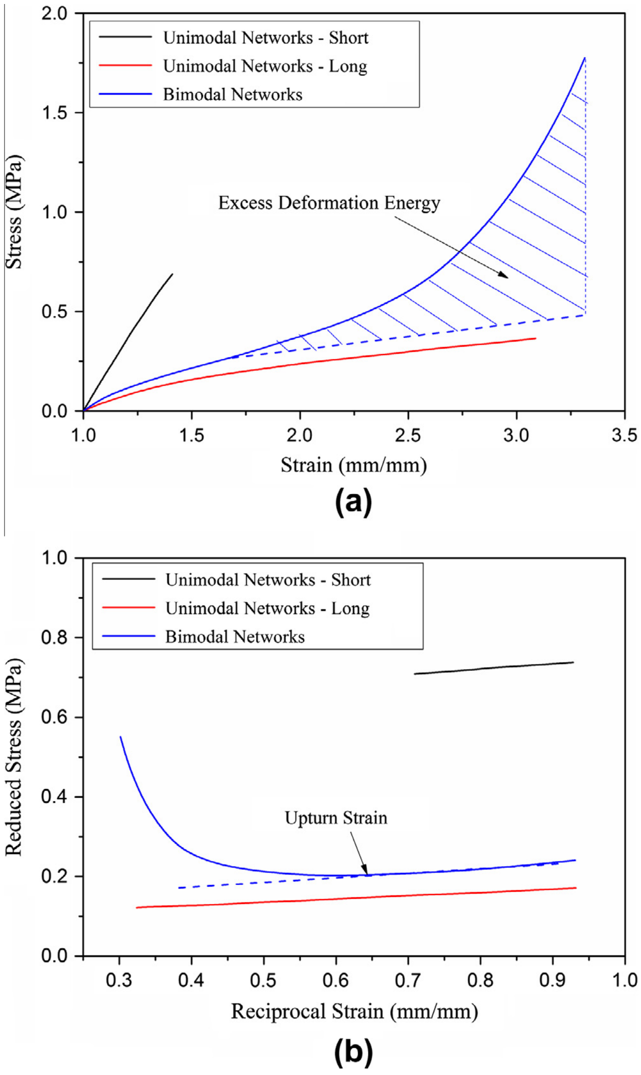


Fig. 1. Typical stress–strain curves (a) and Mooney–Rivlin plots (b) for unimodal and bimodal networks (referred to literature [23]). The shadow area corresponds to the excess deformation energy and dotted stress–strain curve belongs to the idealized unimodal networks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

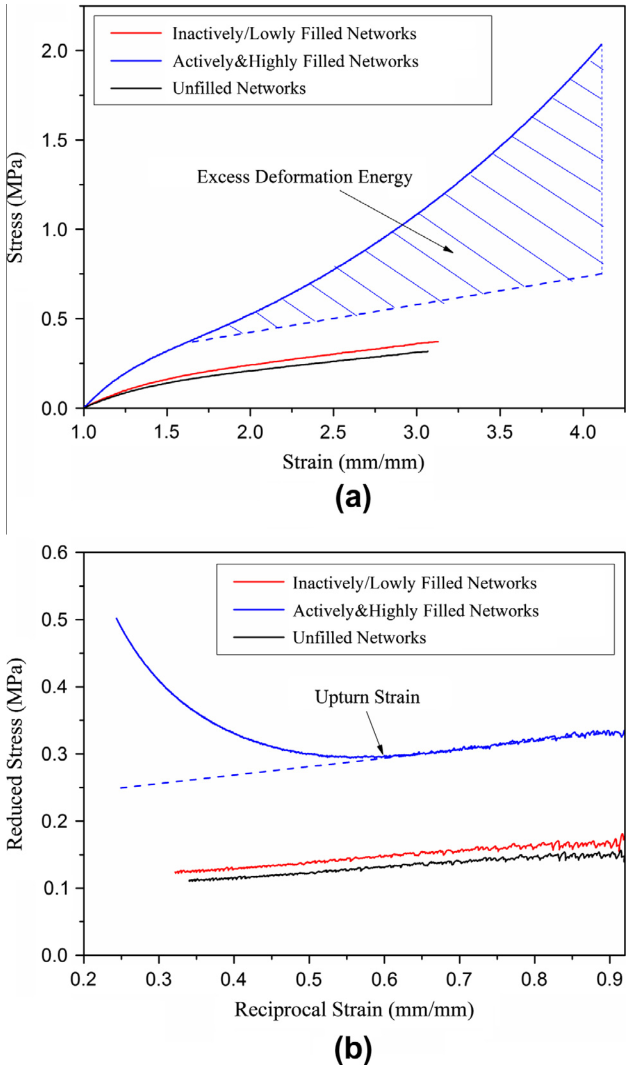


Fig. 2. Typical stress–strain curves (a) and Mooney–Rivlin plots and (b) for unfilled, inactively and actively (lowly and highly) filled networks (referred to literature [25,40]). The shadow area corresponds to excess deformation energy and dotted stress–strain curve belongs to the idealized unimodal networks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The behavior of network chains within filled (unimodal) networks is much more complicated. On top of the behaviors discussed above, the influence caused by filler particles is innegligible or even dominant. For networks filled with inactive fillers like glass spheres [25], Gaussian effect is normally observed (Fig. 2). The chain behavior is mainly affected by the excluded volume effect (or, hydrodynamic effect [26]) from filler particles. And the augmented modulus can be simply characterized by Smallwood–Einstein and other equations using filler's volume fraction [27–29]. For networks filled with active fillers like fumed silica with abundant silanol groups on the surface, chain behavior is affected not only by the excluded volume effect, but also by polymer–filler interaction. Thanks to the adsorption [30–32] and entanglement [33,34], polymer chains are divided into shorter segments. AFM results [35,36] showed that segments can participate in transferring stress and exhibit non-Gaussian behavior before desorption occurs. Thus, the tensile properties of networks filled with active fillers are determined not only by transfer-chains, but also by "transfer-segments". It is obvious that transfer-segments behave differently from transfer-chains under extension. On one hand, segments are more likely to desorb from the particle surface than to rupture at the backbone due to the large energy difference. Specifically, the desorption energy originated from hydrogen bond and van der Waals "bond" (ca. 10–40 kJ/mol [37]) is much smaller than the rupture energy of scission of Si–O bond (361 kJ/mol [2]). On the other hand, shorter segments would be more possible to participate in transferring stress and exhibit non-Gaussian behavior at a lower strain level, just as the short chains in bimodal networks. Similar to the bimodal networks having too few short chains, networks filled with diluted active fillers are also expected to exhibit Gaussian effect. Because the network chains are merely affected by the "effective volume effect" originated from filler volume and the change of network structure caused by polymer-filler interaction [38]. The modulus can be simply characterized by the equations for inactively filled networks using filler's effective volume fraction [39]. Highly and actively filled networks have been demonstrated to show marked non-Gaussian effect and much improved ultimate tensile properties as bimodal networks (see Fig. 2) [40]. Exploring the mechanisms of filler reinforcement has being one of the hot topics in the rubber fields for decades.