Supporting Information

Fracture mechanism of amorphous polyethylene at strain fields

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Normalized Entanglement Percent (NEP):

First, a rough model about chain entanglement is proposed by assuming the following two conditions. (1) 10 united atoms in the chain ends do not entangle, which basically agrees with the entanglement molecular weight of polyethylene[1] and also in consistence with the definition of the entanglement angle. (2) Half of the united atoms of a chain except for 10 end atoms are entangled. This can be explained by the random walk scheme used to generate amorphous polyethylene chains. Assuming a chain ring without ends, which is similar to the middle region of chain packed randomly in three dimensional space, the probabilities of finding an arbitrary atom with entanglement angle of □<90° and with □>90° are the same. So the probability of united atoms in entanglement status is 50%. From this model, we can deduce that the entanglement percent (EP_Model) of a certain chain length system can be calculated as follow

$$EP\_Model_{chain}=(L_{chain}-2\times10)\times0.5/L_{chain} \quad (1)$$

where L_{chain} is the chain length. The calculated entanglement percents (EP_Model) with chain lengths of 100, 200, 400, 600, 800 and 1000 are 0.4000, 0.4500, 0.4750,

0.4833, 0.4875 and 0.49, respectively. To eliminate the effect of strain on the entanglement percent, the entanglement percent of each chain length is normalized.

$$NEP\_model_{chain} = (EP\_Model_{chain} - EP\_Model_m)/(EP\_Model_n - EP\_Model_m) \quad (2)$$

where NEP_model_{chain} is the normalized entanglement percent. In this case m=100 n=1000. So, the NEP_model_{chain} of chain length 100 is always 0 and the NEP_model_{chain} of chain length 1000 is always 1. The NEP_model_{chain} of chain length 100, 200, 400, 600, 800, 1000 are 0, 0.556, 0.833, 0.926, 0.972, 1 respectively, which qualitatively agree with the linear region (strain>0.6) of entanglement percent of different chain length in Figure 6. In order to compare the NEPs from eq(2) and MD simulation, we also calculate the NEP of the MD simulation in ensemble average fashion. The formula is given as follows

$$NEP\_MD_{chain} = \overline{\sum_{strain}^{i} \frac{EP\_MD_{chain}(i) - EP\_MD_m(i)}{EP\_MD_n(i) - EP\_MD_m(i)}} \quad (3)$$

where m=100 n=1000, $EP\_MD_{chain}(i)$ is the entanglement percent of a specific chain length at strain i. $\overline{\sum_{strain}^{i}}$ means that all the calculated data are averaged over every strain. Similarly with eq(2), NEP_MD_{chain} of chain length 100 and 1000 are 0 and 1. It is noted that NEP_MD_{chain} with different temperatures shows a slight difference and a deviation of 1.4% is obtained, which is negligible. So we conclude that at T< 200K, temperature shows a negligible effect on the entanglement of polyethylene. As a result, NEP_MD_{chain} with different temperatures can be also compared directly. The NEP_MD_{chain} of chains with length of 100, 200, 400, 600, 800, 1000 at 100 K are 0, 0.644, 0.703, 0.797, 0.888, 1.0 respectively, and they are 0, 0.571, 0.765, 0.838, 0.963,

1.0 at 150 K. The calculated results qualitatively agree with NEP_Model$_{chain}$. This indicates that the eq(2) model about the chain entanglement captures the major factor affecting entanglement, i.e., numbers of chain ends, which are determined by chain length, play an important role in the entanglement, and temperature is a negligible factor at T<200 K.

References:

1. L. J. Fetters, D. J. Lohse, S. T. Milner and W. W. Graessley, *Macromolecules*, 1999, **32**, 6847-6851.