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Constitutive modeling of carbon nanotube rubber composites on the basis of chain length statistics

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ABSTRACT

A constitutive model for carbon nanotube (CNT) reinforced rubbers is proposed on the basis of the polymer chain length statistics. Rubbers both with conventional fillers like silica or carbon black (hybrid system) and without them are considered. The reinforcement by CNTs is explained by additional cross-linking which influences the probability density function of polymer chain lengths. The change in the probability density function is statistically reasoned and incorporated into a full network model based on the numerical integration over the unit sphere. This full network model is able to describe typical inelastic effects of filled rubbers as for example the Mullins effect, strain induced anisotropy and permanent set. The so obtained model demonstrates good agreement with experimental data on CNT blended rubbers available in literature.

1. Introduction

Since their discovery in 1991 [17] carbon nanotubes (CNT) have appeared to be a very effective mean of reinforcement for elastomeric materials as for example rubbers. Both single- and multi-wall CNTs can effectively be applied with or without conventional fillers (see, e.g., [27,7,15,30,32]). By using along with the conventional fillers like carbon black or silica within a hybrid system even a relatively small volume fraction of CNTs suffices in order to reach a significant improvement of mechanical characteristics. For example, Lorenz et al. [24] reported that with the increasing concentration of CNTs the stress-strain response of the composite becomes stiffer while the strain at break slightly decreases (see also [13,10]).

The mechanism of this reinforcement is still not thoroughly studied. However, there is a consensus that CNTs introduce additional cross-links and influence thus the entropy of the filler-polymer system [21,29]. Thus, the cross-link density increases with the CNT concentration up to some critical value [35,31]. Litvinov et al. [23] found out that the mobility of the rubber matrix is restricted by the adsorbed polymer chain fragments which form physical junctions with the filler. Bokobza [4] also reported that the interaction between the filler and the matrix could increase the effective degree of cross-linking. This is especially the case for fillers with reactive surface groups as for example CNTs.

There are relatively many works focusing on small strain behavior of CNT polymer composites (see, e.g., [28,1,2]). Odegard et al. [28] proposed an equivalent-continuum modeling method for polymers reinforced by nanotubes with different lengths, concentrations and orientation. Ashrafi & Hubert [2] utilized the Mori-Tanaka method in addition to the finite element analysis to determine elastic properties of random and oriented twisted CNT array/polymer composites. Anumandla & Gibson [1] also considered the waviness of nanotubes for estimating the effective elastic modulus of CNT reinforced composites.

However, there are very few studies dealing with the large strain response of CNT reinforced elastomers. A phenomenological model for multi-wall CNT rubber composites was proposed by Cantournet et al. [5]. The model is based on the rule of mixtures. The rubber phase is simulated by a compressible version of the eight chain model [3] while the CNT-phase is described by a polynomial expression in terms of the CNT stretch. The model shows good agreement with own experimental data of the authors. Córdova et al. [6] further extended this model to inelastic behavior of the rubber phase in order to take softening and residual strains into account. Georgantzinos et al. [14] presented a finite element model of single-wall CNTs blended rubbers. The representative volume element of the model includes a CNT inside of rubber and an

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interfacial layer between them. The CNT is described by a modified Morse potential with 19% strain at break of carbon–carbon bonds. The model is applied to small and moderate strains but is not compared to any experimental data.

In this paper, we present a constitutive model for CNT reinforced rubbers. The model is based on the polymer chain length statistics recently applied in order to describe rubber elasticity and anisotropic softening [18,20]. The reinforcement by CNTs is explained by additional cross-linking which influences the probability density function of chain lengths. Polymer chains are assumed to split by the cross-links into shorter chains, which leads to the stiffening of the composite. The change in the probability density function by the additional cross-linking is statistically reasoned.

CNTs are much stiffer than the surrounding polymer phase, which also causes a reinforcing effect. Additional stiffening also results from the rotational constraint of CNTs whose length is very large in comparison to the diameter. In the proposed model these effects are not directly considered but taken into account by means of the above mentioned change in the probability density function of polymer chain lengths.

The paper is organized as follows. In Sect. 2 we recall the above mentioned chain length statistics. Its change due to the additional cross-linking by CNTs is discussed in Sect. 3. The so resulting probability density function is further incorporated into a full network model based on a numerical integration over the unit sphere (Sect. 4). Finally, in Sect. 5, the model is validated in comparison to experimental data available in literature. Abbreviations used in the paper are listed and explained in Table 1.

2. Polymer chain length statistics

According to the classical statistical theory of polymerization the probability that a linear polymer molecule is composed of exactly k segments is given by the expression [12].

$$P(k) = p^{k-1}(1-p), \quad k = 1,2,\ldots, \tag{1}$$

known as the geometric probability density function, where $0 < p < 1$ denotes the probability of the chain propagation while $1-p$ represents then the probability of the chain termination. These are exactly the events that the polymer chain connects to a free radical (monomer) with either two or one active end, respectively. Representation (1) is based on the assumption of the classical polymerization theory that p remains constant over the whole polymerization process.

The chain length statistics briefly presented above assumes the minimal number of chain segments available in the distribution to be 1. The probability density function (1) can, however, be generalized to an arbitrary minimal number of chain segments n as follows

$$P(k) = p^{k-n}(1-p), \quad k = n, n+1,\ldots \tag{2}$$

It a priori satisfies the normalization condition

$$\sum_{k=n}^{\infty} P(k) = 1 \tag{3}$$

for any n.

In the following we will need a continuous form of this probability density function. In this case we set

$$P(u) = ap^{u-n}(1-p), \tag{4}$$

where u is a real valued number of segments and a is a normalization factor. The latter one results from the normalization condition

$$1 = \int_n^{\infty} P(u)du = a\frac{p-1}{\ln p} \tag{5}$$

as $a = \ln p/(p-1)$. By this means, the continuous probability density function (4) can be given in the following exponential form (cf. [33,34])

$$P(u) = \frac{1}{\Delta}e^{\frac{n-u}{\Delta}}, \tag{6}$$

where

$$\Delta = -\frac{1}{\ln p}. \tag{7}$$

The most of the network models operate with the average (mean) number of chain segments N. Thus, it is convenient to express $P(u)$ in terms of N. To this end, we first obtain

$$N = \mathrm{E}[u] = \int_n^{\infty} P(u)udu = n + \Delta, \tag{8}$$

where $\mathrm{E}[u]$ denotes the mean value of a random variable u while

$$\Delta = N - n. \tag{9}$$

Thus, the parameter Δ (7) of the probability density function (6) represents the difference between the average and the minimal number of chain segments available in the distribution. In the following, Δ will be considered as a material constant.

The probability density function (6) is illustrated in Fig. 1 for $n = 1$ and different values of Δ.

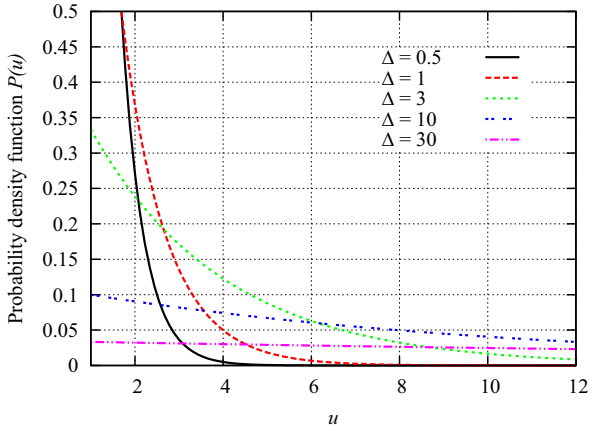

Fig. 1. Continuous probability density function (6) of the number of chain segments for $n = 1$ and various values of the parameter Δ.

Table 1
Abbreviations used in the paper and their expansions.

Abbreviation	Expansion/meaning
CNT	Carbon NanoTube
phr	Parts per Hundred Rubber
CBR	Chlorinated Butyl Rubber
BR	Butadiene Rubber