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# Prediction of Tensile Curves of Rubber Materials by Different Network Models

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**Summary:** The paper presents application of rubber elasticity theory to the predictive model of tensile mechanical properties. Poly(methyl methacrylate) was chosen as a model polymer. The input dates were crosslink density and type of chain. The crosslink density was taken from swelling experiment. Two types of chain were analyzed, namely worm like and chain with the realistic function of dihedral potential. Dihedral potential function was derived from molecular model of chain segment. Predictive tensile curve was compared with experimental one. The similarity of potential functions of selective polymers (polypropylene, poly-vinylchloride, poly-vinylalcohol, poly-vinylfluoride, polystyrene) enables to generalize this procedure.

**Keywords:** mechanical properties; Monte Carlo simulation; rubber elasticity; tension

## Introduction

Application of different types of networks can lead to more generalized models in field of structure –properties relations of rubbery materials. In such materials, some macroscopic properties are controlled by entropy.[1] The entropic component of the deformation properties can be calculated by rubber elasticity theory.[2,3] One of the basic network models was proposed by Termonia.[4] Termonia applied this model to analyze the deformation behavior of spider silk. Particularly, to analyse influence of reinforce effect of β-sheets and interphase layer between rigid β-sheets and amorphous matrix on tensile deformation of spider silk. The input data for the model were derived from the real tensile curves and output was a comparison of real tensile curve and hypothetical tensile curve without β-sheets or without reinforcing layer.

Enhancement the predictive ability of the model leads to develop more generalized models of rubber elasticity theory. Building the generalized model can not be realized in one step. The process consists rather by a series of small steps, where each step will analyze single structural factor. As the first step we used the Termonia‘s model to predict tensile curve of simpler materials without reinforcing inclusions, specifically for poly(methyl methacrylate) (PMMA). As input data relevant parameters of chemical structure have been used. The data especially crosslink density were obtained from swelling experiment by Flory-Rehner equation.[5] The potential functions describing the energetically changes at the molecular level, that we need in model in study, were taken from literature.[6,7] The model was applied to the poly-methylmethacrylate above glass transition temperature. The results published in paper of Ogura and Takahashi[6,7] were used for verification. There are presented tensile curves and swelling experiment measured at the same samples.

Termonia’s model utilized a Kuhn chain network. This type of chain respects size of segment but the orientation of the segment is random. Utilizing this model Treloar[8] derived stress-strain function (1).

$$\sigma = \frac{1}{3} E\sqrt{N} L^{-1}\left(\frac{\lambda}{\sqrt{N}}\right) \tag{1}$$

where

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$\lambda$ is a draw ratio of the chain
$E$ is the elastic modulus, that is a function of crosslink density, expressed as $E = 3\ \nu kT$ and
$\nu$ is a chain density.
$L^{-1}$ is an inverse function to Langevin function: $L(\beta) = \coth(\beta) - \beta^{-1}$, $\beta = \lambda/N^{0.5}$

This model has some restriction as a real structure concern. Specifically, if the model is applied to real structure one parameter called Kuhn length (length of single segment) have to be estimated from experimental stress-strain curve.[9]

For enhancement the predictive power, the Kuhn chain must be replaced by worm like chain (WLC)[10] in the network model. One version of WLC is freely rotating chain. The orientation of adjoining segments is mutually influenced. This state should be express via two parameters: segment length and so called bending angle. For example in carbon backbone the length of segment can be reduced to single bond and bending angle can be represented by bond angle.

Another possibility is to use so-called self-avoiding type of chain. Self-avoiding factor for the materials is based on presumption that the field of non bonding energy is homogenous in entire volume of network with one exception i.e. atoms are in close contact. In this case, chain does not intersect with itself.[11,12]

In our paper, a chain with realistic dihedral potential was used. Particularly, in classic models of rubber elasticity the concept of dihedral angle is neglected and it is considered that all the dihedral angles are equivalent. In reality, the potential energy of conformation is not uniform and it leads to prefer some selected conformation states. In case of carbon chains, the preferred conformation states are three: trans, gauche+ and gauche- that corresponds to three dihedral angles π, π/3 and 5π/3, respectively.[12]

## Model

The material structure in the not deformed state was modeled as tetra-functional network. The chains in that network were modeled with the support of a realistic dihedral potential[13,14] utilizing the material studio software. The segment of PMMA's chain was chosen as modeled example. The input data were coordinates of atoms and their linkage. The results was the dihedral potential $U(\theta)$ (See Figure 2). The dihedral potential was used for estimation partition function, $q$. Basically this function describes the probability of segment‘s place in real dihedral angles. The potential was transformed into partition function $q_i$ (2), which detects a probability of conformation in given dihedral angle.[11]

$$qi \approx \frac{\exp\left(-\frac{U(\theta)}{RT}\right)}{\sum_{i=1}^{n} \exp\left(-\frac{Ui(\theta)}{RT}\right)}. \tag{2}$$

where

$U(\theta)$ and $U_i(\theta)$ are potential functions of given angle, and potential function of in range $\langle 0,2\pi \rangle$
R- is Molar gas constant
T is a temperature.

The exponential term for selected dihedral angle is divided by a sum of exponential terms for each possible dihedral angle in a system.

The whole single chain was generated with knowledge of partition function. It was generated by a perl-script implemented into Materials Studio software. Result of generation was a set of backbone atom coordinates by Monte Carlo method. Position of consecutive atom added into existing chain was limited by the position of its three precedent atoms and random dihedral angle.

To build up the network model of material structure (PMMA) we need to know the mean value of chain length that in the molecular terminology called end-to-end length.

The end-to-end length was calculated as a function of number of bonds separating two atoms. By means of a statistical set of randomly generated chains the network was constructed. The result of statistical approach leads to cumulative distribution function (CDF) of end-to-end lengths. The mean length was then calculated as the inflexion point of CDF. The mean length is a building block for network.

Now we subject this model to tensile deformation. From the molecular point of view this deformation causes elongation of individual chains. There is no change in the shape of CDF function in non deformed and deformed state. The difference is only in the shift in end-to-end length end. From the thermodynamic point of view it means that the entropy of the system decreases. The change of the entropy can be expressed by:

$$S = k \ln \Omega \tag{3}$$

where

$\Omega$ is to number of possible arrangements.
$\Omega$ is numerically derivative of CDF in narrow interval near the inflexion point. Constructing the macroscopic curve we need to express beside deformation also the force. The force was calculated by fitting the relation force versus deformation of worm like chain

$$\frac{Fl_p}{kT} = \frac{\lambda}{L} + \frac{1}{4\left(1-\frac{\lambda}{L}\right)^2} - \frac{1}{4} \tag{4}$$

where

$l_p$ is persistence length,
$L$ is contour length,
$\lambda$ is the extension
$F$ is the force.

The contour length ($L$) is a length of linear chain in the all-trans positions.

Above described network presumed zero volume of nods. In real structure, crosslinking agent has a volume that depends on its molecular structure. The molecules of crosslinking agent were represented in the present model as undeformable reinforcing components.

This model was derived for PMMA, however for applied this procedure to another polymer the relevant dihedreal potential function must be chosen.

For the chemical similar groups of polymers (e.g. PVA, PVC, PS, PVF) the relevant dihedreal potential function can by derived. The condition by deriving the dihedreal potential function is that cumulative distribution function (CDF) lies between the function derived for most flexible - freely rotating chain, and function derived for most rigid chain - controlled by Ryckaert and Bellemans polynomial for linear carbon chain[15], respectively.

## Results and Discussion

The tensile curve reflexes a macroscopic behavior of polymer in study. From molecular point of view the influence of two parameters: (i) self-avoiding of chains and (ii) dihedral angle potential function was investigated. Both the factors can be mutually influenced each by other. Therefore, their influence must be investigated separately.

The set of 10000 freely rotating chains with self-avoiding function was generated. The self-avoiding consists in repulsion of atoms in close contact by energy minimization method. The result was a pair of cumulative distribution functions (CDF) of end-to-end length with self-avoiding and without self-avoiding function shown in Figure 1.

It was found that behavior chain is almost independent on that factor. There is only slight difference increase of inflexion points (length of chain), but without effect to chain rigidity. The elimination of the self-avoiding step is very advantageous, because the computer time consuming.

Dihedral potential energy function distribution was calculated by Materials Studio software using Dreiding force field.[16] The function for most flexible - freely rotating chain must be constant function. The function for most rigid chain was described by Ryckaert and Bellemans polynomial.[15]

The dihedral potential energy function obtained from molecular simulation of

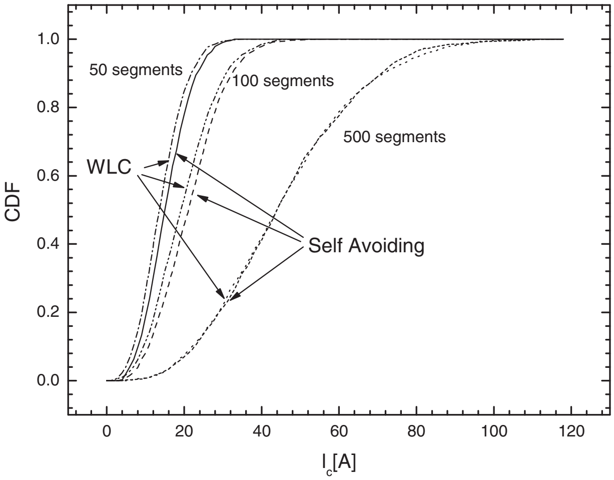

***Figure 1.***
Cumulative probability function (CDF) of end-to-end vectors; Difference between classic worm-like chain (WLC) and self avoiding WLC for different chain lengths 50, 100, and 500 segments.

PMMA structure is shown in Figure 2. In Figure 2 there are also shown another dihedral potential energy functions for similar groups of polymers.

The Figure 2 shows that the polymer in study can be dived into two groups. The first group has the dihedral potential energy function of three preferred positions of dihedral angles with the same preference. This group contained poly methyl methacrylate, polypropylene, poly vinylchloride, and one variant of poly styrene.

The second group has the dihedral potential energy function that has slightly lower potential in trans-position in compression with the gauche-positions. In this group, there are poly vinylalcohol, poly vinyl fluoride and one variant of poylstyr-

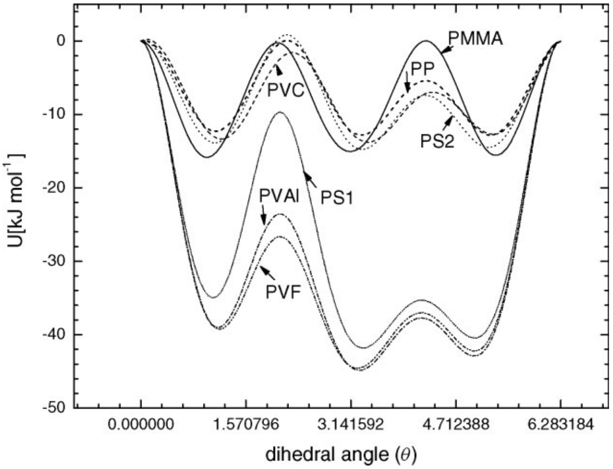

***Figure 2.***
Dihedral potential functions numerically calculated structures with minimized energy influence of side groups: Group 1 with weakly interacting side chain: PP, PVC, one version pf PS and PMMA; Group2 is with strong attractive interaction: PVAl, PVF and second version of PS.

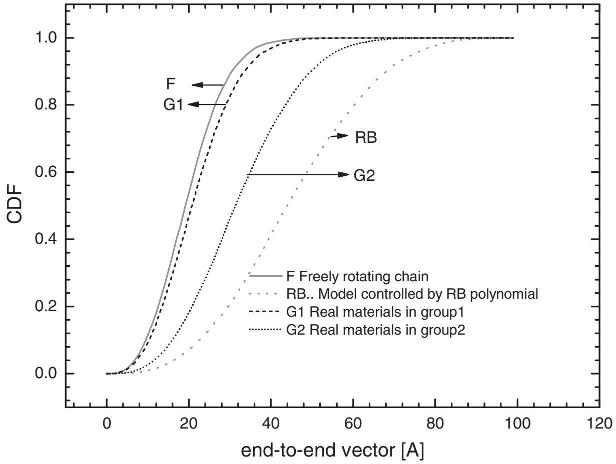

***Figure 3.***
Cumulative distribution function of end-to end vectors of chains with 100 segments; Chains with different dihedral potential: F,RB Limit model cases; G1, G2 groups of materials from Figure 2.

ene. The variants of polystyrene were differing probably by orientation of phenyl group.

The dihedral potential energy function was applied to calculate the cumulative distribution function (CDF) of statistically generated set of chains. The CDF for two groups of polymers (see Figure 2) and for two limits cases (the most flexible and the most rigid chain, respectively) are presented in Figure 3.

The CDF forms are similar for the first group of polymers and for the most flexible case (see Figure 3). This fact enables to describe the deformation behavior of one chain using only one function.

The CDF for the second group of polymers was located between the most flexible (freely rotating) and the most rigid model chain.

The calculation of tensile curve of PMMA was modeled in three steps (see Figure 4). In the first step, the network was modeled as Kuhn chains with zero-volume nods. In this step also the deformation of chains was calculated by means of analytical relation (Equation 1.). In the second step, the Kuhn chains were replaced by network of freely rotating chains. The deformation of freely rotating chains was calculated utilizing the cumulative distribution function. In the third step, the nods of network were replaced by undeformable nods with defined size (1 nm).

The predicted tensile curves and the experimental curve approach each other but nevertheless its coincidence is only above $\lambda \geq 3$. The model and experimental curves differ significantly in region of low deformations and they differ also in the region of middle deformations. Not exact defined type of chain, crosslink density and presence of slip-links and weak physical crosslinks can cause this declination.

The type of chain can be verified by persistence length of chain. The persistence length of the chain reflects the deformation as well as structural behavior of chain. The persistence length can be derived from any polymer utilizing rheometric experiment. The experimental estimated persistence length of PMMA was 0.15 – 0.20 nm.[17] The numerical estimated persistence length of freely rotating chains was 0.2 nm. We can state that the freely rotating chain was good approximation to real PMMA chain model.

The difference between experiment and model can be probably associate with properties of network. Difference of model and real network structure is in presence of slip-links and weak physical crosslinks. This factor is included in real tensile curve but is

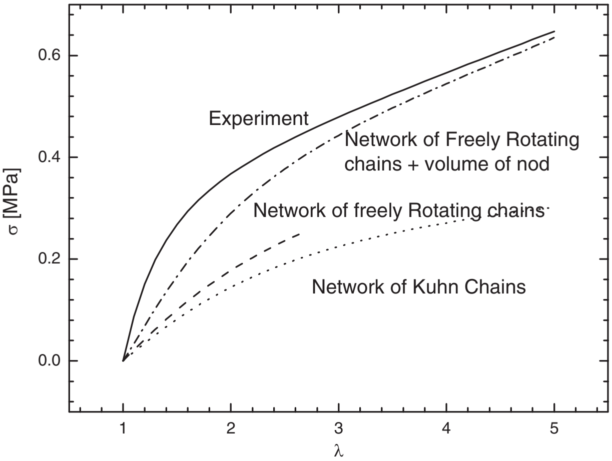

***Figure 4.***
Deformation properties of chains based on replacement real chain by freely rotating chains, and real model of PMMA; Dotted: network of Kuhn chains, dashed: Network of freely rotating chains with zero volume of chains; dash-dotted: Network of freely rotating chain where the volume of nod was calculated from molecular structure of nods; solid- comparison to experimental tensile curve.

missing in swollen state. The difference between swollen and unswollen state is interpreted as a presence of slip links just in the constrained junction models.[1]

The effect of weak crosslinks as a function of deformation must follow the difference between model and experimental tensile curve from Figure 4. The relation between concentration and deformation of network is more highlighted in glassy polymers.[18] According to Stachurski, the tensile curve of glassy PMMA is divided to three regions: low deformation – relaxations of chains, middle deformation – breaking of constriction points and high deformation – engagement of entanglements. In the rubbery materials, the chains are more flexible in comparison to glassy state. The flexibility of chains leads to formation of quickly dissociable nods in the low deformation phase. Quick disappearance and re-appearance of temporary nods increases the crosslink density and the modulus of material. With increasing deformation, the flexibility of chains decreases up to middle deformation region. The presence of quick slip-links decreases and there are only constriction points which are realized by weakly entangled chains. That is why the difference of real and model tensile curve is lower, but it is still observed. In high deformation phase, the effect of constriction points disappears and there is only the effect of crosslinks.

The behavior of constriction points can be detected by the strain hardening. Hoy and Robbins[19] presented the model of glassy network during the strain hardening. They assumed that the model of glassy polymer is an entangled network. In contrast to entropy- controlled networks, the strain hardening modulus in real materials is decreasing with increasing temperature. Thus the molecular structure of constriction points must be separable only by thermal motion.

## Conclusion

The combination of rubber elasticity and molecular modeling was applied to predict the tensile curve of poly(methyl methacrylate) (PMMA). The predicted curve was compared with experimentally measured curve. The results can be summarized in following point:

In the low and middle deformation area ($\lambda < 3$) the predictive curve differs from experimental one. The reason of this difference is in the topology of network in dry and swollen state, respectively. Specifically, with increasing deformation this difference decreases.

There is only a small difference in using two types of chains in build up the network (worm-like versus real molecular chain with correct dihedral angle potential function).

It was confirmed that the procedure used to predict the tensile cure of PMMA can be used to polymers with carbon backbone and arbitrary side group. Specifically, there are two groups of polymer that can be described by two dihedral potential functions.

First group including also PMMA had the similar cumulative distribution function end to end length as the freely rotating chains. The second group had a different cumulative distribution function end to end length (longer mean value of end to end length).

The generalization the procedure using for predicted the tensile curve of PMMA opens the way to widespread the prediction of tensile behavior to other polymers as well as to take in account another type of load.

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