Computational study of mechanical properties of modified Polypropylene

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Abstract. We theoretically investigate the mechanical properties of homo-PP modified by titanium dioxide fillers. As the inorganic filler particles are usually of much larger size comparing to the polymeric chain, the filler is treated as an equivalent “solid” TiO2 substrate on which the PP chains are physically adsorbed. The computational method takes into account the molecular weight distributions and stiffness of PP chains. All parameters of the model are obtained from experimentally known properties of the PP homopolymer. The terminal mechanical properties of the system are studied by generating an equilibrated network in which the microscopic simulation of fracture phenomena, caused by the application of tensile stress perpendicular to the interface is simulated. The network is deformed assuming a kinetic MC method at a constant strain rate. Results based on structural grounds and on estimations of the stress-strain curves are derived and compared.

1. Introduction
The inherent physical properties of polymers can be modified by adding inorganic fillers. The addition of fillers though retains their characteristic processing ease; it affects the basic mechanical properties.

In this article we focus on the polypropylene (PP) system filled with TiO2 [1-3]. We study the PP/TiO2 as it is one of the mainly used, commercially available polymeric systems. The TiO2 filler do not usually alter the morphological characteristics of the polymer, except that the filled samples are less opaque than homo-PP samples. Actually, it is has shown experimentally that although the melt and the glass transition temperature of homo-PP remain essentially unchanged by filling, the room temperature stiffness is significantly improved. It is assumed that the inorganic filler particles are of much larger size comparing to the polymeric chain [4]. We have therefore considered appropriate to model the PP/TiO2 interface by envisioning a TiO2 matrix, treated as an equivalent «solid» substrate, on which the PP chains are physically adsorbed, extending into a bulk PP phase. In order to model realistic polymeric interfacial PP/TiO2 systems, we assume that both the free and adsorbed PP should have a polydispersity index (PDI) different from unity (usually rather high).

2. Theoretical model
In this work we apply the self-consistent field model (SCF) for the PP/TiO2 interface. The conformations and concentration profiles at our interface is the SCF lattice model [5]. Actually, we have applied a
modification of the plain SCF theory, in which we have properly accounted for conformational stiffness and for polydispersity [6]. In this approximation, it is usually convenient to map the many-chain system on a lattice. In addition the segment weighting factors are estimated, which describe the probability of finding a specific chain segment at some lattice site. Although the formulation of the partition function for a dense system on a lattice and the derivation of the free energy for this partition function is not a formidable task, it is rather cumbersome or sometimes practically infeasible to derive final expressions for useful physical quantities. In most cases it is legitimate to work exclusively with the maximum term in the partition function, ignoring all other terms which are the source of the fluctuations. This approach, based on the neglect of some fluctuations in the system, is classified as a mean field approximation, due to the fact that each chain is described as feeling the mean field of all surrounding chains. Usually, we describe and estimate this mean field in a self-consistent manner. Within an iterative procedure, the input local concentration produces a local mean field which is used in order to estimate a new conformational distribution, hence a new value for the local concentration. A self-consistent scheme is successful when the sequence of approximations for the local density converges. The full description of the SCF methodology applied in the present work can be found in reference [6].

In this SCF methodology the use of the lattice has the advantage of lowering the available number of configurations to a representative subset of the real configurations. Among the possible choices for the lattice segment size, we use the Flory segments. A Flory segment can be defined such that a chain will have the same maximally extended length (end-to-end distance in all-trans conformation) and volume in the Flory segment representation as are measured experimentally. We then apply to the PP/TiO$_2$ interface an algorithm for generating polymer entanglement networks [7]. Our guides for the generation of the polymer network are the configurational distribution functions derived from the SCF results on the interface. Entanglement points are placed along the contour of each chain at equal distances, corresponding to the experimentally measured molecular weight between entanglements. The spatial distribution of entanglement points in the direction perpendicular to the surface follows the statistical weights of the mean field theory. Our initial guess for the positions of the entanglement points of each chain parallel to the interface obeys Gaussian statistics. The polymer network created by this procedure is not in equilibrium. Overstretched strands are relaxed by a Monte Carlo method involving moves that preserve the placement in the directions perpendicular to the interface. The equilibrated network is our starting point for the microscopic simulation of fracture phenomena, caused by the application of tensile stress perpendicular to the interface.

The specimens generated are not in detailed mechanical equilibrium. We then apply a method [8] for relaxing the network with respect to its density distribution, and thereby imposing the condition of mechanical equilibrium, without changing the network topology. Our method rests on minimizing a free energy function characterizing the network, with respect to the coordinates of all entanglement points and chain ends. Contributions to the free energy include (a) the elastic energy due to stretching of the chain strands, and (b) the free energy due to the repulsive and attractive (cohesive) interactions between segments. In order to calculate the interaction energy, a simple cubic grid is superimposed on the network. The repulsive interactions are calculated within each grid cell. The attractive interactions are calculated from contributions between cells and within each cell. The fully relaxed networks serve as a starting point for the mesoscopic simulation of fracture phenomena, caused by the application of tensile stress perpendicular to the interface. The network is deformed at a constant strain rate and the network topology evolves according to elementary mechanical processes of chain scission, chain slippage, disentanglement, and reentanglement. Chain slippage across an entanglement point occurs according to a Zhurkov activated rate equation with parameters derived from viscosity data. Each cycle of the kinetic MC algorithm used to track the deformation process consists of the imposition of a small incremental strain on the network,
relaxation to mechanical equilibrium, introduction of the micromechanical processes mentioned above, and again relaxation to mechanical equilibrium. The MC cycles are repeated until fracture occurs [8].

3. Results and conclusions

As the size of the TiO$_2$ particles is of the order of 0.5 $\mu$m [4] and the radius of gyration of the longest (100kg) PP is of the order of $R_g=25$nm, we conclude that our assumption for treating TiO$_2$ as an “infinite” substrate is valid.

In order to study the PP phase by means of the SCF lattice model, we construct a lattice bounded by a flat substrate, the size of each site being equal to the polymer Flory segment. Isotactic polypropylene is a very well studied polymer [9]. In order to estimate the Flory segment we need expressions for the density as a function of the pressure and temperature [10]. In the results we present here we have assumed that the temperature of our system is 235 °C, temperature at which the sample are usually prepared. Then the samples are cooled down to room temperature abruptly, so we assume that the thermodynamic equilibrium state corresponds to the high temperature. In order to estimate the bending energy a value for the characteristic ratio ($C_\infty$) is needed; in this work we use 5.7 [11]. For PP at this temperature, the Flory segment length is $l_F=6.1$Å.

We expect the mechanical properties to depend mainly on the number of entanglements between adsorbed and free chains. An estimate of this region where adsorbed and free chains coexist, is obtained by the interfacial width $w_{\text{int}}$, with $w_{\text{int}} = 4 \int_0^\infty \varphi_a \varphi_f \, dz$. In this expression $\varphi_a$ and $\varphi_f$ are the volume fractions of the adsorbed and free chains and the factor 4 is set in order to get the correct limit for interfaces of hyperbolic tangent shape.

By systematically investigating case of various molecular weight (MW) distributions, we found that the interfacial width is a monotonically increasing function of the for monodisperse samples (figure 1(a)). Once we assume polydisperse samples we have shown that the interfacial width does not increase monotonically, but it levels off (see figure 1). This means that we can not improve the mechanical properties of polymer by either increasing its MW or its DPI.

![Figure 1](image_url)

(a) Plot of the effective interfacial width ($w_{\text{int}}$) as a function of (a) the number average molecular weight for fixed DPI (circles for monodisperse and squares for DPI=2) and (b) the DPI for fixed number average molecular weight of 50kg/mol.

Using a kinetic MC algorithm [8] we proceed to the simulation of deformation and fracture of the polymeric sample. In order to do so we need to simulate properly the elementary mechanical processes of chain scission, chain slippage, disentanglement, and reentanglement. In order to estimate the rate constant of an elementary slippage event the activation energy and the frequency factor are needed, which are
estimated by means of the temperature dependence of the viscosity [8]. In the present study we ignore processes where the adsorbed segments of a chain are removed from the surface.

From figure 2, we clearly observe that the polydisperse sample is more difficult to break in accordance to predictions on structural ground (figure 1(b)).

![Figure 2](image)

**Figure 2.** True stress-draw ratio curves for sample with molecular weight of PP of 50kg/mol. The deformation occurs at strain rate 1% per second. The dotted line corresponds to a monodisperse sample and the solid line corresponds to a polydisperse sample of DPI=4.

In conclusion, one can say that the observed results are in good agreement with both available experimental expectations and predictions from our previous work. Moreover, the procedure followed in this work in order to track deformation to fracture of an entanglement network is rather general; it can easily be applied to polymeric systems of different chemical constitution and topology.

4. Acknowledgment. This work was supported by the Greek Secretariat for Research and Technology (GGET) by a grant (PENED 01ED529).

5. References

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