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Relazione Scientifica conclusiva
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During the stage at Leiden Institute of Chemistry, at the Leiden University, the research activity has been focused on the achievevement of a better understanding of the morphology of PEBAX 2533 membranes by using mesoscopic techniques. The copoly(amide-12b-ethylene oxide) named PEBAX®2533 is composed of rigid polyamide, Nylon 12 (PA-12) at 20 wt% interspaced with flexible polyether (PTMO) chains and shows micro-separation between the components and a very low crystallinity percentage (≈ 3 %)[1]. The need to include the degree of crystallization firstly into the pure co-monomer PA-12 and then into the PEBAX material, has driven our research during this stage in Leiden University.
PEBAX, highly versatile materials, are plasticizer-free thermoplastic elastomers. They have been utilized in high performance industrial articles, medical textiles and sports-wear exhibiting specific and interesting transport properties [2-7]. We know that the microdomain morphology is very complex, and despite the great deal of experimental work [1-11], there's a lack of information about the morphological behaviour of PEBAX.

The main scientific goal of the collaborative research project is the advance in knowledge of the morphology of PEBAX. Mesoscale simulations have been performed in order to investigate the phase behaviour and the miscibility between hard and soft domains in the spatial range of mm.
The previous studies with the Dynamic Density Functional Theory (DDFT) [12-18] methodology, conducted by modelling collections of flexible chains, have shown that PEBAX®2533 is in a disordered, completely amorphous state. The DDFT study treating the system as a collections of flexible chains indicated the impossibility to consider a complex morphology with of hard and soft moieties and that is not suited to address the properties of PEBAX®2533.
It is necessary to introduce a certain degree of stiffness, owing to the presence of PA-12, into the method, which is most easily done with the Dissipative Particle Dynamics (DPD) methodology.

In DPD, collections of connected soft-core repulsive particles move according to Newton's equations of motion and interacts dissipatively through simplified force laws (e.g. Groot and Warren [19]). In this way, a full hydrodynamics description is recovered.

Setting the masses of all particles equal to 1, the time evolution of the positions ($r_i(t)$) and velocities ($v_i(t)$) is given by:

$$\frac{dr_i}{dt} = v_i(t) \qquad \frac{dv_i}{dt} = f_i(t) \tag{1}$$

The force acting on the particles is a combination of three contributions:

$$f_i(t) = \sum_{j \neq i} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R \right) \tag{2}$$

The conservative force between two beads *i,j* separated by a distance *rij*:

$$F_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij}/r_c)\hat{r}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \leq r_c \end{cases} \tag{3}$$

where a_{ij} is the maximum of the linear potential between particles i and j , $r_{ij} = r_i - r_j$, $r_{ij} = |r_{ij}|$, $\hat{r}_{ij} = r_{ij}/|r_{ij}|$, and r_c is the cut-off radius.

Note that the conservative force is always finite even at zero separation. The other two forces are the dissipative and the random force, which are given by:

$$F_{ij}^D = -\gamma w^D(r_{ij})(\hat{r}_{ij} \cdot v_{ij})\hat{r}_{ij}$$

$$F_{ij}^R = -\sigma w^R(r_{ij})\theta_{ij}\hat{r}_{ij} \tag{4}$$

where $\hat{v}_{ij} = \hat{v}_i - \hat{v}j$, ω^D and ω^R are weight functions tending to zero for $r = r_c$ and θij is a randomly fluctuating variable with zero mean and unit variance. Español and Warren [20] showed that the weight functions and constants γ and σ (denoting the friction coefficient and the noise amplitude for all particles, respectively) in Eq. (4) can be chosen arbitrarily, but should obey:

$$[\omega^R(r_{ij})]^2 = \omega^D(r_{ij}), \quad \sigma^2 = 2k_B T \gamma \tag{5}$$

where k_B is the Boltzmann constant and T the temperature of the fluid. The equations are solved using the modified velocity-Verlet algorithm as described by Groot and Warren [19]. The random force weight function: $\omega^R(r_{ij})$ is defined as $1 - (r/r_c)$, where $r_c = 1.0$.

Since DPD is a coarse-grained model and individual atoms or molecules are not represented directly by the particles but they are grouped together into beads, these beads represent local 'fluid packages' able to move independently.

Connections between beads, i.e. a polymer molecule, are established by adding a spring between beads. Thus, beads can be interconnected to highly complex topologies, e.g. branched architectures, and additional spring forces should be added to Eq. (2).

Choosing the correct spring force deserves closer examination. Two types of spring force have been considered in literature. Groot and Warren advocated the use of the harmonic spring:

$$F_{ij}^{spring} = k \cdot r_{ij} \tag{6}$$

where k is the spring constant. In this way the mean distance between two consecutive chain beads is governed by the spring force and the repulsive interaction. The value of the spring constant is chosen such that the mean spring distance corresponds to the distance found at the maximum of the pair correlation function of the polymer beads when the spring constant is equal to zero. However, in this manner connected beads are not prevented to be located far more than r_c apart. This is highly undesirable as hydrodynamic interaction between beads within the same polymer chain is lost and it would be easy for polymer chains to cross each other without ever experiencing any mutual interaction. This is comparable to neglecting the Zimm corrections [21] on the dynamical chain behaviour as predicted by the Rouse model [22]. Of course, a stiffer spring could be modelled by choosing a larger spring constant, but, essentially, this would also imply an increase in the density of the polymers.

Chain stiffness is modelled by a three-body potential acting between adjacent bead triples in a chain:

$$U_{i-1,i,i+1} = k_2\left[1-\cos(\phi-\phi_0)\right] \qquad (7)$$

where the angle ϕ is defined by the scalar product of the two bonds connecting the pairs of adjacent beads *i-1. i. i+1*: in general, the bending constant k_2, and preferred angle ϕ_0 may be specified independently for different bead type triples allowing the chain stiffness to vary along a molecule's length. A preferred angle of zero means that the potential minimum occurs for parallel bonds in chain.

The mapping procedure from the full atomistic to the coarse grained representation is based on the notion that packing constraints are most important in pattern formation, hence, it relies on matching atomic and coarse grained volumes. In general, bead radii are constraint below by the persistence length at atomistic resolution.

The volume of the sphere of a single segment of amorphous PTMO, $V_{PTMO,}$ has been calculated from geometric considerations on structural data extracted by MD models: a single segment has been considered as one bead.

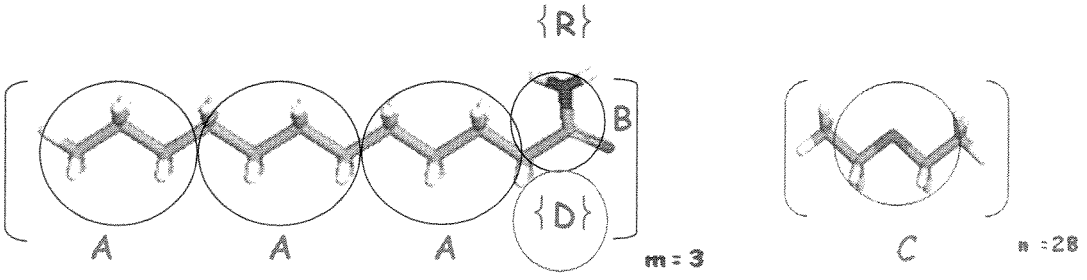

Figure 1 - Coarse grained modelling of PA-12 (left) and PTMO (right) monomers from atomistic model.

According to the estimated volume V_{PTMO}, the PA-12 aliphatic chain has been divided into 3 beads of similar volume (calculated from geometric considerations on structural data of crystal of PA-12 [24]), while the stiff part (amidic group) of polyamide has been considered as one bead of (smaller) volume. Actually beads have the same volume.

From experimental data it is known that the most stable crystalline phase of PA-12 is α phase [24] consisting of planar sheets of hydrogen-bonded chains with sheets stacked upon one another and displaced along the chain direction by a fixed amount.

Consequently DPD simulations of PA-12 and PEBAX®2533 have been carried out: the incorporation of a certain degree of crystallinity is unprecedent in this respect. PA-12 has been modelled as a collection of rigid rods of compositions $A_3B\{R\}\{D\}$, where A represents the aliphatic chain bead, B the polar amidic group bead; $\{R\}\{D\}$ are perpendicular to the segment bond and do not represent physical entities but play the role of acceptor and the donor groups. They have been introduced in order to define the interchain interactions between different PA-12 chains.

A number of 167 chains with three repetitive units $A_3B\{R\}\{D\}$ has been inserted in the simulated volume. Stiffness has been introduced by making use of angle potential of Eq. 3, setting $a_{ij} = 2$, k_2= 180-200 and $\theta = 0$. Also a high value to the bond interaction type (k3) has been introduced with a value between 180-200.

The interaction parameter a_{ij} (Eq. 3) is a measure of the repulsion between every pair of bead. This captures the chemical nature of the molecules, or segments of molecules, that each bead represents. The a_{ij} parameters as they are used Culgi [25] are the dimensionless $a_{ij}^* = (a_{ij} / k_B T) \cdot h$.

The interaction parameters a_{ij}^* between AA and AB type beads are set to high values, and to low values for $\{R\}\{D\}$ groups (respectively 130 and 2) in order to ensure repulsion between beads of the same type and of the same chain and strong interactions between different chains.

Temperature has been set to low value for "freezing" the system and to decrease the entropy. The temperature: 0.1. The Time step: 0.01. The Box Dimension: 10 X 10 X 10, and the Bead number density: ~3.0.

DPD simulations have been conducted for 100000 iterative steps and the final frame is reported in Figure 2:

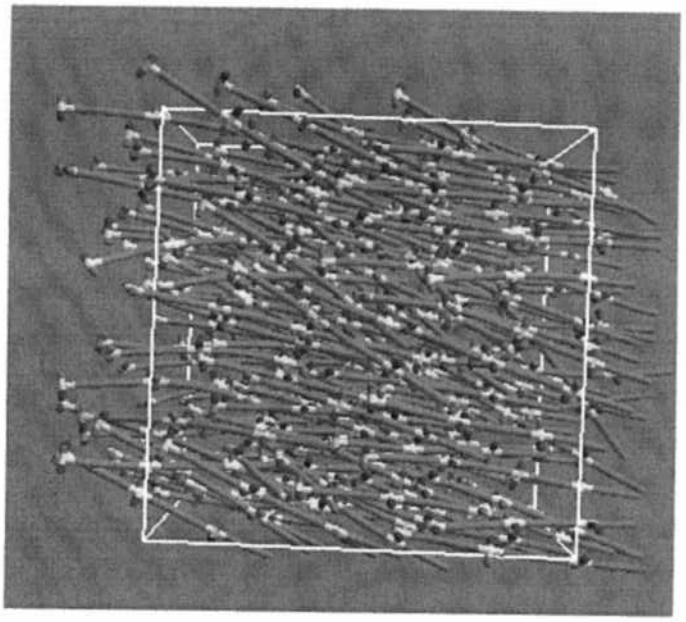

Figure 2 - Last frame of PA-12 DPD simulation: a PA-12 chain is modelled as $A_3B\{R\}\{D\}$, with A coloured in grey, B in yellow, $\{R\}$ in red, $\{D\}$ in blue.

From a quick visual analysis of Figure 2, the PA-12 chains are "rigid" rods in an almost parallel reciprocal orientations. To estimate the degree of alignment of PA-12 beads with respect to the main direction, i.e. to describe the alignment of the rigid PA12, the Maier-Saupe Parameter (MS) has been measured, $MS = \sqrt{3[(\cos\phi)^2 - 1]}$ In Figure 3 the interaction parameters has been modified keeping constant k_2 and k_3. The structure is rigid along the simulations in the wide range of simulated interactions.

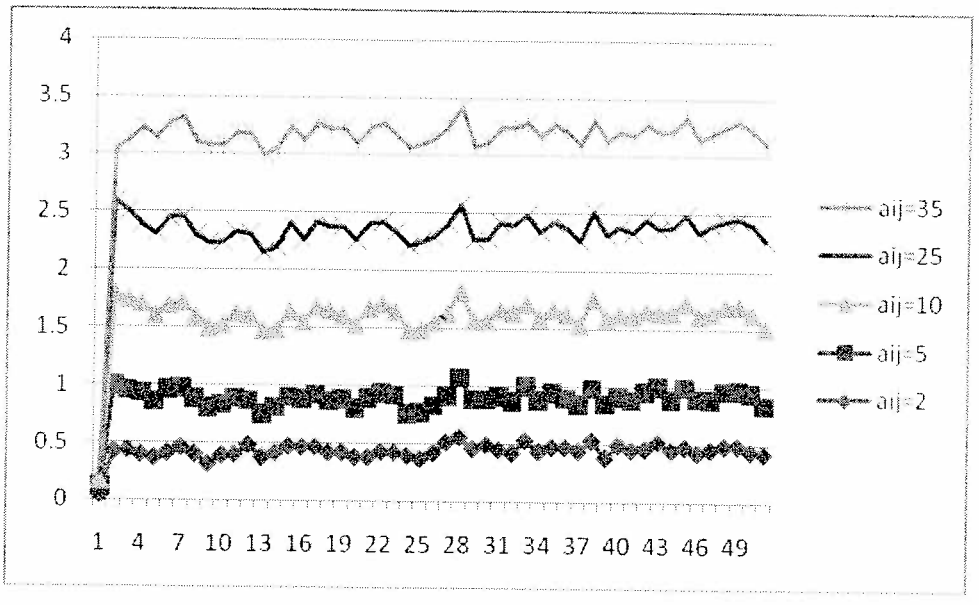

Figure 3 - Description of alignment of the rigid PA12.

DPD simulations of PEBAX®2533 have been performed using the rigidity parameters introduced for PA-12. The PTMO beads (C) have been introduced. The composition of PEBAX repeating unit is set to be $[A_3B\{R\}\{D\}]_3\ C_{28}$.

The a_{ij} parameters have been calculated using the Flory Huggins procedure, $\chi = (0.286 \pm 0.002)\Delta a$, with $\rho = 3$ following the indications of Groot and Warren [19], combined with the calculated value from V.V. Ginzburg et al. [26], of $\chi = 9.66$. The pair interaction parameters for all couple of beads are indicated as follows:

Pair interaction parameters:

Type1	Type2	a_{ij}
A	C	34
B	C	34
D	R	2

The other parameters that have been fixed are: K_2=180, K_3=200, ϕ=0 , Temperature: 0.1, Time step: 0.01, Box Dimension: 30 X 30 X 30, number of beads: 1761 and Bead number density: ~3.0

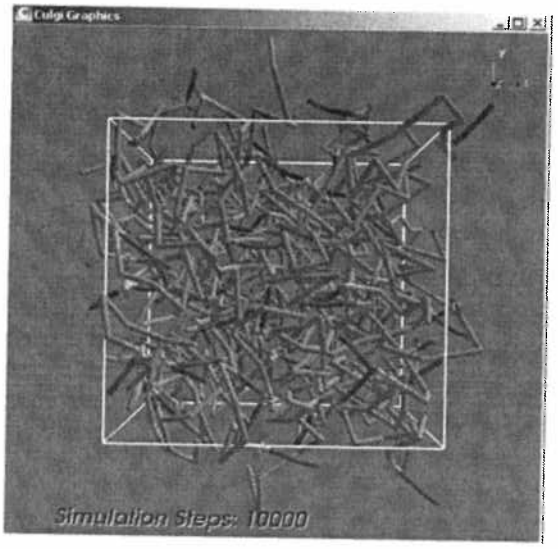

Figure 4- Last frame of PEBAX®2533 DPD simulation.

The software used is Culgi, developed in the same host institute, which contains a variety of mesoscopic methods including both Dissipative Particle Dynamics (DPD) and Dynamic Density Functional Theory (DDFT).

The visit at the Leiden Institute of chemistry has been quite positive in terms of strenghtening collaborations with the Soft Matter Chemistry Group on complimenting experimental-theoretical studies with mesoscopic techniques and generating a more complete investigation of the PEBAX®2533 morphology, thus widening the length and temporal range of simulation effort with respect to the fully atomistic investigation by MD.

As a further step DPD simulations will be carried on in order to analyze the influence of the different percentages of PA-12 into the PEBAx series. This will be done to provide more detailed insights on the chain architecture of hard PA-12 and soft PTMO domains.

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