

Determination of plasticizers efficiency for nylon by molecular modeling

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Abstract Polyamides are semicrystalline polymers useful in a wide range of applications in the plastics industry. Some applications require higher flexibility and workability of the polyamides, therefore, plasticizers are added to ease compounding and processing procedures and produce the desired product properties. The goal of this study was to estimate plasticizers efficiency in plasticizing Nylon 66/6 copolymer (molar ratio 80/20, respectively) using computational tools and to compare the calculated estimations to experimental results. Four plasticizers were studied: glycerin mono stearate, benzene sulfonamide, methyl 4-hydroxybenzoate (M4HB), and diethylhexyl phthalate. Plasticizers efficiency was determined by calculating cohesive energy density, solubility parameters, free volume and interaction intensities of pristine nylon, and the nylon–plasticizer blends. It was found that the efficiency of the plasticizers increases with the degree of interaction intensity between the plasticizer and polymer chains and that M4HB molecules cause the largest changes in free volume. This finding correlates with the experimental results, based on reduction of polymer glass transition temperature (T_g). The highest calculated plasticization efficiency was obtained for M4HB, for which the decrease in T_g was the most significant.

Keywords Polyamides · Plasticization · Solubility parameter · Interactions

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Introduction

The mixing of polymers with various additives to achieve desired properties for specific applications is a well-known approach. For example, plasticizers are able to reduce the modulus, tensile strength, hardness, density, melt viscosity, and glass transition temperature of a polymer, while at the same time increasing its flexibility, elongation at break, workability, and extensibility [1]. Plasticizers are incorporated in the amorphous parts of polymers while the structure and size of any crystalline part remains unaffected [2].

Plasticizer efficiency is defined as a measure of the concentration of plasticizer required to impart a specified softness to a polymer [2]. Plasticizer efficiency is greatly influenced by structural effects of the plasticizer. For example, Krauskopf and Arndt [3] explored ester plasticizers for poly(vinyl chloride) PVC and found that for a given acid constituent of an ester, plasticizer efficiency decreases as the carbon number of the alcohol chain increases. Also, phthalate and adipate esters were both considerably more efficient than their trimellitate equivalent and the linear plasticizers were found to be more efficient than the branched ones [3]. On the other hand, Lindström and Hakkarainen [4] found that plasticizing efficiency was improved by higher degree of branching. They examined linear and branched poly(butylene adipate)s with molecular weights ranging from 2,000 to 10,000 g/mol as plasticizers for PVC [4]. In another study [5], acetyl tri-*n*-butyl citrate and poly(ethylene glycol)s (PEGs) with different molecular weights (from 400 to 10,000) were used to plasticize poly(L-lactic acid). The plasticizing efficiency of PEG increases with decreasing molecular weight [5]. The efficiency of plasticizers for the corn protein gluten was related to many physicochemical characteristics of those molecules [6]. The polar plasticizers studied were efficient because of their low molecular weights, whereas amphiphilic molecules, such as dibutyl tartarate and octanoic acid, could interact efficiently with the proteins, through structure similarities [6].

The interactions formed between the polymer chains and the plasticizer molecules, while reducing polymer–polymer chain interactions, play a crucial role in plasticization mechanism. De Brabender et al. [7] studied the plasticizing properties of ibuprofen (IBP) on hot-melt extruded ethyl cellulose (EC). They confirmed the existence of hydrogen bonds between IBP and EC using Infrared spectroscopy [7]. Domjan et al. [8] determined the plasticizing efficiencies for glycerol and PEG 400 as softening materials in amorphous chitosan films. They found that the two plasticizers were similar in mechanical tests, but different in the three-dimensional (3D) H-bonded structure, monitored by solid-state NMR spectroscopy. Their findings were supported by density functional theory calculations indicating formation of three H-bonds for glycerol with chitosan, and only one for PEG 400 [8]. In another study, it was found that hydrogen bonding played an important role in plasticizing starch films by monosaccharides and polyols, as indicated by FTIR spectra [9].

Among the theories describing plasticization effects, the gel theory [10] and the free volume theory [11] are the most notable.

Gel theory suggests that polymer rigidity is a consequence of its 3D honeycomb structure formed by attachments of the active centers (polar side groups for example) along the macromolecular chains [10]. Free volume theory is an extension of gel theory. Free volume is defined as the fraction of the volume not occupied by the polymer [10, 11]. Free volume enables motions of the polymeric main chain, its ends, and side chains. Plasticizers increase the free volume of the resin and thus increase its flexibility and consequently lower its glass transition temperature. The amount by which plasticization can increase the free volume is limited by the size of the plasticizer and the inherent free volume of the polymer matrix [10, 11]. Experimental probes for free volume at molecular and atomic scales and volume distribution of holes in amorphous polymers is possible using small-angle diffraction, fluorescent spectroscopy, and positron annihilation lifetime spectroscopy [11, 12].

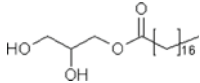
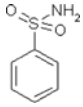
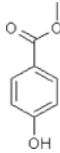
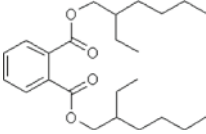
A plasticizer is mixed with a polymer in order to make it more flexible, durable, and processable by lowering its second-order transition temperature. Therefore, glass transition temperature T_g is a good measure of material plasticization, and it may serve as an indicator of plasticizer efficiency [2]. Recently, plasticizer efficiency for polyamides was determined in our group by measurement of the lowering extent in T_g caused by a given amount of plasticizer [13].

Only few works were published concerning estimation of plasticizer efficiency using computational tools. Tarvainen et al. [14] used quantitative structure activity relationship based method (VolSurf with GRID) as a novel tool for the prediction of plasticization efficiency for the film-former starch acetate, plasticized with each of 24 tested compounds. A decrease in glass transition temperature of the plasticized free films was used as an indicator for plasticizer efficiency. They found a good correlation between the 3D molecular structure of the compounds obtained by molecular modeling and the experimental data. Favorable structural properties identified for the potent starch acetate plasticizer were strong hydrogen bonding capacity and a definitive hydrophobic region on the molecule [14]. Quantitative structure property relationship was used by Chandola and Marathe [15] to establish plasticizer efficiency for PVC. They scanned 25 molecules as plasticizers and used low temperature flex point, T_f , as an indicator of plasticization efficiency. The correlation of physical and structural descriptors derived from the plasticizer molecule alone was not very good. Therefore, a model containing two PVC chain segments along with a plasticizer molecule in a simulation box was constructed, using molecular mechanics. A good QSPR equation correlating physical and structural descriptors to T_f of the plasticized resins was obtained for that model [15].

Free volume distributions have been studied theoretically by using kinetic theories and molecular dynamics. Chow [16] has modeled the size and volume distribution of holes in amorphous polymers and has provided a good description of the non-Gaussian spreading observed in position annihilation experiments.

The goal of this study was to apply computational tools to estimate plasticizers efficiency of several plasticizers (see Table 1) for a polyamide, the random copolymer Nylon 66/6, and to compare the calculated results to the experimental ones obtained in our laboratory [13]. Various parameters which are connected to plasticizer efficiency were calculated: Solubility parameters of the pure nylon, the

Table 1 Description of plasticizers

| Chemical name | Structure | Phase at RT | Molecular weight (g/mol) | Melting/boiling temperature (°C) |
|---------------------------------|-----------------------------------------------------------------------------------|-------------|--------------------------|----------------------------------|
| Glycerin mono stearate (GMS) |  | Solid | 359 | 74/240 |
| Benzene sulfonamide (BSA) |  | Solid | 157 | 152/NA |
| Methyl 4-hydroxybenzoate (M4HB) |  | Solid | 152 | 131/270-280 |
| Diethylhexyl phthalate (DOP) |  | Liquid | 390 | -52/386 |

pure plasticizers, and their mixture may serve as an indication to their compatibility. The free volume of the plasticized polyamide was calculated and compared to the free volume of the pure polymer. The major interactions between the polymer chains and each plasticizer were also calculated. All calculations were conducted in the atomistic level.

Experimental

Computation details

Two simulation modules included in the molecular modeling package Material Studio (by Accelrys) were used:

Discover—a forcefield simulation tool performing molecular mechanics and molecular dynamics tasks. The forcefield used was COMPASS [17].

Amorphous cell—a simulation tool capable of building 3D periodic boundary cells [17].

The computational procedure was as follows:

1. A random copolymer, Nylon 66/6, with monomers ratio of 80/20 (M.W. 5,886) was built and minimized using Discover module. The polymer molecular weight was chosen so that the 3D model is large enough to represent the actual

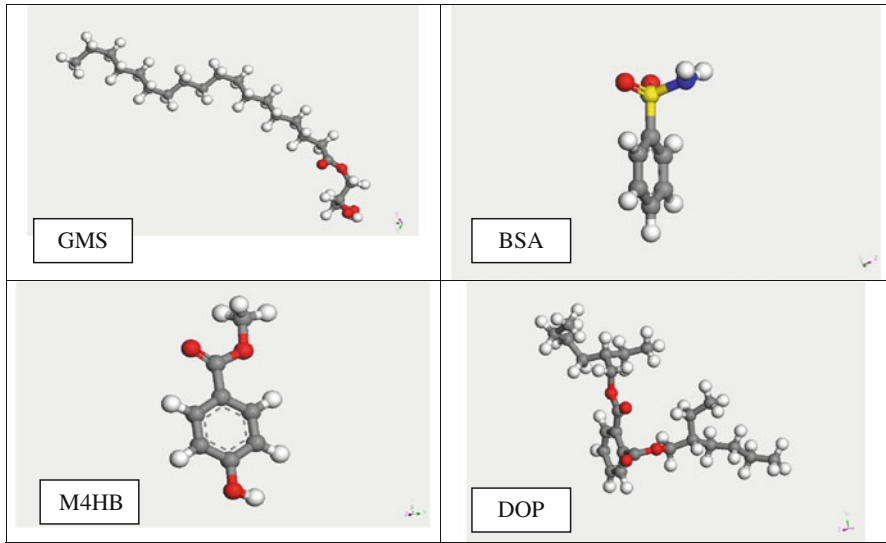


Fig. 1 Plasticizers structure after minimization

material behavior while maintaining a reasonable cell size to avoid long computation time. Each of the four plasticizer molecules (see Table 1) were built and minimized as well. The minimized molecular structures of the four plasticizers used in this study are shown in Fig. 1.

2. Five simulation cubic boxes (about 20 Å edge) were constructed for each of the following: (a) pure copolymer; (b) pure plasticizers; (c) plasticized copolymer. A simulation box of nylon with benzene sulfonamide (BSA) is shown in Fig. 2. The boxes were built using Amorphous cell module at their experimental density [18] and at a temperature of 298 K. The plasticizer concentration in the plasticized nylon was chosen to be between 10.9 and 11.8 wt% according to the concentration range used in the parallel experimental research [13]. To reach that concentration, each simulation box was constructed with one nylon chain to which plasticizer molecules were added according to their molecular weights: 5 molecules of methyl 4-hydroxybenzoate (M4HB) or BSA, and 2 molecules of diethylhexyl phthalate (DOP), or glycerin mono stearate (GMS).
3. The cell building procedure was repeated for the free volume calculation, only that four helium atoms were added to each box. Mean square displacement (MSD) of the helium atoms served as a probe for the free volume.
4. The cells containing the nylon, the plasticizer and their blends (with and without helium atoms) were subjected to a refinement stage of 100,000 dynamic steps (1 fs for each step) followed by a data collection stage of additional 300,000 steps.
5. The resulted dynamic trajectories were analyzed using Amorphous cell module analysis tools. The following properties were calculated:
 - a. *Cohesive energy density (CED) and solubility parameter* of the pristine polymer and its blends with the plasticizers. In atomistic simulations, the cohesive

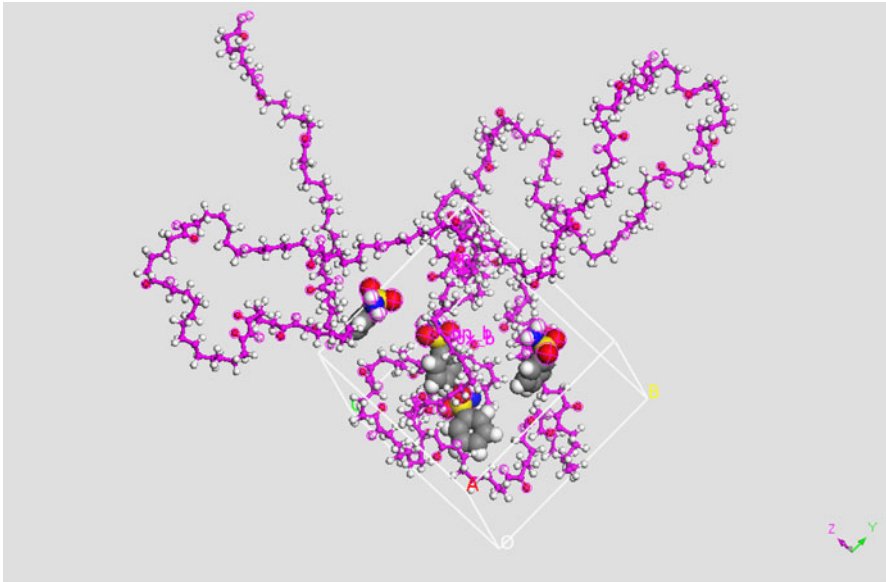


Fig. 2 A simulation box of BSA-plasticized Nylon 66/6 copolymer

energy is defined as the increase in energy per mole of a material if all intermolecular forces are eliminated. The CED corresponds to the cohesive energy per unit volume. Solubility parameter δ is the square root of the CED.

- b. *MSD* of the helium atoms in the polymer or polymer blend may serve as a probe for the free volume of the pristine polymer and its blends. MSD calculation is implemented in the Amorphous Cell module as one of the dynamic analysis options [17]. The limiting slope of the MSD as a function of time enables to estimate the self diffusion coefficient of an atom undergoing random Brownian motion in three dimensions. MSD is averaged over the time period of the dynamic run (300 ps in this case), and the diffusion coefficient of the helium atom can be calculated by:

$$D = a/6$$

where D is the diffusion coefficient and a is the slope of the MSD trajectory versus time [17]. MSD trajectories and the helium diffusion coefficients in the pristine polymer or the plasticized polymer were used as measures of their free volumes [19].

- c. *Pair correlation function* (also sometimes referred to as the radial distribution function) gives a measure of the probability that, given the presence of an atom at the origin of an arbitrary reference frame, there will be an atom with its center located in a spherical shell of infinitesimal thickness at a distance r from the reference atom [17]. Pair correlation function may serve as a tool to estimate intermolecular interactions like hydrogen bonding.

Results and discussion

Plasticizers molecular structures and volumes

The minimized molecular structures of the four plasticizers used in this study are shown in Fig. 1. It can be seen that while M4HB and BSA are rigid molecules due to the aromatic rings which are their main constituent, GMS is a very flexible molecule due to its long aliphatic chain. DOP is less rigid than M4HB and BSA, but is much less flexible than and GMS because of the aromatic ring and the branched aliphatic chains. The molecular volumes of the plasticizer molecules were calculated using the “Atom volume and surface” tool in the Material Studio visualizer [17]. The volume calculated were as followed: DOP (441 Å³), GMS (420 Å³), M4HB (140 Å³), and BSA (133 Å³).

Solubility parameter calculation

The solubility parameter δ (which is the root of the CED) of the pure nylon, the pure plasticizers, and their mixture was calculated using the analysis tool of Amorphous cell module [17]. The solubility parameter results are shown in Table 2. The rigid plasticizers, namely, M4HB and BSA, have solubility parameter values of 24.6 and 22.6 [J/cm³]^{0.5}, respectively, which are very close to that of the nylon (23.2 [J/cm³]^{0.5}). This might be attributed to the ability of those molecules to participate in hydrogen bonding, similar to nylon. GMS is also capable of creating H-bonds due to its hydroxyl groups, but its long aliphatic chain decreases the impact of that ability, giving it an amphiphilic character. DOP has the lowest δ because of the absence of H-bond creating groups in that molecule. The solubility parameters of the mixtures of each plasticizer with nylon can indicate the intensity of the mutual interactions [19]. Whereas DOP or GMS have solubility parameters of 17.9 and 19.4 [J/cm³]^{0.5}, respectively, the mixtures of DOP or GMS with the polymer have both a δ of 22.4 [J/cm³]^{0.5}. This value is lower than that of pure nylon (23.2 [J/cm³]^{0.5}) but significantly higher than δ of the pure plasticizers. This might indicate that the interactions between the nylon chains were only slightly affected by the presence of those plasticizer molecules. The solubility parameters of M4HB- and BSA-plasticized nylon are 22.8 and 22.6 [J/cm³]^{0.5}, respectively, closer to the value of pure nylon than the other two plasticizers. This small decrease in δ might be

Table 2 Solubility parameters δ calculation results of pure nylon, pure plasticizers and plasticized nylon

| Substance | δ of pure substance [J/cm ³] ^{0.5} | δ of the mixture nylon–plasticizer [J/cm ³] ^{0.5} |
|------------|----------------------------------------------------------------|-------------------------------------------------------------------------------|
| Nylon 66/6 | 23.2 | – |
| GMS | 19.4 | 22.4 |
| BSA | 22.6 | 22.6 |
| M4HB | 24.6 | 22.8 |
| DOP | 17.9 | 22.4 |

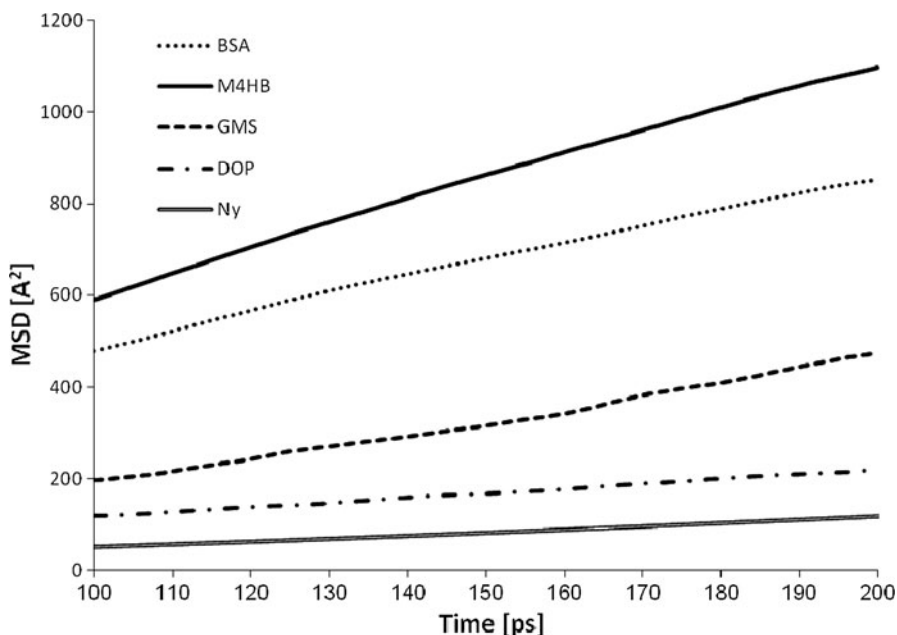


Fig. 3 MSD results of four helium atoms in pure and plasticized nylon

attributed to these plasticizers compatibility with nylon as indicated by the pure plasticizers δ results.

MSD calculation

The results of MSD calculation for the pure nylon and its mixtures with each of the four plasticizers are shown in Fig. 3. The simulation time appears in the x axis, and the MSD of the helium atoms in pure nylon or in the nylon–plasticizer blend appear in the y axis. The limiting slope of MSD as a function of time enables to calculate the diffusion coefficient. The calculated diffusion coefficients are presented in Table 3. It can be seen that the MSD of helium atoms in pure nylon is the lowest as well as the diffusion coefficient ($3.9 [\text{m}^2/\text{s} \times 10^{10}]$), which indicate, as expected, small free volume. The MSD values and diffusion coefficients of helium atoms in the plasticized nylon are much higher for all four plasticizers. The highest values were obtained for M4HB-plasticized nylon (diffusion coefficient of $85.1 [\text{m}^2/\text{s} \times 10^{10}]$), indicating that M4HB molecules cause the largest changes in free volume. The order of the four plasticizers according to their free volume introduction capability (estimated from diffusion coefficients results) in ascending order is:

1. M4HB
2. BSA
3. GMS
4. DOP

Table 3 Helium diffusion coefficients in pure and plasticized nylon

| Substance | Diffusion coefficient [$\text{m}^2/\text{s} \times 10^{10}$] | Correlation factor |
|---------------------|----------------------------------------------------------------|--------------------|
| Nylon 66/6 | 3.9 | 0.999 |
| Nylon 66/6 and GMS | 56.7 | 0.998 |
| Nylon 66/6 and BSA | 62.0 | 0.999 |
| Nylon 66/6 and M4HB | 85.1 | 0.996 |
| Nylon 66/6 and DOP | 53.3 | 0.999 |

Pair correlation calculation

The results of hydrogen bonding calculated by pair correlation function for the pure polymer and its mixtures with the plasticizers are shown in Figs. 4 and 5. Whereas hydrogen bonding interaction between the nylon chains in pure and plasticized nylon are demonstrated in Fig. 4, the hydrogen bonding interaction between the nylon and the plasticizers molecules in plasticized nylon are shown in Fig. 5. It can be seen from Fig. 4 that hydrogen bonding between the nylon chains is not significantly modified by the introduction of plasticizers to nylon. Still, hydrogen bonding peaks in the blends are slightly wider than the peak of pure nylon, indicating a larger average interaction distance. This might imply on somewhat weaker hydrogen bonding between the nylon chains in plasticized nylon.

Figure 5 shows the interaction between the plasticizer molecules and nylon chains. The interaction between the M4HB hydroxyl group and the nylon's amide group is much more pronounced than the interactions of the other plasticizers indicating M4HB is

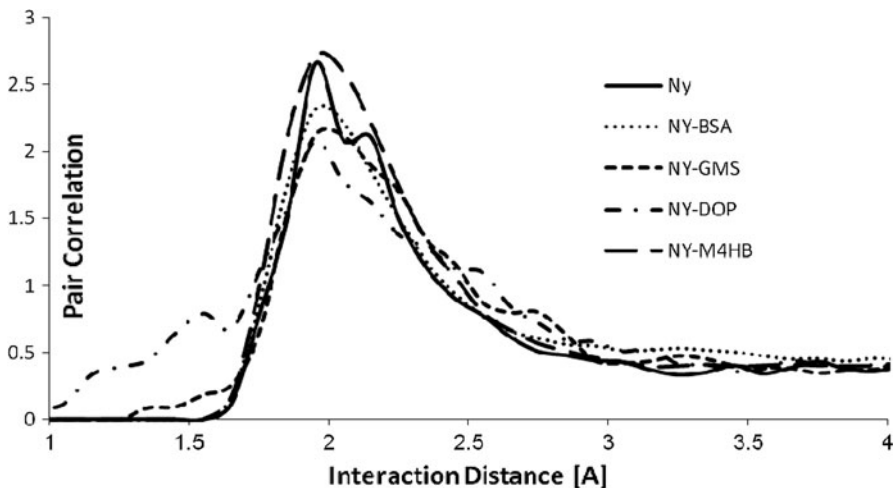


Fig. 4 Hydrogen bonding interaction between the nylon chains in pure and plasticized nylon, calculated by pair correlation function

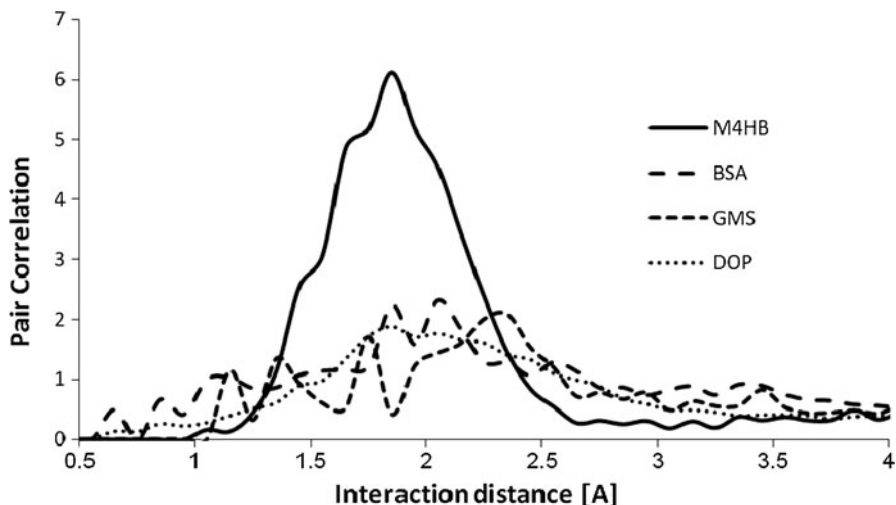


Fig. 5 Hydrogen bonding interaction between the nylon and plasticizers molecules in plasticized nylon, calculated by pair correlation function

Experimental evidence

Recently, plasticizer efficiency for Nylon 66/6 copolymer with monomers ratio of 80/20 was determined in our laboratory by measurement of the lowering extent in T_g caused by a given amount of plasticizer [13]. The plasticizers used were GMS, BSA, M4HB, and DOP, the same plasticizers explored in the presented simulation work. The results are shown in Fig. 6. It can be seen that M4HB reduced T_g with the highest efficiency, BSA was the second, GMS the third, and DOP reduced copolymer glass transition to the lowest extent.

Conclusions

Determination of plasticizing efficiency of four plasticizers for nylon was performed using molecular modeling tools. Various parameters which are connected to plasticizer efficiency were calculated: Solubility parameters, free volume changes, and interactions between the polymer chains and plasticizer molecules. As mention before, two main factors mostly affect plasticizer efficiency:

1. Plasticizer–polymer interactions [8, 9].
2. Enlargement of free volume caused by the plasticizer [10, 11].

Plasticizer–polymer interactions were estimated by solubility parameters and by pair correlation function. It was found that M4HB and BSA have solubility parameter values which are very close to that of the nylon, indicating similar intermolecular interactions. Hydrogen bonding interaction between the nylon chains and M4HB in plasticized nylon, calculated by pair correlation function, was the most pronounced by far. According to these parameters, M4HB is the most efficient plasticizer.

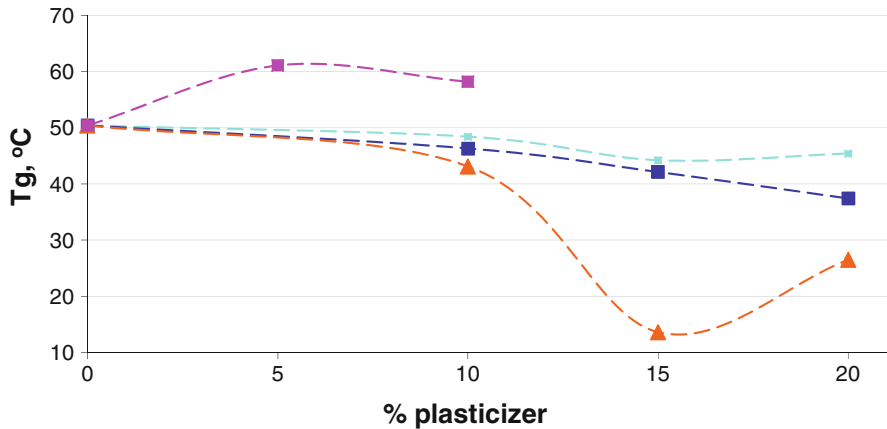


Fig. 6 Experimental results of T_g measurements (determined by DMTA) versus plasticizer content of pure and plasticized nylon [13]

Free volume enlargement caused by introduction of the plasticizer to the nylon was estimated by the MSD of helium atoms in pure nylon or in the plasticized nylon. The order of the four plasticizers according to the free volume enlargement they create (estimated from diffusion coefficients results) in ascending order is: M4HB > BSA > GMS > DOP.

According to all checked parameters, the plasticizer that introduces the largest free volume change and forms the strongest interaction with nylon is M4HB, and therefore is the most efficient plasticizer for nylon (of the four plasticizers examined).

According to the gel theory [10], intensive interaction between a polymer and plasticizer leads to the reduction of the amount of the polymer–polymer attachments, and thereby relieves the rigidity of the truss-like 3D structures. The same argument applies to the introduction of a larger free volume between the chains [11]. Both phenomena lead to a more pronounced plasticization of the nylon and thus may serve as indicators for plasticizing efficiency.

In this computational study, the plasticizer content taken was around 11 wt%. According to the experimental results [13], at that content the largest T_g lowering is induced by M4HB and the order of plasticizer efficiency is M4HB > BSA > GMS > DOP. Hence, the assumption that both the interaction intensity between the plasticizer and the polymer and the plasticizer capability of increasing the free volume correlates with the plasticizer efficiency, is indeed approved by this study for the first time to the best of our knowledge, by a computational study.

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