Mathematical modeling of alkyde resin paint modified by carbon nanotubes

Artem Rukhov¹, E Tugolukov², S Juboori¹,², K Brankin¹ and Anton Rukhov⁴

¹Department "Chemistry and Chemical Technologies", Tambov State Technical University, 106 Sovetskaya street, Tambov 392000 Russia
²Department "Technology and Technology of Production of Nanoproducts", Tambov State Technical University, 106 Sovetskaya street, Tambov 392000 Russia
³Chemical Engineering Department, University of Technology, Mohamid PO Baghdad, 35023 Irak
⁴Department "Operation of Motor Transport and Car Service", Tambov State Technical University, 106 Sovetskaya street, Tambov 392000 Russia

¹E-mail: rukhov.av@gmail.com

Abstract. The purpose of the paper is to develop a hypothesis of the alkyd resin modification process. Using the method of molecular mechanics, a mathematical simulation of the alkyd resin-carbon nanotubes system was carried out under equilibrium conditions. It is shown that the surface of carbon nanotubes is able to structure polymer chains with the formation of additional hydrogen bonds, that can explain the increase in hardness of the film by 10-60%, obtained experimentally. Practical recommendations on the development of industrial technology for the production of modified alkyd paints have been discussed.

1. Introduction

Primers are widely used to ensure adhesion and to reduce paint consumption for subsequent staining with enamels of wooden and metal surfaces applied in the construction, repair and decoration works [1, 2]. Among the requirements, priming compound should effectively treat the surface, totally close its pores, quickly dry, create highly stable film and should not shrink when processing and operating the surfaces. However, currently produced primers do not always provide desired depth of it’ penetration into the treated surface, then, good adhesion to the enamel or varnish layer, high elasticity, and impact strength [1, 3].

Due to high mechanical strength, heat resistance, large specific surface, and hydrophobicity, carbon nanotubes (CNTs) may be considered as promising modifier of primer as shown before [4, 5]. The purpose of the modification is to improve the quality characteristics of the primer, for example, regulated by the documents GOST 25129-82 Primer GF-021 (Russia). For example, it is expected that the mechanical strength of CNTs embedded in the primer base will make it less sensitive to incision. Previously we have shown [6] that alkyd-based primer containing 0.01% wt. of CNTs has film hardness 10-60% higher than the primer without CNTs. However, there are still no data about mechanisms of the processes taking place on the molecular level when the priming compositions are modified with carbon nanotubes, that limit primer introduction into the practice. Meanwhile, in most cases it is not necessarily to carry out experiments to obtain data on matter’ structure and composition, since it can be obtained on the basis of mathematical modeling. The purpose of our work is to propose
a hypothesis about modification of alkyd resins, that would explain an increase of film hardness after modification of polymer.

2. Calculations

Despite many benefits of quantum-chemical methods of modelling [7], they need high power requirements to computer device and poorly used for considering molecular systems with more than 50 atoms. Contrary, reliable data about the structure of CNTs distributed in alkyd resins demand of examining system of dimension no less than 10^3 of atoms, that cannot be studied by quantum-chemical methods.

In our work we modelled the molecular system based on GF-021 primer (alkyd resin and solvent) modified with CNTs "Taunit-M" (NanoTechCenter Ltd., Tambov, Russia). Carbon nanotubes in alkyd resin was introduced in the following way. At room temperature, a suspension of nanotubes in a solvent with a concentration of about 0.1% of the mass was obtained. For high-quality dispersion, ultrasonic treatment was used, with a specific power of 18 W/g for 40 minutes. In the process of ultrasonic treatment the suspension was cooled with running water. The resulting suspension in different ratios described in [6] was introduced into the alkyd varnish and intensively moved in the homogenizer for 1.5 hours at a shaft rotation speed of 10,000 min^{-1}. During the mixing process, the modified varnish was cooled with running water. The systems was examined in equilibrium state by the help of the method of molecular mechanics (MM+), which generally treats atoms as Newtonian particles interacting with each other through potential fields given on the basis of the empirical laws of physics. Here, the potential energy of interaction depends on bond length, bond and torsion angles, and non-covalent interactions (including van der Waals forces, electrostatic interactions and hydrogen bonds). It should be noted that the molecular mechanics method is applicable if the De Broglie wavelength of an atom is much smaller than the interatomic distance, particularly, for particles with a weight more than 10 atomic units and temperature higher than 10 K [8].

The force fields of the potential energy of a molecular system are generally given as the sum of pair atomic-atom interactions, which depend only on the distance between atoms [9, 10]. For calculating system potential energy we used MM+ method developed for organic molecules, that took into account the potential fields formed by all atoms of the calculated system and allowed flexible modifying the calculation parameters depending on the problem, which makes it, on the one hand, to be universal, and on the other it sharply increases the necessary resources in comparison with other methods of molecular mechanics.

In the MM+ method the molecule potential energy is considered as follows:

\[ U = U_b + U_v + U_{\varphi} + U_f + U_q + U_{LJ} + U_{hb} \]  

(1)

where \( U_b \) – chemical bonds; \( U_v \) – valence angles; \( U_{\varphi} \) – torsion angles; \( U_f \) – flat groups and pseudorotation angles; \( U_{LJ} \) – Van der Waals contacts; \( U_q \) – electrostatic interactions; and \( U_{hb} \) – hydrogen bonds.

The energy of valence interactions and vibration energy of valence angles were described by parabolic potentials. The potential energy for torsion angles, plane groups and pseudorotation angles was given by the Fourier series [11, 12]. The interaction between atoms not connected by a valence bond (van der Waals interaction and the formation of hydrogen bonds) was described using the Lennard-Jones potential [13]. The potential energy of interaction of charged atoms was characterized by an electrostatic potential.

The formulation of the problem of calculating the geometry of the molecular system of alkyd resin-CNTs, which was in equilibrium at a local minimum of the value of the potential energy, had the following form:

\[ \{ \vec{r}_{n,m} \}_n \text{; } n=1..N_a; m=1..3; \]  

(2)

\[ l_i = f_i(\vec{r}_{n,m}); \alpha_h = f_{\alpha_h}(\vec{r}_{n,m}); \varphi_g = f_{\varphi_g}(\vec{r}_{n,m}); t=1..T; h=1..H; g=1..G. \]  

(3)
where $\mathbf{r}$ is the matrix of the coordinates of $N_a$ atoms in 3D space; $l_i$ is the length vector $T$ of chemical bonds; $\alpha_i$ is the vector of values of angles $H$ of chemical bonds; $\varphi_i$ is the vector of values of torsion angles $G$ of chemical bonds.

$$
U = U_h(\bar{l}) + U_v(\bar{\alpha}) + U_\varphi(\bar{\varphi}) + U_f(\bar{\varphi}) +
+ U_q(\bar{r}) + U_{LJ}(\bar{r}) + U_{hb}(\bar{r}) \rightarrow \min
$$

where $K_{h,i}$ is the effective stiffness of the valence bond; $l_{0,i}$ is the equilibrium chemical bond length.

$$
U_h(\bar{l}) = \frac{1}{2} \sum_{i=1}^{H} K_{h,i} (l_i - l_{0,i})^2 ,
$$

where $K_{v,h}$ is the effective elasticity of the valence angle; $\alpha_{0,h}$ is the equilibrium value of the chemical bond angle.

$$
U_v(\bar{\alpha}) = \frac{1}{2} \sum_{i=1}^{H} K_{v,h} (\alpha_i - \alpha_{0,h})^2 ,
$$

where $K_{v,r}$, $K_{f,r}$ are constants determining the heights of the potential barriers of dihedral angles; $V_{g,r}$ is the contribution of the harmonic to the potential of the torsion angle ($-1 < V_{g,r} < 1$); $s_{g,r}$ is the torsional barrier multiplicity; $\delta$ is the phase shift; $s$ is the harmonic number; $S$ is the number of harmonics.

$$
U_q(\bar{r}) = \sum_{i=1}^{N_a} \sum_{j=i+1}^{N_a} \left[ q_i q_j \epsilon W_{i,j} \right],
$$

where $q_i$, $q_j$ are partial charges on atoms; $\epsilon$ is the medium dielectric permittivity; $W_{i,j}$ is the distance between $i$ and $j$ atom, $W_{i,j} = |\mathbf{r}_i - \mathbf{r}_j|$.

$$
U_{LJ}(\bar{r}) = \sum_{i=1}^{N_a} \sum_{j=i+1}^{N_a} \left[ \frac{A_{i,j}}{W_{i,j}^{12}} - \frac{B_{i,j}}{W_{i,j}^{6}} \right],
$$

where $A_{i,j}$, $B_{i,j}$, $A'_{i,j}$, $B'_{i,j}$ are constants determining the depth of potential wells and the location of their minimum depend on the types $i$ and $j$ of the atoms involved in the interaction.

Initial conditions:

$$
\{ \mathbf{r}_{n,m} \}_{0} = R_{N},
$$

Limitations:

$$
\{ \mathbf{r}_{n,m} \} \in \Omega_{N_{a},3}; 
I_{\min} \leq I_i \leq I_{\max}; 
\alpha_{\min} \leq \alpha_i \leq \alpha_{\max}, 
\varphi_{\min} \leq \varphi_i \leq \varphi_{\max}.
$$

It was necessary to find variable parameters as $\mathbf{r}$ - coordinates of atoms in three-dimensional space (2), under which the criterion of optimality (the potential energy of the system) (4) tended to a minimum under conditions (4) - (13).
The solution of problem (3) - (12) with allowance for the constraint (13) was obtained using the method of conjugate gradients by the Polac-Ribiera (Pshenichny) algorithm [14] implemented in the Gromacs software product.

3. Results and discussion

According to the analysis of calculation results, the surface of carbon nanotube placed in an alkyd resin under noted conditions has a structuring effect (Figure 1). The polymer changes its configuration and forms new intramolecular hydrogen bond in its chain (black arrow on the Figure 1). The formation of a hydrogen bond is determined by the condition that the distance from electronegative atom to hydrogen donor is less than 3.2 Å, and the angle of the covalent bond between donor and acceptor is less than 120º. There are many polymers which properties are determined by the presence of hydrogen bonds, as cellulose, nitrocellulose, and nylon [15]. In alkyd resin this bond has an energy of about 20-25 kJ/mol and most likely performs an auxiliary function. Thus, it is possible to explain hardness growth of modified primer film by forming an additional hydrogen bond in the polymer. When the film is bent or stretched, this bond is easily torn by allowing polymer to rearrange. After removing the load, in the presence of favourable conditions, this hydrogen bond is formed again. This explains why the hardness of film increases although its fragility does not augment.

![Figure 1. Results of the calculation of the equilibrium state of the molecular system of alkyd resin-CNTs. Arrow shows a new hydrogen bond.](image)

There are several possible options for the practical implementation of this method of modifying alkyd resins by modernizing the traditional technology for the production of alkyd primers, typically in periodic synthesis of alkyd glythaldehyde primers shown in Figure 2.

In order to improve GF-021 primer characteristics, it is proposed to introduce an additional stage into the traditional technological scheme by including the step of CNTs solvent modification. The hardware design of the new stage includes container for CNTs, dispenser, container for mixing CNTs in a solvent and ultrasonicator providing uniform distribution of nanotubes in a solvent.

The problem of agglomeration of CNTs in an organic solvent is still unsolved [16], however, as research shows [17] application of hydrophobic surfactants reduces nanotubes aggregates since they absorb on the phase interface. So, it is advisable to equip a new stage also by feeding the surfactant into the slurry prior to its ultrasonic treatment. Another variant to improve traditional technology for
primer preparation may involve the introduction of CNTs during preparation of dry mixture of fillers, chalk and microtalc, followed by its processing in inkjet machine. In this case, in the technological scheme it is necessary to install only container for CNTs and dispenser. It was also considered a variant of technology modernization - introduction of CNTs into semi-finished alkyd varnish.

**Figure 2.** Technological scheme of production of alkyd glyptal primers in a periodic way:
1 – container for pigments; 2 – hopper-funnel; 3 – auger; 4 – feeder; 5 – kneading machine; 6 – container for mixing; 7 – roller mill; 8 – mixer; 9 – colloid mill.

**Conclusions**

Using the method of molecular mechanics (MM+), the mathematical modeling of the molecular system of alkyd resin-CNT in equilibrium conditions has been carried out. For the first time it is proved that in certain configurations the surface of carbon nanotubes is able to structure alkyd polymer chains with the formation of intramolecular hydrogen bonds. The calculated data on the formation of hydrogen bonds with energy of 20-25 kJ/mol explains the increase in the film hardness by 10-60%, obtained experimentally earlier [6]. The formation of additional bond in the polymer allow us to propose a hypothesis about the processes of alkyd paint modification by carbon nanotubes. When the film is compressed or stretched, this bond is easily broken allowing the polymer to rearrange. After removing the load, in the presence of favorable conditions, this hydrogen bond is formed again. As the hardness of the film increases, its brittleness remains constant. The obtained results of modeling and the formulated hypothesis allow us to follow the conclusion about the high prospects of alkyd composition modification by carbon nanotubes. In this regard, we propose to introduce the process of alkyd modification by CNTs in industrial scale, that opens up prospects for the creation of new durable paints. The formulation of the hypothesis about the modification processes requires its comprehensive experimental confirmation. Future works of the
authors will be focus on the experimental study of the alkyd paints modification with carbon nanotubes.

Acknowledgments
This research is supported by the grant of Tambov region (Russia) for young scientists in 2017, agreement No. 1-17/MU, project No. 14 MU-17.

References
[1] Elrebii M, Kamoun A and Bouf S 2015 Waterborne hybrid alkyd–acrylic dispersion: Optimization of the composition using mixture experimental designs Prog. Org. Coat. 87 222
[2] Berge C B and Henley A 2009 Paint, varnish, stain and wax The Ecology of Building Materials 18 381
[3] Abdel N A and Madkour M Potential use of smart coatings for corrosion protection of metals and alloys: a review J. Mol. Liq. 253 11
[4] Dyachkova T, Anosova I, Galunin E, Orlova N and Tkachev A 2017 Preparation of TiO$_2$/carbon nanotubes composites and a study of their adsorption on organic dyes Nano Hybrids and Composites 13 135
[5] Burakova E, Galunin E, Rukhov A, Memetov N and Tkachev A 2016 Effect of ultrasound on a mixed oxide-based catalyst in the synthesis of carbon nanostructured materials Res. Chem. Intermed. 42 7045
[6] Filatova E and Rukhov A 2011 Study of soil compositions modified by carbon nanostructured material Taunit-M Prov. Int. Conf. "Perspective Innovations in Science, Education, Production and Transport 2011", 21-30 June, 2011, Odessa, Ukraine
[7] Clark T 1985 A Handbook of Computational Chemistry: A Practical Guide to Chemical Structure and Energy Calculations (Wiley, Moscow) p 383
[8] Rapaport D C 2004 The Art of Molecular Dynamics Simulation (Cambridge University Press), p 565
[9] Mc Cammon J A 1984 Protein dynamics Rep. Progr. Phys. 47 1 46
[10] Kalinichev A G and Kirkpatrick R J 2002 Molecular dynamics modeling of chloride binding to the surface of calcium hydroxide, hydrated calcium aluminate, and calcium silicate phases. Chem. Matter. 14 3539
[11] Tormena C F 2016 Conformational analysis of small molecules: NMR and quantum mechanics calculations Progress in Nucl. Magn. Resonance Spectroscopy 96 73
[12] Peng-Yuan C, Lin Z, Shun-Guan Z and Guang-Bin C 2017 Role of intermolecular interaction in crystal packing: A competition between halogen bond and electrostatic interaction J. Mol. Struct. 1131 250
[13] Kaplan I G 1982 Introduction to the Theory of Intermolecular Interactions (Nauka, Moscow) p 312
[14] Nguyen A, Reiter S and Rigo Ph 2014 A review on simulation-based optimization methods applied to building performance analysis Appl. Energ. 113 1043
[15] Raj P H, Bajgai M P, ChuanY, Nirmala R, Nam K, Baek W and Kimd H Y 2010 Effect of successive electrospinning and the strength of hydrogen bond on the morphology of electrosyn nylon-6 nanofibers Colloid Surface A 370 87
[16] Piao-Hao S, Kim-Hwan M, Choi-Jin H, Nirmala R, Lee H and Park J J. Ind. Eng. Chem. 2017 Dispersion state and rheological characteristics of carbon nanotube suspensions 52 369
[17] Nomède-Martyr N, Disa E, Guérin K, Bonnet P and Dubois M 2018 Effect of fluorination on the stability of carbon nanofibres in organic solvents Cr. Chim. 21 791