Surface modification of PVC by silica sol

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Abstract. One of the most important and widely used modern materials is polymeric composite materials based on PVC. One of the possible ways to improve the properties and increase the reliability of polymer products is their surface diffusion treatment with liquid nanomodifying components. The study investigated the possibility of using silica sol to strengthen the surface of rigid PVC. It is shown that as a result of diffusion impregnation of PVC in silica sol to a certain degree of saturation and subsequent heat treatment (in order to fix the modifier), the resulting composites have enhanced surface properties. As a result of the diffusion of silica sol into the PVC matrix and its physicochemical interaction with the latter, a modified surface layer is formed with a structure and properties that vary in its thickness. Modifying the surface of finished PVC products without changing the inner part, allows you to strengthen the whole material as a whole and increase its resistance to various external factors. At the same time, the consumption of the modifying additive is significantly reduced in comparison with the adding into the volume of the material, and its effectiveness increases due to the high local concentration on the surface.

Keywords: polyvinyl chloride, silica sol, surface modification, diffusion, microhardness.

1 Introduction

Material science has achieved great success in creating polymer composite materials, including nanosystems, with a range of positive physicochemical properties. The traditional methods of polymers synthesis – polymerization and polycondensation – largely exhausted themselves and the probability of occurrence polymers with characteristics significantly exceeding the achieved certain level decreased significantly. However, all of the properties of these materials are generally uniform in cross-section of products and structures. Meanwhile, the surface of polymer articles is exposed during operation to various aggressive factors (mechanical, physical, chemical and other), which are distributed not uniformly throughout the volume of the article, but are concentrated on the surface containing an increased number of local stresses and defects associated with the processing technology. Surface defects are the most dangerous, mechanical destruction, chemical corrosion, aging, thermal and thermal-oxidative degradation begin from the surface, which reduces the durability of the finished products during operation [1–3].

Strengthening or other functional modification of the surface of polymer materials and articles practically without changing the structure of the inner part is accelerated in recent years and is a promising direction, which allows to develop technologies for obtaining qualitatively new materials with a complex of improved physical-chemical and operational properties on the basis of known polymers.

There are a lot of possible ways to strengthen the surface layers. Traditionally, it is common to modify the surface of polymers by mechanical [2, 3], energy [4] and diffusion [5–8] action on the surface layers of the material in finished products without changing the structure and composition of the inner layers. Surface treatment with various liquid reagents is the most effective. As a result of the
diffusion of liquid into the polymeric material, a modified surface layer is formed with a structure and properties that vary in its thickness, that is, a gradient layer. It is not so much a protective coating, that is created as a new layer of modified polymer with a modifier concentration decreasing into the depth of the volume of the base material. By changing the temperature-time parameters of diffusion impregnation, it is possible to control the penetration depth and thereby the thickness of the surface gradient layer. The diffusion method, which allows filling pores with a low molecular weight substance in the polymer structure, is a fundamentally new method for modifying polymers in products [3].

The surface strengthening of polymer products is due to the initial heterogeneity of the polymer at the submicroscopic structure level. This is typical mainly for amorphous polymers, which are distinguished by local heterogeneity of molecular packing and the presence of dense globular formations. Interglobular regions have more defects, in addition, there may be defects in the macromolecules themselves. This weakened portion of the block polymer has a lower strength and hardness than the closely packed domains or globules, less resistance to thermal degradation and to aggressive environments. In this regard, microdefects arising and developing due to local stresses [9–11]. These weak zones of the polymer material must be strengthened, since they are most accessible for diffusion impregnation.

Creation of gradient interpenetrating networks (IPNs), and, in fact, polymer composites with a structure that varies in thickness, contains great potential for controlling the properties of polymer materials for various operating conditions and the purpose of the products made from them. Then polymerization is carried out to obtain the second polymer, the concentration of which in the matrix polymer has a gradient. As a result, systems are formed whose properties differ both from the properties of individual polymers and from IPNs obtained in the traditional way. If the matrix polymer is linear, then semi-IPN structures are formed [12–14]. Sequential curing for receipt of polymer composite materials is a fundamentally new, promising modification method. It allows solving the problem of strengthening their surface, to widely control properties, in particular surface hardness, wear resistance, resistance to hydroabrasive wear and diffusion penetration of chemically aggressive environments. The method is much more effective and more economical than volumetric modification (modifier consumption is reduced by 3-10 times).

The structural and kinetic principles of creating gradient IPNs with high technical properties are realized using two amorphous polymers as an example: linear polyvinyl chloride (PVC) and polymethyl methacrylate (PMMA); The features of the formation of gradient layers were revealed, their structural models were proposed taking into account the heterogeneity of the submicroscopic structure of the base polymers [15–17].

According to Ivanchev’s [18], polymer systems are natural nanostructured formations, have a complex submicroscopic internal structure (coil, globule, crystallite) with a different arrangement of constituent elements in space and a different nature of the interaction between them, and the polymer crystallite size is 10-20 nm (macromolecule can enter several crystallites, since its length is 400 nm). It follows from this that “macromolecular formations and polymer systems, by virtue of their structural features, are always nanostructured formations” [18]. Therefore, surface modification of polymer products, taking into account modern concepts of nanostructured and nanoreactor formations, can be represented as surface nanomodification.

2 Materials and methods
The studies were carried out on PVC specimens with sizes of 20×20×4 mm, obtained by rolling and subsequent pressing of a composition consisting of 100 parts by weight PVC and 3 parts calcium stearate. Silica sol was used as a low molecular weight diffusant, which is a lyophilic colloidal system with spherical nanoscale particles with an average size of 5-9.5 nm (Figure 1). Silica sol has a density of 1200 kg/m³, a viscosity of not more than 20.0 cSt and a mass concentration of SiO₂ of 330-340 g/l.
The modification method was as follows: initially, virgin PVC specimens were saturated in silica sol at various temperatures to an equilibrium degree of swelling. Then the specimens were exposed to heat treatment at 100 °C for 1 hour.

**Figure 1.** The silica sol particles distribution in sizes.

### 3 Results and Discussion

Use of nanostructure-forming inorganic modifier silica sol as the diffusant allows to adjust the character of nanostructured formations and hence the strength properties of PVC materials. It should be noted, that only small doses of the sorbed low molecular weight diffusant (up to 1.5 wt. %) are required to realize this method of modification. The first stage of the modification process is the swelling of PVC in nanomodifying component – silica sol. Kinetic curves are typical saturation curves (Figure 2). An increase in temperature leads to a decrease in time required to reach an appropriate degree of swelling. In the samples obtained by diffusion impregnation during different periods of time, with varying degrees of swelling (mass and volume) changes the actual concentration of modifier in the surface layer. The maximum degree of impregnation (up to 1.4 wt. %) corresponds the modifier concentration more than 6 %.

**Figure 2.** Kinetic curves of saturation of PVC in silica sol at room temperature (1) and at 60 °C (2).

The modifier concentration gradient in the surface layers causes the changes in the properties over the thickness of the samples. There is a definite relation [19, 20] between the concentration of the diffusant and parameters such as the microhardness of the sample. So the change in microhardness can indirectly determine the nature of the modifier distribution in the surface layer of the polymer sample.
Figure 3 shows the curves of the distribution of microhardness over the thickness of the flat sample (plate 4 mm thick).

![Microhardness Distribution](image)

**Figure 3.** Distribution of microhardness over the thickness of the PVC samples containing 0 % (1), 1.4 % (2), 1.4 % (3) silica sol before (2) and after solvent removal (3).

In studying the processes of surface nanomodification we are dealing with a complex system, which involves several components: the dissolved nanomodifier, the solvent (water) and the surface layer of the polymer block. The penetration diffusion layer of the solvent in the polymer block is always greater than of nanomodifier. Diffusion modification is not only loading of modifying component in the most critical surface layer, but also improving the structure and physical state of the surface layers of polymer products, firstly, due to the formation of hydrogen bonds and the ordering of water structure in the polar groups of PVC, second, due to the structuring effect of free d-orbitals of silicon and unshared electron pairs of chlorine and oxygen of the polymer, due to the formation of bonds of the donor-acceptor character. After removal of physically bound water (free) there is a further increase in the microhardness on the surface because of the structural changes that lead to the transformation of both the molecular and supramolecular nature. The most thermodynamically equilibrium structure formed.

In order to study the emerging structure, electron micrographs of the surface layer of the modified PVC were obtained (Figure 4). Silica sol forms a thin film on the surface, which, at a larger magnification (Figure 4b), represents a friable "flaky" structure that can heal dangerous defects and fill internal micropores.
Figure 4. Scanning electron microscopic (SEM) photographs of the surface layer of modified PVC at magnifications of 1000× (a) and 50,000× (b).

The chemical compositions of gradient layers at different depths were analyzed by high-resolution scanning electron microscopy to estimate the changes in the silica sol concentration in the surface layers. The content of the modifier was identified by the lines of the spectra of silicon (Si) and oxygen (O). Quantitative surface analysis based on the proportionality of the intensity of spectral lines of atomic concentration of the test element. The chemical state of the surface of untreated PVC practically coincides with the characteristic of modified PVC at a depth of 250 μm (Figures 5-6), where the silica content is minimal. The distribution profile of various elements for modified PVC is characterized by a monotonic change from the surface into the interior of the sample (Figure 6). The concentration of carbon atoms (C) and chlorine (Cl) inherent in PVC is lower, which begins to increase as it deepens into the specimen. A monotonous decrease in the concentration of silicon (Si) and oxygen (O) elements corresponding to silica sol indicates that the distribution of the diffused modifier is along the gradient.
Figure 5. The chemical composition of the modified PVC at a depth of 50 µm (a), 150 µm (b) and 250 µm (c).

The state of the surface layer affects the macro-properties of polymer material which significantly altered by changing the packing density. For example, the elastic modulus of surface-modified samples was higher (Figure 7). This can be explained by the fact that the action of nanomodifier causes the unique physical “crosslinking” of the polymer which leads to its compaction and, consequently, to an increase in strength and elastic modulus of the polymer system.

![Graph showing concentration of elements from surface deep into the sample](image)

**Distance from surface, µm**

Figure 6. Changing the concentration of elements (C, Cl, O, Si) from the surface deep into the sample for the modified PVC.

![Graph showing temperature dependence of elastic modulus](image)

**Figure 7. Temperature dependence of the elastic modulus for pure (1) and the modified PVC (2).**

4 Conclusions
Thus, specifics of the formation of specific nanostructures in the polymer and the realization of their nanostructural characteristics were observed. Improving the complex of physical and mechanical characteristics and changes in the structure was achieved with the loading of fine nanoscale inorganic particles into the surface layer of polymer block, and to implement the desired effect only small
amounts of additives (1.5 wt. %) are required. Polymer system in the surface layers is transformed into organic-inorganic polymer composite material by means of the formation of nanoscale structured zones – a hybrid system based on the incompatible by nature components. The principles of nanochemistry and nanotechnology in the polymer materials can greatly increase the efficiency of polymer systems, to improve their properties and operational characteristics.

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