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Hydrophobic Composition Based on Mixed-Molecular Weight Polyethylene

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Abstract. The paper presents investigations of compositions based on low and high molecular weight polyethylene so as to synthesize a hydrophobic composition for moisture protection of timber. X-ray phase analysis and measurements of the tear-off force of hydrophobic coating needed to apply to the timber surface and the limiting wetting angle are carried out to detect the hydrophobic, adhesive, electrophysical, and physicochemical properties of compositions. Kinetic dependencies are given for moisture absorption of timber specimens. It is shown that the preliminary formation of the texture by the surface patterning or its treatment with low-temperature plasma with the following protective coating results in the improvement of hydrophobic properties of the suggested compositions. These compositions can be used in the capacity of water repellents to protect building materials from moisture including restoration works.

INTRODUCTION

Along with the moisture protection hydrophobic materials possess such properties as corrosion resistance and organic and inorganic pollution resistance. Thus, the creation of hydrophobic materials and coatings, investigations of their physicochemical and operating properties is the relevant trend of the modern materials science [1]. Currently, a wide range of organic and inorganic compositions is used for the reliable and efficient protection of building materials from moisture. The surface pretreatment techniques are intensively used to improve the quality of hydrophobic coatings such as polymerization with the formation of vesicular phase on different surfaces; chemical sedimentation out of ordered structure vapors; plasma etching of polymer surfaces; sublimating film coatings; organic and inorganic fillers with the multimodal distribution of particles; controlled aggregation of particles on the surface resulting in multimodal roughness; etc. [2-11]. The surface pretreatment techniques give the surface texture not only water-repellent properties but also create chemical bonds between the surface texture and substrate that improves the resistance of such coating while operation. Process conditions of the surface coating and treatment are usually selected empirically.

Due to some of its properties, low molecular weight polyethylene (LMWPE) of the lubricating type is one of the promising hydrophobic materials. First, it possesses proper adhesion to any hard dry surfaces, namely: wood, concrete, metal, glass, plastic, and others. Second, LMWPE is a by-product of high molecular weight and polyethylene (HMWPE) that allows resolving ecological problems of polymer recycling. One of LMWPE disadvantages is viscidity observed after its application to a surface which is retained for rather long time. This creates a sort of discomfort while in operation of the building material since the outer side of the water repellent intensively adsorbs various impurities on its surface. To avoid this phenomenon the viscidity substance should be transferred to a solid-like state with retaining or insufficient reduction of high adhesion values.

The aim of this work is to synthesize a LMWPE-based hydrophobic composition for timber protection from moisture.

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MATERIALS AND METHODS OF STUDY

Investigations included the modified compositions of low molecular weight polyethylene represented by the amorphous crystalline material having about 16% crystallinity degree and comprising linear and branched molecules with unsaturated bonds and bimodal molecular mass distribution within the interval from 50 to 4500 units. LMWPE was used to compensate LMWPE plasticity since it reduces its viscidity. All the components were mixed at heating and studied in relation to their physicochemical properties. Moreover, either slow or rapid cooling of the mixture components was used to control the ratio between the crystalline and amorphous phases of composition. These modification techniques allowed purposive compensating the properties of hydrophobic compositions.

The value of the surface adhesion was detected estimating the relative tear-off force of hydrophobic coating needed to apply to the timber surface and the limiting wetting angle of water drop. The values of vapour permeability and electrophysical properties of compositions were obtained in compliance with the State Standard 25898-2012. The X-ray phase analysis was used to determine the degree of crystallinity of specimens using DRON-3 diffractometer. The timber specimens were subjected to the low-temperature plasma treatment (LTP) by the methodology described in the work of Volokitin *et al*. [12]. The capillary-porous pine wood was selected for this experiment. The surface hydrophobization of the material was provided by dipping from the melt.

EXPERIMENTAL RESULTS AND DISCUSSION

X-ray phase analysis shows that the ratio between high and low molecular weight polyethylene is considered to be optimum at LMWPE: HMWPE = 12:1 by weight composition because this ratio provides high hydrophobic properties of the solid phase without viscidity. This composition is obtained at slow cooling of the melt. The experimental findings of the optimum composition are presented in Fig. 1 and Tables 1-3.

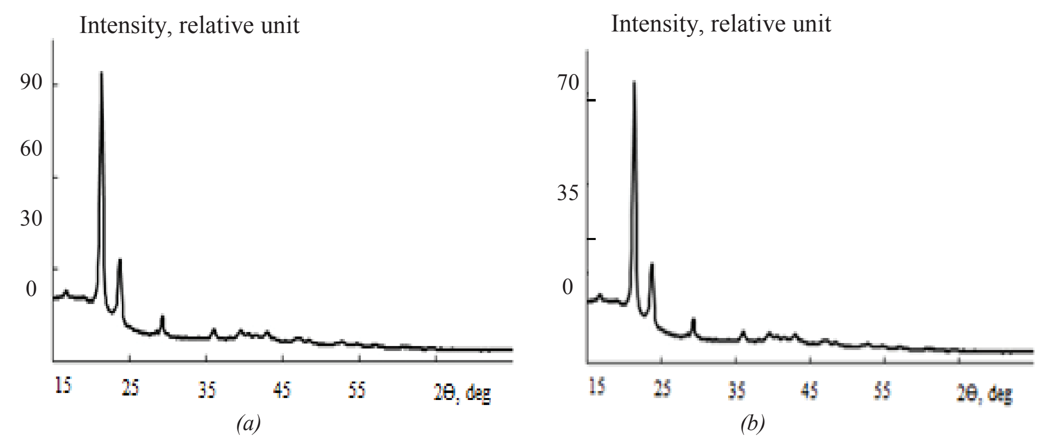


FIGURE 1. XRD patterns of HMWPE /LMWPE mixture composition: *a* – slow cooling; *b* – rapid cooling

As shown in Fig. 1, the ratio between 20, 24 2Θ diffraction maximums indicates the increase of crystallinity of the composition at slow cooling of the melt which results in the elimination of viscidity.

Since the adhesion ability of hydrophobic material is one of its important properties, the behavior of adhesion, cohesion, and the drop spreading coefficient are determined by the limiting wetting angle of water drop and the tear-off force of hydrophobic coating needed to apply to the timber surface. Experimental findings are presented in Tables 1 and 2.

TABLE 1. Limiting wetting angle values depending on water drop and specimen surface contact time

Specimens	Wetting angle, degrees						
	Min 0	5	10	15	20	30	60
LMWPE/HMWPE mixture composition(12:1)	104	104	104	103	103	102	98
Test specimen (original timber)	34	2	0	0	0	0	0

TABLE 2. Adhesion parameters of LMWPE/HMWPE-based composition

Slow cooling composition				
$F_t \times 10^{-3}$, N	$W_t \times 10^{-3}$, J/m^2	$W_a \times 10^2$, J/m^2	$W_c \times 10^2$,J/m^2	f, J/m^2
1.0±0.1	6.1±0.2	9.8±0.3	31.1±0.4	-21.3±0.7
Rapid cooling composition				
1.2±0.1	6.7±0.3	11.0±0.4	35.2±0.4	-24.2±0.7

Notation: $F_t = ma$ is the tear-off force; $W_t = h/S$ is adhesive strength; $W_a = (1 - \cos\Theta)/b$ is adhesion behavior; $W_c = 2W_a/(1 + \cos\Theta)$ is cohesion behavior; $W_t = F_t h/S$; $f = (W_a - W_c)$ is the drop spreading coefficient; h is the film thickness, m; S – is the film surface area, m^2; b is the film width, m; Θ is the wetting angle.

The limiting wetting angle larger than 90^0 and its insignificant change in time as given in Table 1 indicates the timber surface hydrophobization. However, the increase of the crystallinity degree results in the decrease of the adhesive and cohesive ability relative to the timber surface (Table 2). Cohesion as a low molecular weight polyethylene is partially observed on the timber surface after the hydrophobic coating was torn off the surface at the negative value of the drop spreading coefficient.

Table 3 gives some of physicochemical properties of hydrophobic material that define its performance characteristics. Surface coatings of this composition are characterized by the low water absorption and high electrically protective properties.

TABLE 3. Physicochemical properties of modified low molecular weight polyethylene

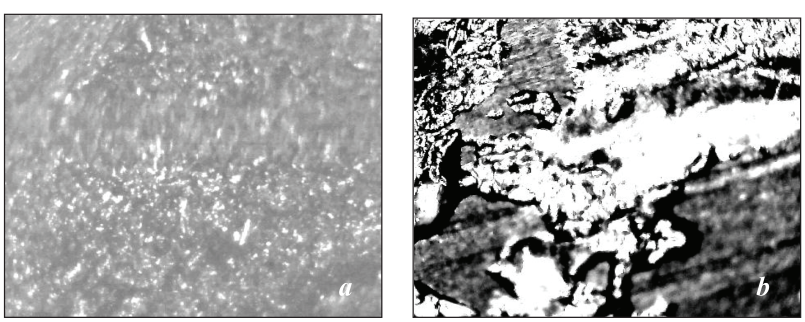
R, mg/h×m^2	W, %	T, ^{0}C	ε, rel. unit	$tg\delta$, rel. unit
0.0032	0.12	90-110	4.2-4.6	(3-5) ×10^{-4}

Notation: R is vapor permeability; W is water absorption (during 1 h); T is the melting point; ε is the dielectric permeability; tgε is the dielectric loss tangent at 200 GHz.

Table 4 shows the kinetics of water absorption in test specimen and specimens treated with hydrophobic composition. These compositions possess rather high water resistance. However, it should be noted that a long-term contact between hydrophobic timber and water leads to the structural change of the surface layer as shown in Fig. 2 that requires additional investigations of the coating resistance to natural conditions.

TABLE 4. Water absorption kinetics of timber treated with hydrophobic composition

Specimens	**Absorbed water percentage *vs*. specimen-water contact time**					
	Min 5	10	15	30	60	3600
Test specimen (original timber)	6.3	7.5	8.5	9.7	10.9	15.2
LMWPE/HMWPE mixture composition (12:1)	0.03	0.05	0.05	0.07	0.12	0.21



(*a*) (*b*)

FIGURE 2. Micrographs of hydrophobic timber surface modified by LMWPE: *a* – before and *b* – after contact with water for 3 days (×80 magnification)

Experimental findings given above are obtained for the timber surface regardless of its roughness. It is known that the efficiency of hydrophobization, besides the chemical composition, depends on the surface texture, a method of coating application, and modes of homogeneous and heterogeneous wetting, while the limiting wetting angle can be obtained from:

$$cos\Theta = S/S_o \times cos\ \Theta_o = r \times cos\ \Theta_o, \quad (1)$$

$$cos\Theta = (f \times r \times cos\Theta_0 + f) - 1, \quad (2)$$

where Θ and Θ_0 are limiting wetting angles of homogeneous and heterogeneous surface parts, respectively; f is the fraction of wetted surface area; $r = S_0/S$ is the roughness coefficient; S_0, S are true and apparent surface areas, respectively.

According to Eqs. (1) and (2), the surface roughness of a solid and the decrease of f and r values provide the decrease of the limiting wetting angle. Therefore, in order to achieve high values of the timber moisture resistance it is necessary not only to control the roughness coefficient but also preselect its values and a share of wetted surface area as well. For example, at the wetting angle larger than 90°, the roughness coefficient is sufficient to be 2 for the wetting angle to exceed 160° that indicates to the super-hydrophobic state of the surface.

The preliminary surface texture is formed by its patterning resulting in the ordered rectangular projections and linear cavities as shown in Fig. 3.

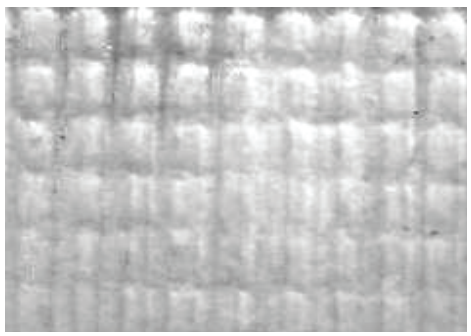


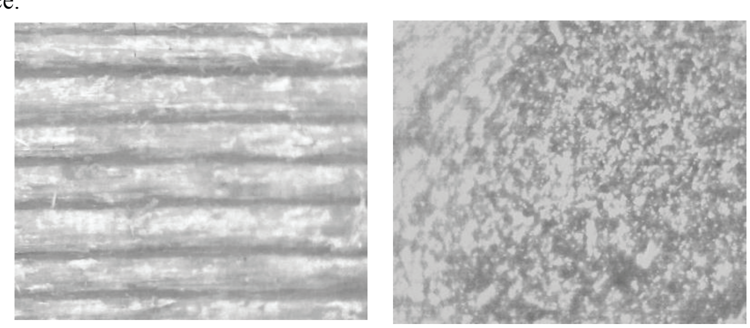
FIGURE 3. Micrograph of timber surface texture (×40 magnification)

The subsequent LMWPE film coating of this texture type allows increasing the limiting wetting angle up to 128° as compared to the original texture of timber.

Therefore, setting the height, size and distance between the textural elements, it is possible to vary the roughness coefficient within the broad range and to purposefully control the hydrophobic properties of polymer coatings.

In order to produce the materials with large limiting wetting angles it is advisable to use a combined effect of rough surface and chemical structure. Most of the methods currently used in this field allow the production of super-hydrophobic materials based on disordered textural surfaces. In this case, process conditions of the surface coating are selected empirically. At that, the formation of such texture should be achieved, the water repellent application to which results in super-hydrophobic surface modification.

One of these methods is the low-temperature plasma (LTP) treatment. Fig. 4 contains micrographs of timber surfaces before and after the LTP treatment that produces the formation of dispersed carbon particles having almost similar sizes and ordered structure that creates conditions for the improvement of hydrophobic properties of timber surface.



(*a*) (*b*)

FIGURE4. Micrographs of timber surface texture: *a* – before and *b* – after LTP treatment (×40 magnification)

Hydrophobic coating of such timber surface increases the limiting wetting angle by (8-10)° as compared to the untreated surface. The increase of this angle can be explained by 1) the impossibility of creating highly hydrophobic surfaces at dense packing of monodispersed particles regardless of their sizes [2] and 2) the plurality of structural defects in self-organized layers appeared due to LTP treatment that have an effect on the hydrophobic nature. These disadvantages can be eliminated by the process optimization of the LTP treatment.

CONCLUSIONS

1. The suggested hydrophobic composition based on the mixture of low and high molecular weight polyethylene for coating timber surfaces has the following physicochemical and service characteristics: 0.0032 mg/h×m^2 vapor permeability; 0.12% water absorption; 90-110 °C melting point; 4.2-4.6 rel. units dielectric permeability; 200 GHz dielectric loss tangent; (3-5) ×10^{-4} relative unit; 31.1 J/m^2 cohesion; 9.8 J/m^2 adhesion; 106° limiting wetting angle.

2. The preliminary surface texture formed by its patterning resulted in the ordered rectangular projections and linear cavities with the subsequent hydrophobic coating provided 16° increase of the limiting wetting angle of water drop.

3. The low-temperature plasma pretreatment of the timber surface enhanced its hydrophobic properties.

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