Scientific basis for the use of microwave radiation to improve the technological properties of polymeric insulating coatings

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Abstract. This article discusses an approach to improve technological and operational properties of polymeric insulating coatings of pipelines by their treatment by the electromagnetic field radiation of microwave range. In recent years, it has become quite widely used to find the electromagnetic radiation of a microwave (MW) range. Because it has several advantages: intensifies the energy exchange in the matter by the converting of the radiated energy into the kinetic energy of molecular vibrations; provides a uniform treatment of the substance in the irradiated volume and high stability of the energy flow due to lack of persistence within the varying its power.
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Introduction

One of the major problems of the fuel and energy complex of the Russian Federation is to ensure the reliability and safety of exploitation of pipeline systems, the total length of which is more than 2 million kilometers [1]. Polymeric coating which are widely used in the industry that is applied to the outer surface of pipes during repairs usually do not provide prolonged protection due to hard conditions of piping exploitation, combining the effects of corrosive media and mechanical loads of different nature [2]. Typical coating defects, arising in such circumstances are offset, discontinuity, the degradation of the structure, as well as the development of those defects which have appeared due to the non-compliance of the repair technology. Therefore relevance of the new insulating coatings with higher performance becomes obvious.

In recent years it has become quite widely used to find the electromagnetic radiation of a microwave (MW) range for the heat treatment of soil (soil reinforcement in the piping routing area), increase of the strength of foam concrete in house building, the activation of various chemical reactions, the increase of the selectivity of catalysts, etc. The microwave radiation is also used to increase the hardness of epoxy compound and to improve properties of high strength polyethylene, which is directly adjacent to the insulation coating by the application field [3-5].

Methodology and research methods

The research methodology was gradual study of the penetrating ability of microwave radiation in polymers of different nature, the influence of various parameters of the energy flow to the structure of polymers, peculiarities of the formation of the physical and mechanical properties of polymers in the course of this type of treatment. To realize the processing of polymeric materials by microwave radiation it is necessary to examine regularity of the changes in some of the most important parameters, which include the depth of penetration of the radiation into the material. Calculation methods are not applicable, since no analytical expressions to describe the real and imaginary parts of dielectric and magnetic penetration ability of polymers are not received, as well as for their absorption capacity, depending on the frequency of the radiation and the temperature in the corresponding period of the technological cycle. To investigate the depth of penetration of microwave radiation in polymeric materials with the assistance of the author it has developed a universal microwave laboratory unit, allowing not only to determine the depth of penetration of the electromagnetic radiation in polymeric materials, but also to process them by microwave radiation (figure 1). Conformational changes in the structure of the polymers were evaluated by the studying of results of breaking strength, water absorption and electrical resistivity.

The influence of the energy flow of microwave radiation on the evolution of the structure of polymeric insulating materials was carried by the images of their structure, obtained by means of a probe scanning microscope of high resolution NT-MDT Integra Prima in atomic-force mode using probes type NSG 11. The evaluation of the effectiveness of microwave radiation on the change of the adhesion of the insulating coating on the basis of PVC was performed during visual observation using an optical microscope (×100) as well as a quantitative evaluation of the film adhesion method of separation (GOST 25812-83).

The main part

The depth of penetration of the radiation was determined on polymers that are widely used in the production of insulating coatings. For these purposes the author developed universal laboratory microwave unit which includes a microwave radiation generator 1 (frequency – 2450 MHz), a connecting waveguide 2, fitted membranes flanges 3 and 5, a waveguide 4, the matching chamber 6, nozzles for water input 7 and output 8 from the chamber 6, thermocouple 9, the voltmeter 10, ammeter 11 and housing 12.

Method of the penetration depth determining of the microwave radiation is based on an assessment of the proportion of the energy, absorbed by the test sample, depending on the height of the irradiated polymer layer.

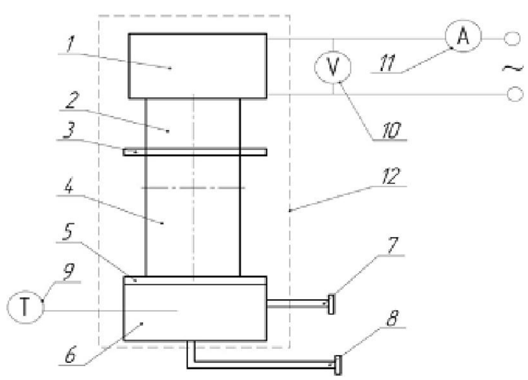

Figure 1. The laboratory microwave unit scheme

During the experiments, there were determined the values of penetration depth of microwave radiation into pellets of polyethylene, terephthalate, polyethylene, polypropylene, cable plastic on the basis of PVC or PVC film (Table 1).

Table 1. The depth of the microwave radiation penetration into polymeric materials

The types of polymeric materials	The penetration depth, m
Polyethylene Pellets	0.412
Poly ethylene terephthalate pellets	0.281
Polypropylene pellets	0.345
Cable plasticate pellets on the basis of PVC	0.195
PVC pellets	0.191
PVC film	0.102

It has been established that the PVC-based materials have a high absorption capacity. The differences between values of the penetration depth of microwave radiation into granules of PVC and onto the film based on them is explained by the fact that the bulk density of granules (750 kg/m^3) is significantly less than the bulk density of the film (1400 kg/m^3). It is established that, unlike polyethylene, polypropylene and polyethylene terephthalate, PVC has a high absorptivity in respect of microwave radiation. This is due to the fact that PVC is a polar polymer, and the molecules have high polarizability. Thus, the dipole moment of the molecules of PVC is $4.8 \cdot 10^{-30}$ ˚C·m, and the rest of the investigated polymers, its values are in the range of (0.8 ... 1.2)·10-30 ˚C·m.

The influence of the microwave range energy and duration of the radiation treatment to change the structure and physic-mechanical properties of polymeric materials based on PVC was investigated using the same laboratory unit (figure 1), by varying the level of radiated energy in the range of from 50 to 400 kJ/kg and processing duration – from 30 to 300 seconds.

Table 2. The experimental values for the aximum breaking load of various polymer materials

Specific energy, kJ/kg	Maximum breaking load, MPa	
	PVC film	Polyethylene film
Without microwave treatment	20.70	11.60
51.0	20.71	11.69
75.8	25.48	11.75
102.5	29.60	11.86
126.8	35.30	12.04
154.2	38.19	12.33
205.8	38.35	15.43
258.0	33.82	12.32
360.0	14.12	12.10

It is experimentally shown that the doubling of the breaking load for materials based on PVC (Table 2) occurs in the range of permissible specific energy of microwave radiation 102.5 ... 205.8 kJ/kg treated for 1-3 min. Further increases in radiation power results in a drastic reduction of the strength properties of the film.

It was also found that under similar conditions the water absorption materials based on PVC is reduced by about three-fold, indicating the formation of cross-links in the polymer, resulting in an increase in the density of the spatial grid. In addition, further study of the thermal stability of PVC and coatings based on it using the method of "Congo Red" showed that previously established range of values of the specific heat of the microwave radiation the time of the thermal stability of PVC is increased by 6 minutes at an average. Consequently, the improvement of the mechanical strength of the samples of PVC film is the result of transformation of the structure, initiated by microwave radiation. Finally, an indirect confirmation of the conformational changes of the molecular structure of PVC film is substantial (approximately 2.7 times) increase in its electrical resistivity [6].

The confirmation of a significant thermal stability of the samples treated by microwave radiation PVC films is their high glass transition temperature. It should be noted that the samples PVHS-70, the partial melting peak is shifted to the higher temperatures area. The temperature of the glass transition (85 ... 89°C) (table 3) slightly exceeds the value characteristic of PVC (82 ... 83 °C). This phenomenon is explained by a decrease in flexibility of the chain macromolecules PVC and cross-links formation, due to the high polarization ability of molecules [7].

Thus, the values of start and end temperatures of the glass transition process (table 3) confirms that the effect of microwave radiation on the PVC leads to increased degree of crystallinity, resulting in increase of the strength of the polymer film. Moreover, the crosslink of the polymer macromolecules is not observed, which occurs at the higher microwave energy radiation, which prevents the loss of elasticity of the film.

Table 3. Influence of the energy of microwave radiation on the temperature of the various stages glass

Radiated energy, kJ/kg	Temperature of start glass-transition, °C	Glass-transition temperature, °C	Temperature of finish glass-transition, °C
Without microwave treatment	81.73	82.30	85.44
102.5	81.99	85.06	88.81
205.8	83.44	89.28	93.32
258.0	83.23	88.76	92.11
309.0	82.50	84.47	89.93

By the increasing the glass transition temperature of the PVC under the influence of the microwave radiation the heat resistance of polymeric materials increases, thereby the upper temperature of exploitation limit significantly increases, which greatly expands the practical use of PVC during processing and exploitation of the finished products. The images of the PVC film structure (figure 2), obtained in the contact mode using an atomic force microscope NT-MDT Integra Prima, showed that it was significant evolution in the process of microwave radiation. The untreated PVC film has predominantly amorphous structure (figure 2a,b). Under the influence of microwave radiation in the PVC, the orientation of the side branches of its macromolecules is changed, which provide the increases of the crystallization centers number, streamlining the structure and reduction of areas of free volume in it. This reduces the total area of the structure of the amorphous fields in favor of the newly formed crystalline phase (figure 2b), which is accompanied by an increase in the degree of order in the arrangement of the polymer macromolecules (figure 2g). PVC molecules begin to rebuild in parallel lines (figure 2d), which is a sign of growth of its crystallinity, providing the improvement of physical and mechanical properties of PVC film.

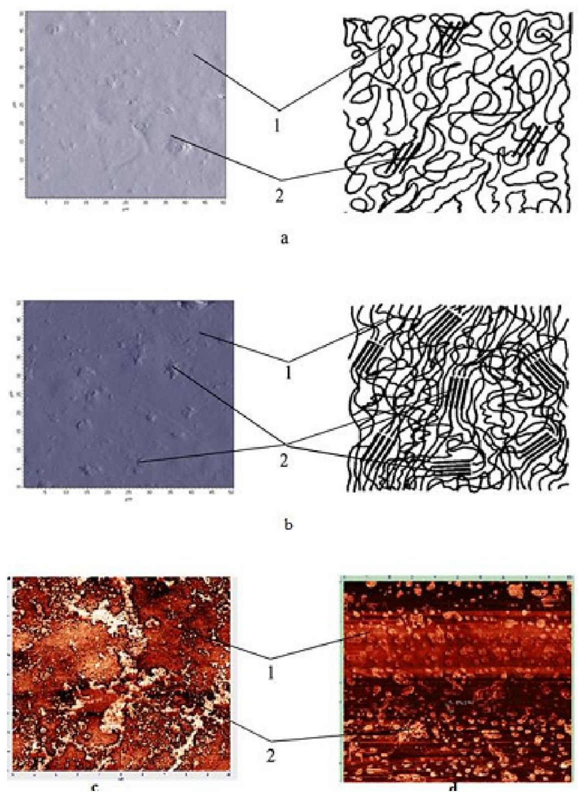

Figure 3. Representation of the structure of PVC film (×10^{6})

1 – amorphous field; 2 – the range of crystallization; a, c – no microwave treatment; b, d – after microwave treatment (specific radiation energy 205.8 kJ / kg)

Thus, it is experimentally demonstrated the possibility of using microwave radiation for the focused the polar polymers structure rebuilding, providing an improvement in their physical and mechanical properties. For its practical implementation there have been designed the microwave units [8, 9], making it possible to produce the main types of insulation materials which are widely used in the oil and gas industry.

The design of a mobile microwave unit is designed on the principle of the developed structures of stationary microwave units for microwave processing of polymeric materials [10]; however, it differs fundamentally by the capability of the operating in the field conditions. A distinctive feature of the design of the mobile unit is the microwave radiation type camera with the unlimited volume, the opening angle of the horn radiator of which is designed so that the electromagnetic radiation could provide the full absorption of the energy of the microwave radiation by the material being processed.

The mobile microwave unit (figure 4) is designed for the polymeric coatings` processing, directly on the pipeline. It includes a cylindrical shell 5, the metal the screen 3, frame 4, platform 6, magnetrons 1with the radiated power of 180 watts, running gear, consisting of the engine 10, the drive gear and chain gears, rollers 2, set at an angle to the shell to provide the reciprocal movement along the pipeline, which is carried out by transmission of the rotation torque from the toothed wheel 7. On it by means of bolts 9 are mounted rollers 8. The unit moves with a linear velocity of 0.0083 m/s.

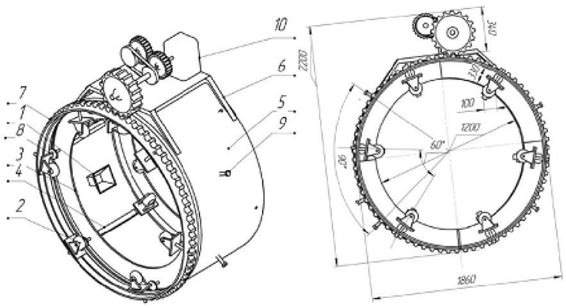

Figure 4. Mobile microwave unit

The research of the influence of microwave energy radiation on PVC coating breakout force from the surface of steel 20 showed that the characteristic of adhesion after the treatment of the film is greatly increased. The maximum value of pull-off force 8.86 N/cm corresponds to the right boundary of the previously set range of the effective values of the specific energy of microwave radiation 102.5 ... 205.8 kJ / kg, which is another argument in favor of the reliability of the above expressed views on the mechanism of microwave radiation on the structure of the polymer film.

After the microwave radiation exposure the adhesion of the substrate to the adhesive surface of the metal pipe also increases. This is because during the microwave treatment of the isolated pipeline the coating temperature increase takes place, and at the moment of the adhesive contact of the glutinous basis with the metal substrate, its viscosity decreases. Thereby, the stronger adhesive interaction of the polymer coating to the surface of the pipeline is achieved.

Conclusions

To implement the developed techniques, we constructed a universal laboratory apparatus by which the entire set of studies of the polymers absorption ability when exposed to microwave radiation and the effect of the latter on their structure and properties was conducted.

1) It is established that the absorption capacity of polar polymer is substantially higher than the nonpolar due to a significant dipole moment, whereby it is possible to achieve a better polar polymers` structure rebuilding under the influence of microwave radiation.

2) During the polymer structure restructuring, when the specific energy of the microwave radiation is in the range of 102.5 ... 205.8 kJ/kg and the treatment time no longer than three minutes, the strength of the insulating material approximately 2 times occurs, as well as the decrease of its water absorption factor of 2.5, increase of the volume resistivity in 3 times and the increase in the glass transition temperature for 3 ... 7 degrees.

3) The usage of the mobile microwave units for insulating polymeric coatings` treatment on existing pipelines, provides not only the improvement of physical and mechanical properties of the coatings, but also the increase of their adhesion to metal surfaces, which leads to increased operational reliability of the pipelines.

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