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Effect of microwave irradiation on the structuring of polyvinyl alcohol

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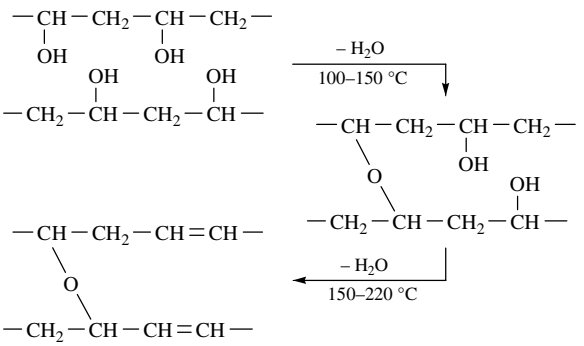
The interaction of microwave radiation with solid polyvinyl alcohol results in the structuring of the polymer accompanied by a change both in the contribution of competitive (both intra- and intermolecular) reactions and in the ratio of reaction products in comparison with the thermal reaction under the same conditions.

The effect of microwave radiation on high-molecular compounds, particularly, polymers in a solid state, is promising for the use of microwave irradiation in the synthesis and modification of polymers.[1–5]

The acceleration of chemical reactions under microwave irradiation results from the effect of an electromagnetic field on the reactants. In addition to a thermal effect (heating), this may also produce specific effects caused by a microwave field on the reactants and resulting in changes in the reaction rate constant.[3–5] A combination of these two components is the origin of the observed acceleration of chemical processes.

A comparison between the two methods of impact, *i.e.*, microwave irradiation and conventional thermal heating, allows one to reveal the difference between these methods and their specific features; such a comparison has been undertaken in this study for reactions of polyvinyl alcohol (PA) as an example. This polymer was chosen due to its ability to undergo dehydration on heating (100–150 °C) resulting in structuring due to the

formation of intermolecular ether bridges.[6] Double bonds are formed at higher temperatures (150–220 °C); the presence of conjugated structures results in a deep colouring of the polymer:



Structured PA is a promising material to be used in aqueous media as a biosorbent or biocarrier, in water filters, *etc*.

A chamber furnace with an MDS-2000 (CEM Corp., USA) radiation source (magnetron) operating at 2.45 GHz with a constant power of 350 W was used as the source of electromagnetic field. The temperature was measured with a fiberoptic probe.

Microwave radiation and thermal heating were applied to solid PA films (with a molecular mass of 70000–100000) formed from an 8% aqueous solution of the polymer. The films were tightly fixed on a quartz case with a probe placed inside; the distance from the detector to the sample was no greater than 1 mm. The maximum swelling index and the amount of the polymer gel fraction were determined for treated films (treating time of 10 min) after repeated by washing specimens in water at 50 °C. The films were analysed by IR and UV spectroscopy (Bruker, EGUINOX-55, Germany and He λ ios α UV-Vis, USA, respectively). The concentration of double bonds was determined with an ADS-4M double bond analyser (NTO, Russian Academy of Sciences, Chernogolovka) based on the amount of ozone absorbed by one gram of a compound.

We found that the exposure of PA films to microwave radiation heats these films, which suggests that the polymer can absorb and then dissipate microwave radiation even in the solid state. In contrast to the behaviour of low-molecular compounds in liquid media, the motion of a PA molecule as a whole in the solid state is unlikely; hence, the heating of the PA film is more likely to originate from the mobility (vibration) of a macromolecule segment or part-segment. On the other hand, the segmental mobility of a macromolecule predefines its flexibility and the polymer glass transition temperature. We found that the rate of the temperature increase of the sample increases by a factor of 1.5–2 upon an increase in the mobility of the polymeric chain due to the transition of the polymer from a glassy state to a high-elasticity state (85 °C).

It can be assumed that, for polymers with higher glass transition temperatures, the temperature increase under microwave radiation will be not so considerable. In fact, polyacrylic acid (PAA, T_{glass} = 106 °C[7]) heats to 70 °C, whereas a PA film heats to 190 °C under the same conditions. The temperatures of samples made from PA + PAA films with compositions of 3:1, 5:1 and 7.5:1 decrease from 172 to 157 and 112 °C, respectively, as the PAA concentration increases.

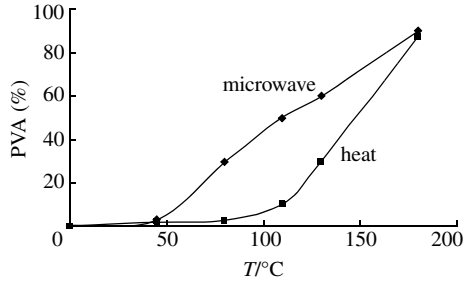


Figure 1 Amount of structured PA following microwave and thermal heating as a function of the treatment temperature; treatment time: 10 min.

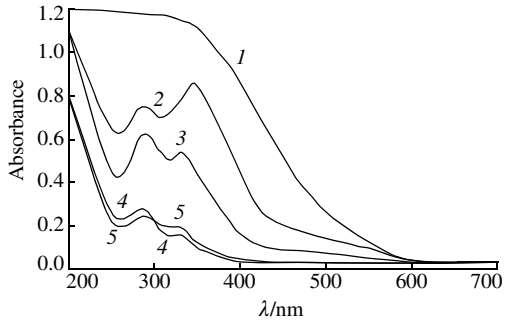


Figure 2 UV spectra of PA films following thermal heating: (*1*, *2*) 178 °C, (*5*) 150 °C, and following microwave heating: (*3*) 170 °C, (*4*) 150 °C; wall thickness: (*1*, *3*) 150 and (*2*, *4*, *5*) 90 μm.

Other conditions being equal, the temperature of the polymer under microwave irradiation increases with the thickness of the PA film. This is accompanied by a decrease in the maximum swelling index. Apparently, for a thin film, heat dissipation from the surface and convective cooling of the material external layers with ambient air are considerable; this determines the temperature profile of the samples and hence their properties.

We performed a comparative study of the properties of PA films under thermal and microwave heating. Analysis of the IR spectra of PA films showed that, in both cases, there is a small decrease in the intensity of the absorption bands typical of OH (3440 cm^{-1}) and CH_2 groups (2940–2910, 1375 and 920 cm^{-1}), an increase in absorption typical of CH bonds (2840–2850 cm^{-1}) and a noticeable absorption increase at 1140 cm^{-1} (C–O–C group); the changes in the spectra are proportional to the sample temperature. Thus, the IR spectra confirm the published data on the structure of the main dehydration products (see the equation) and suggest that the polymer undergoes structuring due to the formation of intermolecular chemical bonds, *viz.*, ether bridges.

The amount of an insoluble (structured) polymer was determined after the repeated extraction of PA films in water at 50 °C. Figure 1 indicates that the degree of polymer structuring under microwave irradiation at 50–150 °C is higher than that in the case of thermal heating. At higher temperatures (≥180 °C), the polymer gets structured up to almost 100% in both cases.

The intense broad-band absorption of the alcohol OH groups (3150–3500 cm^{-1}) and the absorption of acetate groups and water present in PA (1570–1740 cm^{-1}) mask the bands that are typical of unsaturated bonds.[8–10] The UV spectra are more informative in this case. A typical spectrum of PA films after microwave irradiation and thermal heating is presented in Figure 2.

The thermal heating of PA (178 °C) results in a brown colouring, which suggests that a conjugated structure appears.[6] UV spectra show strong absorption in the region 250–400 nm; the increase in the intensity of a band at λ_{max} = 330 nm, which can be attributed to the absorption of polyconjugated unsaturated structures,[10,11] is higher than that at λ_{max} = 280 nm (oxygen-containing oxidation products). On the other hand, when PA films were heated almost to the same temperature (170 °C) by microwave radiation, the colour of the films was different. They turned yellow, and the intensity of the band with λ_{max} = 330 nm

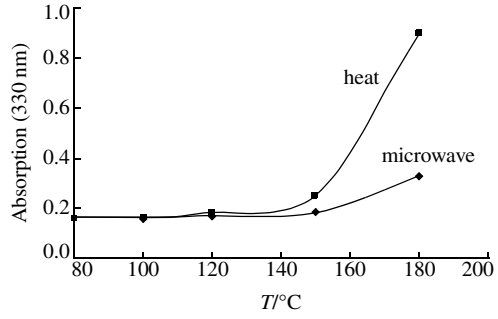


Figure 3 Changes in the absorption intensity at 330 nm for PA films following microwave and thermal heating (10 min).

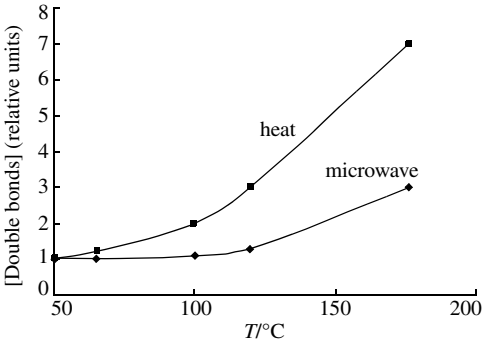


Figure 4 Generation of double bonds in PA upon microwave and thermal heating (10 min).

in the UV spectra increased to a smaller extent. Figure 3 shows that the increase in the absorption intensity at 330 nm for films that have been thermally heated is higher than that following microwave irradiation; this correlates with data on the generation rate of double bonds in treated samples (Figure 4).

Thus, it is believed that an electromagnetic field increases the probability of dehydration *via* the preferential formation of intermolecular ether bridges (though intramolecular cyclisation cannot be ruled out here, either). In the case of convective heating, the intramolecular reaction predominates; it involves both hydroxyl groups and non-polar methylene groups (see the equation). The rate of this reaction becomes particularly considerable at $T > 150$ °C, which results in the fast formation of by-products and in a deep colouring of the polymer.

The selective effect of microwave irradiation on polar groups makes it possible to perform reactions for the structuring of PA applied to polypropylene (PP) and polyethylene carriers, *i.e.*, on supports with a low thermal stability (the working temperature does not exceed 100–120 °C). Figure 5 indicates that microwave irradiation allows one to immobilise PA on a PP fibre more efficiently than in the case of thermal heating, other conditions being equal.

Thus, the results suggest that it is promising to use microwave radiation for the structuring of polyvinyl alcohol. Further accumulation of experimental data will make it possible to expand the possibilities of applying microwave irradiation to the synthesis and modification of high-molecular compounds.

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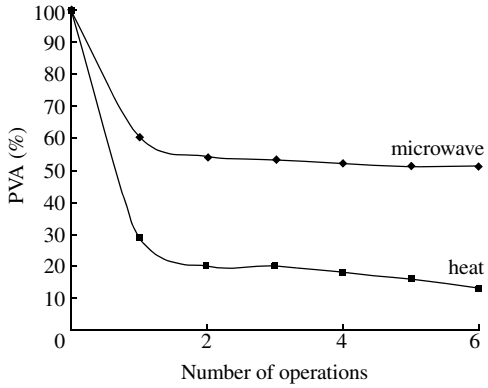

Figure 5 Immobilisation of PA on a PP fibre upon microwave and thermal heating; heating time of 10 min; extraction in water (50 °C) for 1 h.

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