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Microwave assisted processes for producing thin layer materials in the field of nanotechnology

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The possibility of applying a microwave (MW) processes for producing thin layer materials has been studied. The experiments have been carried out with 200 nm thick polyimide (PI) layers prepared by vacuum deposition of PI precursors – oxidianiline (ODA) and pyromellitic dianhydride (PMDA), followed by thermal, MW or mixed treatment. FTIR spectroscopy investigations of the samples have shown that the MW treatment enhances the acylation processes, while not affecting the processes of imidization. The best results have been obtained by combined MW and thermal treatment.

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1. Introduction

Microwave (MW) techniques are now an attractive topic of the combinatorial and parallel strategies in advanced and functional material science [1]. The enhancement of the reactions by MWs could result from a material-MW interaction, leading to thermal and non-thermal effects [2]. MW processing presents an attractive possibility as an alternative to the classical thermal processing, because of the inherent advantage of MW heating which is selective, direct, rapid, internal and controllable.

MW technology has potential advantages for obtaining thin polymer materials, because their dielectric properties predispose them to effective MW- induced curing. Economic analyses suggest that the cost of curing polymers may be reduced from 4-11 $mJkg^{-1}$ to 0,3-0,5 $mJkg^{-1}$ by switching to MWs [3].

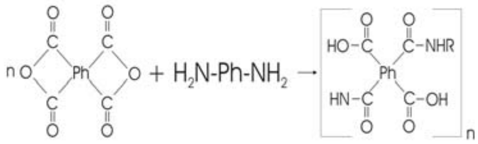
Polyimides (PIs) as polymer materials have found widespread applications, because of their low permittivity, chemical inertia and high thermal stability. Due to this fact, for example, thin PI layers are suitable for MW processing [4].

The aim of the paper is to study the possibility of the MW treatment of VD thin PI layers. This is an attempt to shed light on some aspects of the MW influence on the processes of PI layer production.

2. Experimental

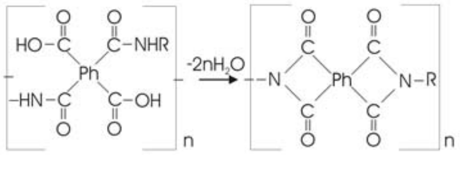
2.1. Thin PI layer formation and MW treatment of the samples

The most widespread method for obtaining aromatic PIs is the interaction of the dianhydrides (Dh) of the aromatic tetracarboxylic acids with the aromatic diamines (AD). This chemical reaction can take place both as a two-step and a one-step process [5]. The two-step method is more popular. In it, the AD first interacts with the Dh and polyamido acids (PAC) are obtained according to the equation (1):



(1)

The second step of the reaction, dehydrocyclization of the PAC (imidization), usually occurs under additional thermal action as in equation (2), leading to the end product of the PI.



(2)

The above equations do not give the right picture of all complications and characteristics of the reaction for obtaining the PI after the two-step method. Our experimental samples have also been obtained on the basis of these reactions by the VD of the PI precursors.

PI layers (200 nm thick) were formed by VD of ODA and PMDA from two thermally heated sources [6] on linearly moving substrates (fixed rates of 5 mm/s).

The base pressure is 5×10^{-4} Pa and the deposition rates were 0.2 to 2 Å/s.

Two different sets of apparatus for MW treatment were used. The first was a domestic microwave oven. The second was an especially developed system for MW treatment, aimed at improving the homogeneity of the MW action (Fig. 1). In this case, however, the samples were MW treated by being placed at an equal distance perpendicular to the direction of the MW dispersion, in a holder of PMMA transparent to the irradiation. The placement of the samples was fixed.

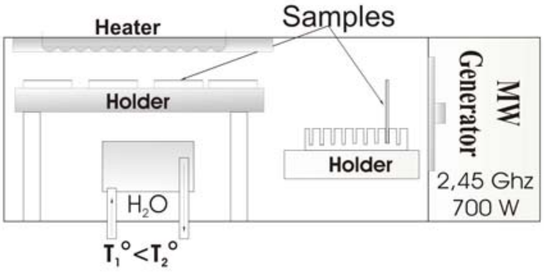


Fig. 1. Apparatus for MW and thermal treatment.

Thus the MWs falling on the sample were equally spread over the entire surface and reproducibility was ensured. A spiral with flowing water was introduced into the treatment chamber, allowing for the removal of the excessive MW energy. A holder was situated under an IR heater, permittingcontrol of the heating temperature. The experimental system made it possible to combine the MW treatment and the following thermal action, under strictly regulated conditions.

2.2. Methods of investigation

FTIR was performed at room temperature using a Perkin Elmer 1600 FTIR spectrophotometer in the spectral range 2000 - 450 cm^{-1}, resolution 4 cm^{-1}, interval 0.2, KBr substrate. FTIR spectra were normalized to the 1500 cm^{-1} peak intensity.

The optical spectra were recorded on a Cary 5E spectrophotometer in the range 200 - 900 nm, using quartz substrates.

3. Results

Our investigations using FTIR spectroscopy showed that in the first step (equation 1) a mixture of a number of products (Fig. 2) was obtained with a prevalence of the A_N (nucleophilic addition) reaction, which leads to the production of isoimide (1400 cm^{-1}) predominantly [6]. As a result of the MW treatment in an inhomogeneous field, the kinetically controlled product of the reaction S_N (nucleophilic substitution) is obtained. Increasing the MW treatment time to 20 min did not yield a significant improvement in the results (Fig. 2).

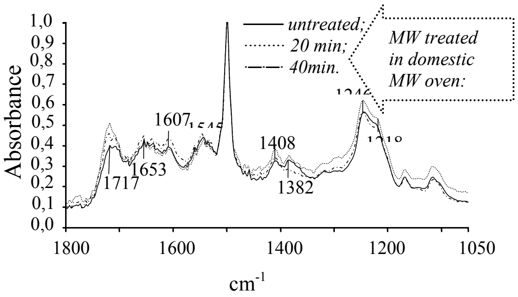


Fig. 2. FTIR spectra of VD – ODA/PMDA layers.

The thermodynamically more stable product PI (1380 and 1720 cm^{-1}) was obtained by additional thermal treatment of the same layers (Fig. 3.), the significant role being attributed to the thermal processing and not to the MW treatment in an inhomogeneous field.

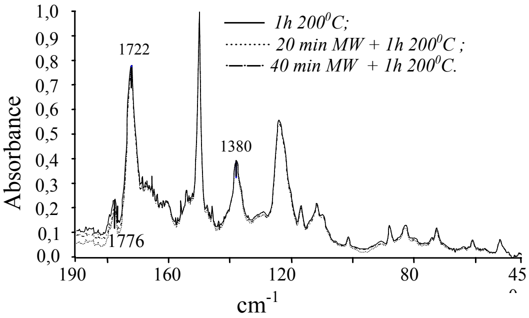


Fig. 3. FTIR spectra of VD – ODA/PMDA layers.

Our preliminary studies of MW treatment in a specially developed system for this purpose, securing a better homogeneity of the MW treatment (Fig. 1), show that an improvement in the PI synthesis and the yield of the end product of higher quality could be attained. The IR spectra of such layers are presented in (Fig. 4) At this stage of our investigations, we have no grounds to assert that there is any concrete dependence on the irradiation time. It is a fact, however, that imidization in this case is also taking place at a lower rate (1380 cm^{-1}), as compared to the generation of isoimide (1400 cm^{-1}).

After thermal treatment of the same layers, spectra typical of the PI were obtained (Fig. 5). Upon inspection of the range characteristic of the degree of imidization-δ (1380 cm^{-1}) it is clearly seen that at this stage the most acceptable results are obtained for 5 min MW treatment followed by high temperature thermal processing (Fig. 5 and Table 1).

Table 1. The dependence of the δ on the treatment.

Treatment conditions	δ /relative units /
5 min MW + 15 min 300 °C	13,81
15 min MW + 15 min 300 °C	13,07
15 min 300 °C	13,27

The differences are not so significant, except for the values shown in Table 1. The peaks at 1340 and 1420 cm^{-1} of the spectra (Fig. 5) are clearly distinguished, and unequivocally testify to a greater quantity of chemical contamination in the layers of type 2 and type 3 from Table 1. The results show that imidization after 5 min MW treatment and additional thermal processing is the best. It is of special importance to note that the high-temperature treatment of the thin layers which are especially sensitive to thermal stress does not lead to defects, except in the case of preliminary MW treatment (as a first stage).

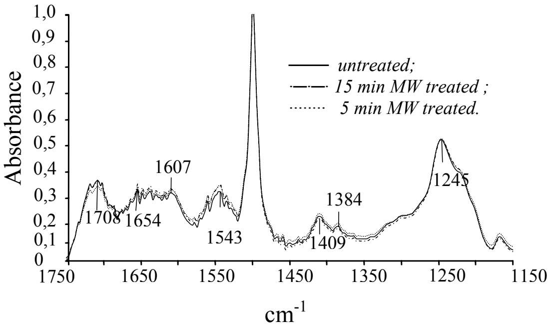


Fig. 4. FTIR spectra of VD – ODA/PMDA layers.

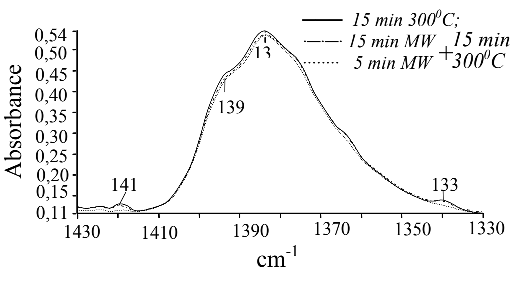


Fig. 5. FTIR spectra of VD – PI layers.

The spectral behaviour of the VD PI layers in the UV-VIS region in transmittance (T) are presented in Fig. 6. The layers show a high T in the range 400 – 800 nm and some bathochromic shift of the absorbance after 15 min MW treatment. This means that MW treatment causes changes in the chromophoric system of the precursors, e.g. mesomerism in amides [7]. After thermal treatment, peaks in the VIS region are not well defined. Only a decrease in the intensity is observed, as a result of the cyclization and interruption of the chromophoric system.

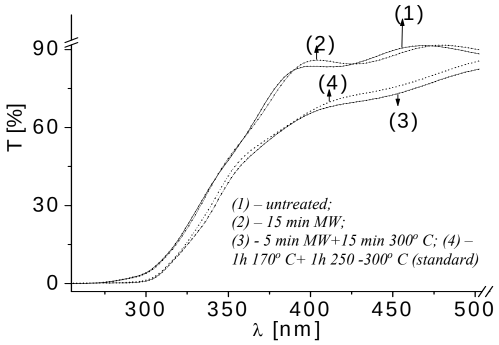


Fig. 6. Optical spectra of PI layers.

The observed picture corroborates our conclusions from the results presented above that the MW treatment does not enhance the imidization process.

4. Discussion

The reaction of acylation (equation 1) considered above represents in itself a S_N at the carbonyl carbon atom, the amine playing the role of an electron-donor and the anhydride being an electron-acceptor. It has been established that monomer links with two isomeric structures (Fig. 7.) have been formed from the PMDA:

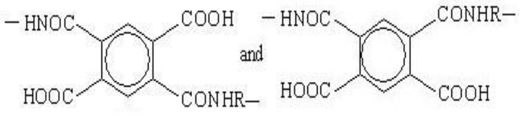


Fig. 7. Isomeric structure of PMDA.

The para- and meta- isomeric link contents exerts an influence on the kinetics of their transformation into PI. Studies of polycondensation have shown that often the reaction capacity of the second functional group is changed after the reaction of the first one [8]. In this way, the so called mono - aminized anhydrides are obtained.

The issue of the balance between the main and side reaction taking place in the process of obtaining PAC is of major importance and great practical significance. The ortho-carboxyamide group may get to cyclization until side products (imido-, isoimido- and anhydride cycles). The carboxyl group situated in an ortho-position relative to the amido bond is prone to internal molecular decomposition and destruction in the macromolecule. The most important issue is the competition between reactions S_N and A_N. The polarization of the carbonyl group makes both reactions equally feasible. The course of both reactions is hard to control, and thus fact methods for controllable synthesis are in high demand. In the course of the S_N reaction, imide is obtained at the next stage, and in the case of the A_N reaction isoimide is the end product. The reaction course is accounted for by stereoelectronic effects, dipole-dipole interactions and the strength of the nucleophile and nucleofugue. The second stage of the process, the imidization itself, depends on the products of the first stage that are in most cases reversible, as well as on the coplanarity of the monomeric links. This is why a suitable spatial positioning of the forepolymer molecules is needed, so that the polycondensation process can be facilitated. This requires the development and implementation of a MW system ensuring sufficient homogeneity of the MW action. The improved system of MW treatment used by us could be considered to be quite close to the fulfilment of these requirements. The introduction of MW treatment in the process of obtaining PI layers offers the possibility of a considerable shortening of the time necessary for the processes of polycondensation and imidization – from 2 hours under the standard conditions to 20-30 min in the case of the combined treatment (Fig. 6.).

5. Conclusions

The following conclusions can be drawn:

- The MW treatment of the PI layers causes an enhancement of the acylation process, but does not affect the imidization process;

- The implementation of MW action focused on the sample or the creation of a homogeneous MW field in the sample area probably creates the possibility for a better spatial arrangement of the molecules in the layers, and hence an improvement in their optical and electrophysical parameters;

- The possibility of a considerable shortening of the whole process is revealed.

Acknowledgements

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