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Curing of liquid epoxy resin in plasma discharge

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Abstract

Epoxy resins in the solid state, liquid state and during polymerisation were treated by microwave oxygen plasma and analysed by FTIR spectra. Curing, etching and oxidation kinetics of epoxy resin were observed. In the liquid resin and polymerising mixture the effect of structure modification was observed more intensively than in the case of solid sample due to a mixing process. A modification of bulk layers of liquid epoxy resin was observed under plasma action. The polymerisation reaction of epoxy resin with amine hardening agent can be released in plasma discharge at low pressure.
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1. Introduction

Future generation of space techniques should be connected with industrial exploitation of unique space conditions. Now the limiting factor of a wide application in industry is the small size of space constructions available in space on Earth orbit and on other celestial bodies. The creation of large-size construction by the way of docking of separate parts is expensive and takes a long time. One of the solutions can be an inflatable construction with following rigidization of material after unfolding [1–4]. It can be realised with the technology of polymerisation of fibre-filled composites and a reactionable matrix applied in free space or on other celestial bodies when the space construction should work during a long period of time [1–4]. For the polymerisation of the construction the fabric impregnated with a long-life matrix (prepreg) is prepared under terrestrial conditions and, after folding, can be shipped in a container to orbit

and kept folded on board the station. In due time the prepreg is carried out into free space and unfolded by, for example, inflating an internal pocket. Then a reaction of matrix polymerisation is initiated. Reaction temperature can be reached by Sun irradiation or additional heating from internal special heaters or from carbon fillers of prepreg. After that, the hard construction can be used for wide applications. In this case, a restriction of the size and form of construction is absent, there is no necessity of some launch vehicles for the creation of large size construction, for example, as for space station [5,6].

However, nowadays this technology is not yet used because clear understanding about polymerisation processes of polymer materials in free space conditions is absent. Conditions of free space have a strong destructive influence on polymer materials. In free space the composite material is exposed in high vacuum, sharp temperature changes, space plasma, micrometeorite fluency and microgravitation [7]. One of the important free space conditions is the space plasma, formed by atomic oxygen (on low Earth orbit), high energy charged and neutral particles as electron, atomic and ion flows, UV and VUV sun irradiation and X-rays fluxes with high energy of photons [8–10].

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Experiments of polymer ageing on Earth orbit show degradation processes occurring in polymer materials under the action of energetic particles. On Low Earth Orbit (LEO) the major factor in polymer degradation is atomic oxygen with a low kinetic energy of about 4.5 eV. Destruction of hard polymers in free space was studied on repeated occasions, including real experiments outside of the space ship on the Earth orbit [11] and laboratory modelling of space action on Earth. These studies showed, that the destruction of epoxy composite, HDPE, LDPE, Kapton, Teflon, polysulfone and others during flight on low Earth orbit is connected with plasma action of atomic oxygen with low kinetic energy [12–14]. Polymer structure changes are observed in a thin polymer surface layer [15]. At low energy flow of atomic oxygen the collision mechanism of destruction is accompanied by chemical mechanism of destruction [16]. The main results of destruction are loss of mass, dehydrating process, formation of amorphous carbon layer, formation of cracks and craters on surface and consequently the decrease of durability of the polymer. Laboratory experiments showed, that the same structural changes of polymers are observed in plasma at low pressure and under vacuum ultraviolet light (VUV) and X-ray irradiation [11]. The formation of rough surface structures, crosslinks and oxidation processes are observed in real free space and in plasma at low pressure. All results were received for hard polymers in glass and elastic states, but not in visco-elastic and liquid states. Some of our experiments with liquid resins were made for ion beam implantation of metal ions for creation of nanoparticles in polymer matrix [17]. But the structure of polymer after ion beam implantation was not analysed. Our previous experiments with curing of liquid resins in high vacuum, plasma and ion beam showed the possibility to carry out a polymerisation reaction under conditions close to free space [18–20]. In the present paper we continue these studies by polymerisation of epoxy resin in microwave plasma reactor.

Results of the effect of plasma treatment on resin in liquid (visco) and hard (glass) state are presented.

2. Experiments

For experiments an epoxy resin based on Bisphenol A and glycidyl ether (average molecular mass 374, viscosity at 25 °C 1 Pa s, Aldrich) with triethylenetetraamine (Aldrich) hardening agents was used. The ratio of resin and hardening agent was 10:1 in weight parts.

The plasma reactor 440G (Technics Plasma GmbH, Germany) with 2,45 GHz plasma frequency, 200 W plasma power with homogeneous distribution in 23 l volume of reactor chamber, 12 Pa pressure of oxygen with flux of 10 sccm was used for plasma discharge. The temperature of samples during plasma treatment in-

creased up to 33 °C after 30 min of treatment. This heating of samples was taken into account at analysis of curing and etching processes of epoxy resin in comparison with control samples.

The thermobox Binder VD23 (Binder GmbH, Germany) was used for heating and vacuum treatment. The pressure was varied from normal atmosphere to 30 Pa, temperature was varied from 25 to 150 °C with accuracy of ±1 °C. Loss of mass for samples was measured on Sartorius balance (weight measurement accuracy of 0.1 mg).

The FTIR transmission spectra were recorded on Bruker IFS-66 spectrometer, resolution 2 cm^{-1}, the number of scans was 100. Resin samples were posited on KBr pellet immediately after mixing of epoxy resin with hardening agent and treated by plasma and vacuum during 10 min. After treatment the FTIR spectra were recorded. Then, the procedures of treatment and spectra recording were repeated. The absorbance values of analysed bands were calculated by peak maximum with base line corrections. The software package OPUS of Bruker was used for spectra analysis. The thickness of sample was determined by weight measurements on balance and by absorbance of FTIR spectra lines.

3. Results and discussion

The experiments with the liquid epoxy resin under plasma action was done without hardening agent. The liquid epoxy resin was put on KBr pellet and treated by microwave plasma at low pressure. The temperature of sample during plasma action increased to 30–40 °C in dependence on the power of plasma discharge and on time in plasma. The FTIR spectra of liquid resin after exposure in plasma discharge are presented in Fig. 1. The intensity of lines at 1184 and 1247 cm^{-1} of ether group, 1610 and 1510 cm^{-1} of aromatic ring of resin, 1455, 1385 and 2966 cm^{-1} of methylene groups and 3487 cm^{-1} of hydroxyl groups decreases with plasma exposure time. The decrease of intensity of all spectra line corresponds to the decrease of epoxy resin thickness by the Lambert-Beer law [21]. With increasing of plasma treatment time the thickness of epoxy resin layer decreases and the optical density of all spectral lines of epoxy resin decrease too. It can be caused as well by an evaporation of epoxy resin into vacuum as by etching of epoxy resin in plasma discharge.

For the estimation of the evaporation process the epoxy resin was exposed under vacuum of 12 Pa in the same plasma chamber without plasma discharge. The spectra of the samples were not changed with time of vacuum treatment. The analysis of evaporation rate of epoxy resin under high temperature and low pressure showed that the epoxy resin film of 30 μm thickness loses about 1% of mass at 12 Pa pressure and 30 °C during

1 h. This value of mass loss rate is too small in comparison with spectral changes under plasma discharge, that the observed mass loss of epoxy resin in plasma cannot be explained by the evaporation. Consequently, the changes of epoxy resin spectra in plasma discharge are caused by the etching process of epoxy resin.

The normalisation of spectra to the optical density of aromatic ring line at 1610 cm^{-1} shows the changes of spectra corresponding to the chemical structure of macromolecules of epoxy resin under plasma effect (Fig. 2). In the normalised spectra the strong 1725 and 1671 cm^{-1} lines of carbonyl groups appear and the optical

density of these lines increases with time of the plasma treatment. The increase of intensity corresponds to oxidation processes in epoxy resin under plasma action. The carbonyl spectral lines have a complex profile, that corresponds to the appearance of different carbonyl containing groups in resin macromolecules after plasma treatment. It can be carboxylic acid, ester and aldehyde groups. The appearance of these groups under plasma action as a result of the destruction processes of macromolecules is a well known process in polymer surface layer [22,23]. In the hydroxyl stretch vibration region the optical density at 3450 cm^{-1} increases in epoxy resin
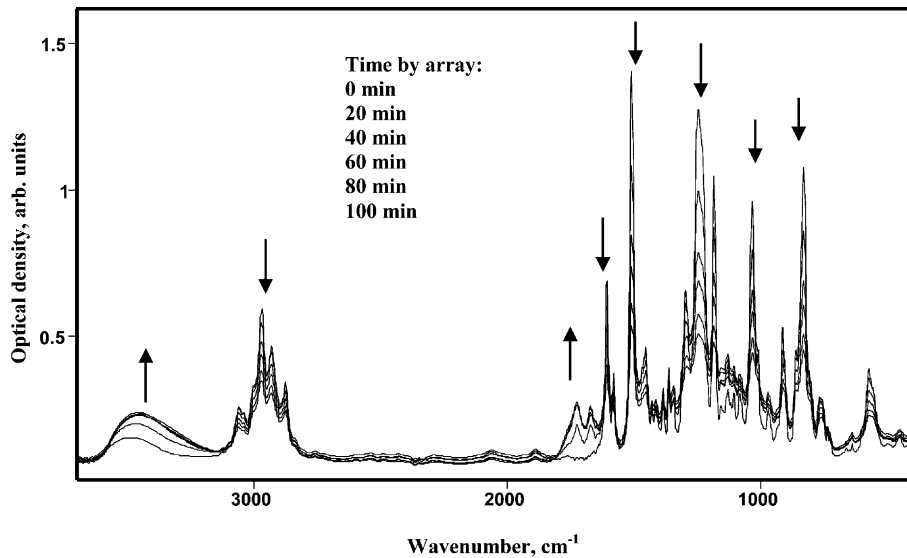

Fig. 1. FTIR spectra of liquid epoxy resin with treatment time in plasma.
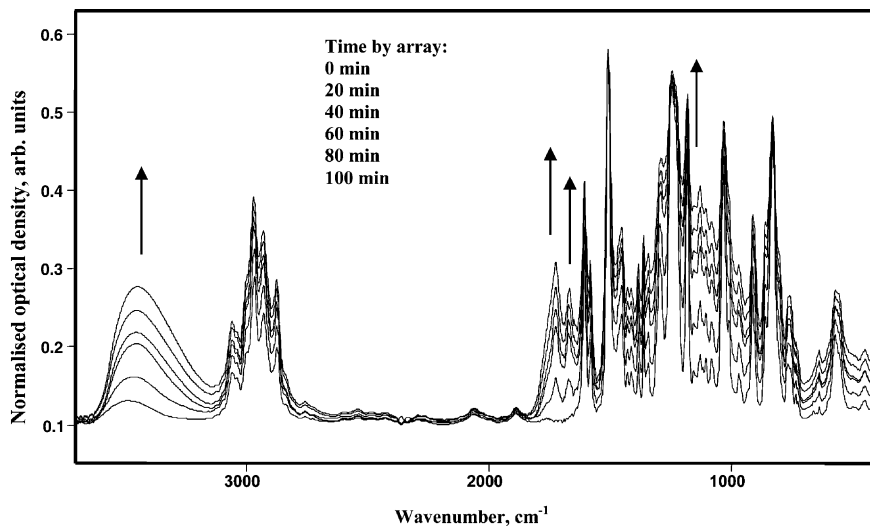

Fig. 2. Normalised FTIR spectra of liquid epoxy resin with treatment time in plasma.

spectra after plasma treatment. This line is interpreted as stretching vibration line of hydroxyl groups and carboxyl groups. Hydroxyl groups exist in initial macromolecule of epoxy resin. The increase of intensity shows the increase of hydroxyl group concentration in epoxy resin under plasma action. These groups appear at destruction and oxidation of epoxy resin macromolecule in plasma too.

Similar spectral changes are observed in spectra of cured epoxy resin under plasma action (Fig. 3). The decrease of spectral lines intensity with time of plasma treatment is observed in all spectral regions. But the spectral changes for solid resin are weaker than liquid resin. In normalised spectra the structural changes of resin macromolecules are observed vaguely. The weak line of carbonyl group stretching vibrations at 1750 cm^{-1} is observed in spectra of treated solid resin. The same weak increasing of optical density line in the region of hydroxyl group stretch vibrations is observed after plasma action. The spectral changes are observed after short time of plasma treatment. At long times of plasma treatment the intensity of carbonyl and hydroxyl group lines does not change. The weak changes of spectra correspond to well known modification of polymers surface in plasma discharge. The weak spectral changes are caused by structural changes of surface layer under plasma modification, whereby a thin surface layer is modified while the bulk resin remains unchanged during plasma treatment.

Similar changes of spectra in liquid epoxy resin with hardening agent after plasma treatment are observed (Fig. 4a and b). In these experiments, the reactionable mixture of epoxy resin and hardening agent was put on KBr pellet immediately after preparation. The decrease of line intensity in all regions of spectra shows the etching processes of composition as in spectra of liquid and solid epoxy resin. In normalised spectra of reactionable mixture the chemical structure changes of macromolecules are observed stronger than in solid resin and they are weaker than in liquid resin. The intensity of the stretching vibration lines of carboxyl and hydroxyl groups at 1734 and 3420 cm^{-1} increases with time of plasma treatment. The polymerisation reaction of epoxy groups with amine groups was observed by the intensity of epoxy ring vibration lines at 915 and 862 cm^{-1}, by the intensity of stretching vibrations lines of methyl group near epoxy ring at 3000 and 3057 cm^{-1}, by the intensity of ether group vibrations lines in C–O vibration region at 1250 and 1130 cm^{-1} and in O–H stretch vibration region at 3420 cm^{-1}. The observed decrease of epoxy ring line intensity and the increase of ether and hydroxyl lines intensity corresponds to the reaction of polymerisation.

The received spectral data were used for a quantitative analysis of reaction kinetics in plasma treated samples and in the control samples. The kinetics of the etching process was observed by the optical density of stretch vibration line of aromatic ring at 1610 and 1510 cm^{-1}. The shape of these lines do not change during etching in plasma and the aromatic ring does not take part in reaction of polymerisation.

In Fig. 5 the dependence of aromatic ring line intensity is presented for epoxy resin in liquid, cured state and during polymerisation. The etching rate of cured resin is lowest that corresponds to highest stability of cured resin in plasma discharge. The etching rate of liquid resin is highest that corresponds to lowest stability of liquid resin in plasma. The etching rate reflects the
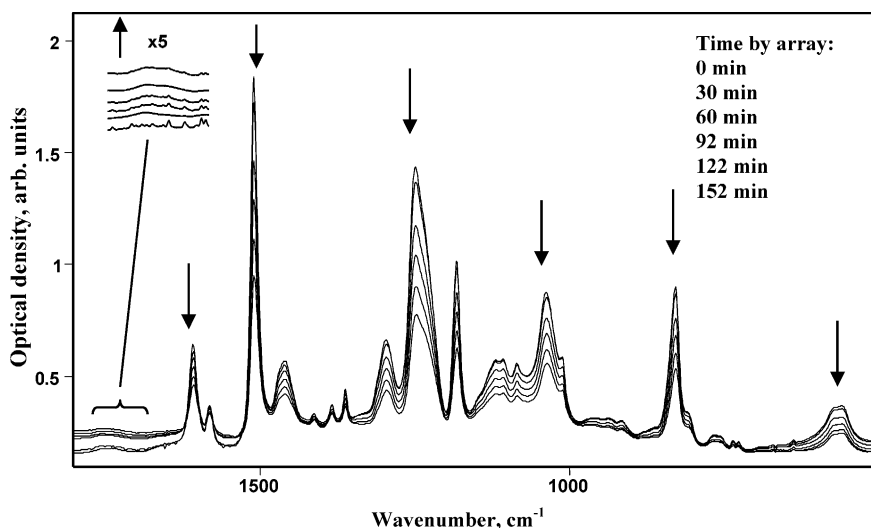

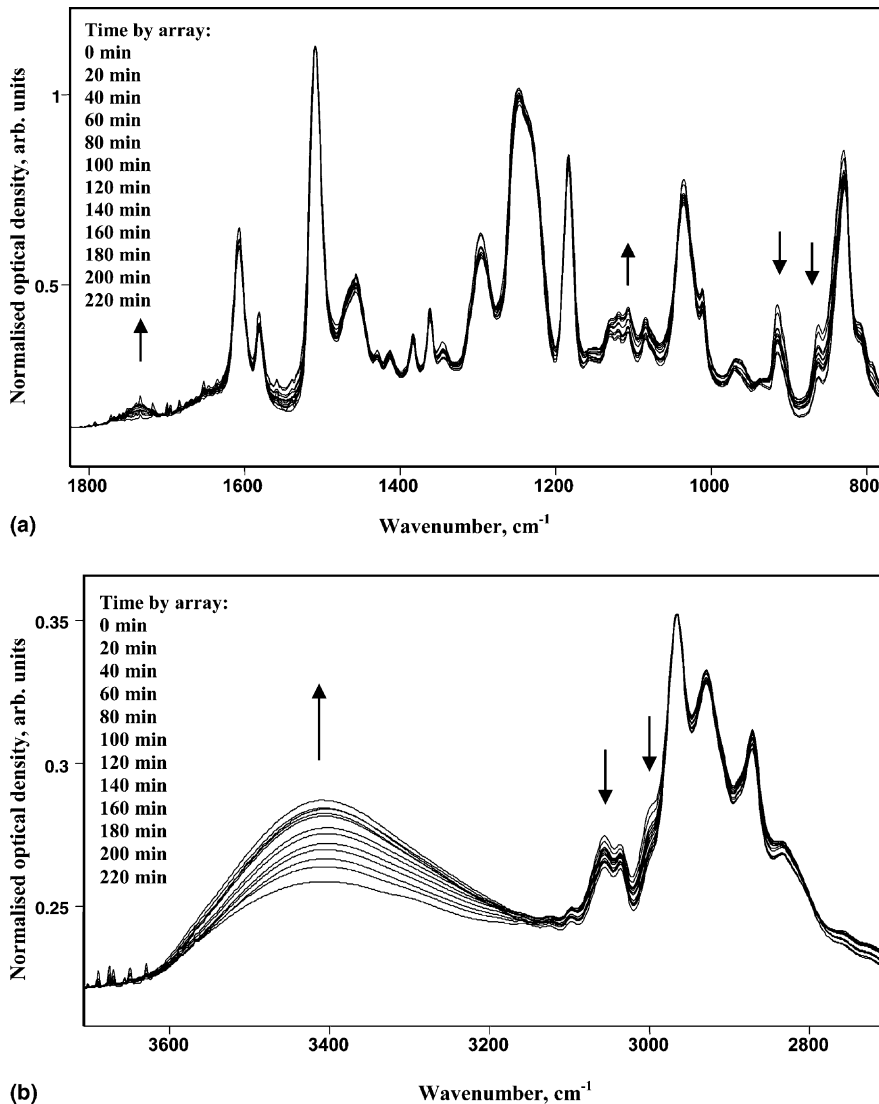Fig. 3. FTIR spectra of solid epoxy resin with treatment time in plasma.

Fig. 4. (a,b) Normalised FTIR spectra of epoxy resin during curing with treatment time in plasma.

ability of resin macromolecules to be cut in separate low molecular parts under the action of plasma particles and to be evaporated into vacuum of plasma chamber. For liquid resin with initial macromolecules the rate is highest due to a possibility of short molecule formation after cut of polymer chain in one chemical bond under action of plasma particles. In cured resin the macromolecules are connected by crosslinks and the appearance of short molecules due to plasma action needs to cut polymer chain in some places. So the rate of etching is lower at the same chemical structure of resin. In this case, the etching rate of epoxy resin depends on molecular weight of macromolecules.

During polymerisation the etching rate of reactionable mixture decreases with time. At the beginning, the rate of mixture is close to the rate of liquid resin and during the reaction of polymerisation the etching rate of mixture becomes equal to cured resin. So, for resin during polymerisation the rate of etching depends on the reaction stage. An average rate of etching for liquid and hard epoxy resin was determined by linear approximated curve of the optical density of 1510 cm^{-1} aromatic ring line in FTIR spectra. The average rate of etching for liquid resin is 83 nm/min, for reaction mixture the rate equals to 40 nm/min and for hard resin the rate equals to 38 nm/min.

The optical density of the carbonyl and hydroxyl lines was used for the kinetics analysis of oxidation process in epoxy resin under plasma action. The dependence of optical density of carbonyl group line at
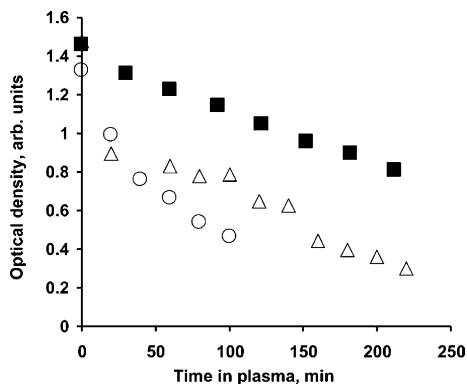
Fig. 5. Optical density of aromatic ring line at 1510 cm^{-1} in FTIR spectra of epoxy resin during plasma treatment. Full: hard resin, circles: liquid resin without hardening agent, triangles: resin at curing in plasma.

1730 cm^{-1} on time of plasma treatment is presented in Fig. 6. In liquid resin a strong increase of the carbonyl group concentration is observed by the increase of optical density of the carbonyl group line. The increase of concentration has extreme character. The same extreme dependence of carbonyl group concentration is observed for reactionable mixture of epoxy resin with hardening agent during curing reaction. But the maximal concentration for reactionable mixture is significantly lower than for liquid resin. The oxidation kinetics for thin and thick layers of the reactionable mixture are different. The maximal concentration of carbonyl groups is higher in thick layer than in thin layer. Taken into account the surface effect of modification in p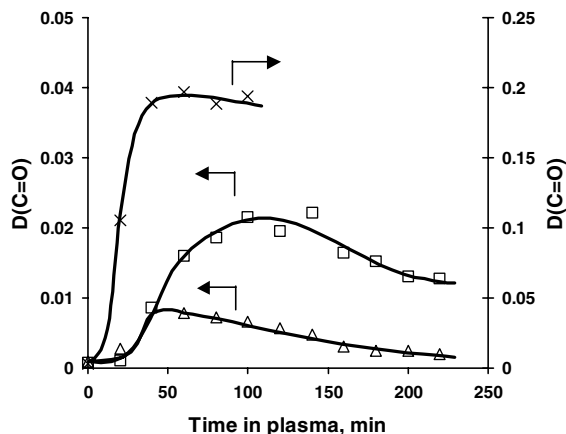lasma discharge, the influence of thickness on oxidation process of epoxy resin can be caused by flows of liquid resin during plasma treatment.

As it is well known, the oxidation process under plasma action takes place only in a thin surface layer of polymer. In the case of solid polymer an oxidised surface layer is attacked by plasma discharge and etched simultaneously. An increase of treatment time in plasma does not lead to an increase of carbonyl groups concentration in epoxy resin more than maximal amount in surface layer. With increasing treatment time the carbonyl groups in the oxidised surface layer of resin are destroyed by plasma particles during the etching process as other parts of macromolecules in surface layer. So, after first period of treatment, the formation of carbonyl groups and the etching process of surface layer reach the dynamical equilibrium and the concentration of carbonyl groups becomes constant. In our spectra of solid polymer under plasma treatment the concentration of oxygen-containing groups is constant during long time of plasma treatment. It can be good viewed by the normalised optical density of carbonyl group line at 1730 cm^{-1} presented for liquid, cured epoxy resin and for reactionable mixture (Fig. 7).

In the case of viscose polymer a movement of different polymer layers is possible due to convection, thermal moving of macromolecules and shrinking of crosslinked layers. The movement of layers can mix treated and untreated layers of epoxy resin during plasma treatment. When oxidised layer comes into bulk due to mixing, the oxygen-containing groups can be protected from plasma etching and collected there with time. It is good observed by spectra of liquid resin without hardening agent. In reactionable mixture, the viscosity of resin increases with time and the collection of oxygen-containing groups is smaller.

The extreme character of carbonyl group dependence is caused by saturation and etching processes. The etching decreases the thickness of the sample up to low value when the mixing process saturates the bulk layers
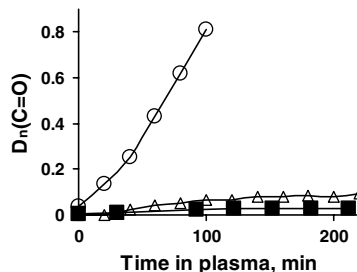

Fig. 6. Optical density of carbonyl groups line at 1730 cm^{-1} in FTIR spectra of epoxy resin during plasma treatment. Crosses (right scale): liquid resin (30 mkm thickness), cubic (left scale): resin at curing in plasma (thick layer, 38 mkm) and triangle (left scale): resin at curing in plasma (thin layer, 10 mkm).

Fig. 7. Normalised optical density of carbonyl groups line at 1730 cm^{-1} in FTIR spectra of epoxy resin during plasma treatment. Full cubic: solid resin, circles: liquid resin without hardening agent, triangles: resin at curing in plasma.

with oxidised macromolecules and the oxidised macromolecules come to the surface again. In this case the destruction of oxidised macromolecules becomes significant and the equilibrium of oxidation and etching process in the surface layer is observed. So the oxidation process of resin reaches a saturation and the optical density of carbonyl groups does not increase.

In the thin sample of epoxy resin the maximal concentration of oxygen-containing groups is smaller. The saturation of bulk layers by oxygen-containing groups is reached quicker and the etching of oxidised macromolecules starts earlier than in thick sample.

The oxidation process was observed by the intensity of hydroxyl group line at 3450 cm^{-1} (Fig. 8). The intensity of this line is constant in spectra of solid epoxy resin at the plasma action. The effect of oxidation in plasma discharge is not observed in transmission of solid resin due to relatively high concentration of hydroxyl groups in cured resin and low extinction coefficient of hydroxyl vibration line. In spectra of curing resin without plasma discharge the intensity of line increases what corresponds to known curing reaction of epoxy ring. In spectra of liquid resin and in spectra of reactionable mixture of epoxy resin and hardening agent in plasma the intensity of hydroxyl groups increases higher than in cured resin. The significant increase of hydroxyl group concentration under plasma is caused by the oxidation process of epoxy macromolecules with formation of hydroxyl and carboxyl groups. The mixing effect of oxidation and initial macromolecules provides the collection of hydroxyl groups in bulk layers and preserves from the action of plasma discharge as it is observed for carbonyl groups. So, the plasma modified surface layer of the liquid epoxy resin penetrates into bulk layers.

The modified layer of resin contains a number of active centres as free radicals, oxygen-containing
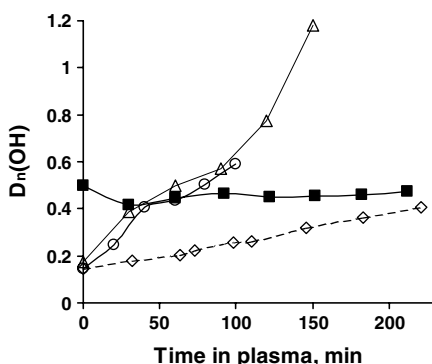

Fig. 8. Normalised optical density of hydroxyl groups line at 3450 cm^{-1} in FTIR spectra of epoxy resin during plasma treatment. Full cubic: solid resin, rhombus: curing at air (control), circles: liquid resin without hardening agent, triangles: resin at curing in plasma.
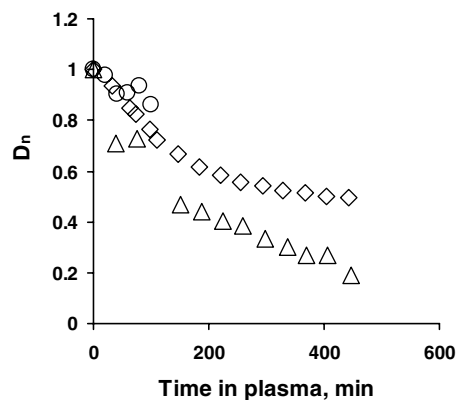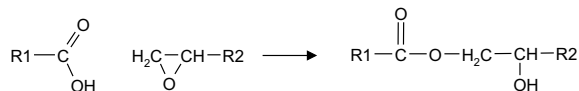

Fig. 9. Normalised optical density of epoxy ring line at 915 cm^{-1} in FTIR spectra of epoxy resin during plasma treatment. Rhombus: curing at air (control), circles: liquid resin without hardening agent, triangles: resin at curing in plasma.
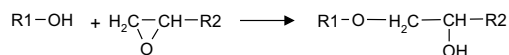
groups and unsaturated bonds. During mixing the treated layer comes into untreated bulk layers of resin and the active centres of modified macromolecules can contact with initial macromolecules of resin. New active centres can take part in the polymerisation reaction.

The curing kinetics was observed by characteristic epoxy ring line. In Fig. 9 the optical density of epoxy ring line at 915 cm^{-1} is presented for resin during curing in plasma and during curing at air for control. Besides that, the optical density of epoxy ring line for liquid resin without hardening under plasma action is presented too. The kinetic curve of the control sample corresponds to the kinetic of second order reaction with autocatalysis. The kinetic curve of resin cured in plasma goes lower than the curve of control sample cured in thermobox. The decrease of epoxy ring line intensity is observed for liquid resin without hardening agent in plasma. This decrease of intensity can be caused by reactions of epoxy ring with products of plasma destruction. One of the ways of such interaction can be connected with the reaction of epoxy group with free radical formed under plasma action in the surface layer of epoxy resin [24]:
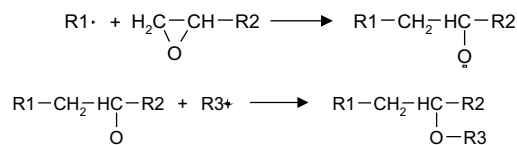
Other reactions can be caused by the presence of hydroxylic and carboxylic groups as the products of macromolecule destruction in plasma:

$$R1{-}OH \ + \ H_2C{-}CH{-}R2 \longrightarrow R1{-}O{-}H_2C{-}CH{-}R2$$

$$R1{-}C{-}OH \ + \ H_2C{-}CH{-}R2 \longrightarrow R1{-}C{-}O{-}H_2C{-}CH{-}R2$$

The reactions of epoxy ring with the products of macromolecule destruction can take place in the epoxy resin with and without hardening agent. Besides that, the free radicals can generate a crosslinking of epoxy resin macromolecules additionally to curing reaction of epoxy ring. As a result, the curing of epoxy resin in plasma discharge was carried out up to deeper stage than under normal conditions at air as it is observed by the decrease of epoxy ring line intensity of spectra.

This acceleration of the curing reaction can be used for initiation of the epoxy resin polymerisation in free space environment where the addition reactions of liquid matrix can be generated under space plasma.

4. Conclusions

The modification of epoxy resin in solid state, liquid state and in reactionable mixture by microwave plasma at low pressure showed, that effects of etching, oxidation and mixing take place in treated resin. The average etching rates for liquid resin (83 nm/min) and for solid resin (38 nm/min) differ not critically to put a liquid epoxy composition in plasma discharge at low pressure. It means that the reaction of polymerisation can be carried out without significant etching of liquid mixture during curing.

In liquid epoxy composition the modified surface layer is mixed with initial bulk layers during plasma treatment. Due to mixing the products of epoxy macromolecule destruction are collected in bulk layers and stored from etching in plasma discharge. In this case the plasma treatment becomes the method of bulk modification of polymers. The products of destruction accelerate the curing reaction of epoxy resin. The effect of curing reaction acceleration is useful for a polymerisation of epoxy resin composition under free space conditions.

Acknowledgements

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