Artículo de investigación

Surface structure of electret polymeric materials in different process conditions by corona discharge

Estructura de la superficie de los materiales poliméricos electretos en diferentes condiciones de proceso por la descarga de corona

Estrutura da superfície dos materiais poliméricos electrote em diferentes condições de processo para o download de corona

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Abstract

The issue of polymeric materials production with defined operating characteristics is under review. Work objective is to define influence on alteration of materials structure under technological processing by corona discharge in particular linear travel of processed material, processing frequency and number of electrodes. It is hereby suggested a surface processing technique of polypropylene and polyethylene terephthalate films. The analysis of corona-induced structural alterations in the samples of polymeric materials has been carried out. Methods of non-contact sensing of electret characteristics and Fourier-transform infrared spectroscopy have been used to study modified packaging polymeric materials. The conclusion is drawn on the grounds of the research made. It is possible to intensify the processing by changing technological parameters of corona discharge influence. It results in uprating of parameters of materials electret state whereby surface oxidation level will be different. It is indicated that bands intensity of spectrum absorption consistent with OH, C=O, C-O groups fluctuating is changed while films are processed

Resumen

El tema de la producción de materiales poliméricos con características operativas definidas está bajo revisión. El objetivo del trabajo es definir la influencia en la alteración de la estructura de los materiales en el proceso tecnológico mediante la descarga en corona en el desplazamiento lineal particular del material procesado, la frecuencia de procesamiento y la cantidad de electrodos. Se sugiere una técnica de procesamiento de superficie de películas de polipropileno y tereftalato de polietileno. El análisis de alteraciones estructurales inducidas por corona en las muestras de materiales poliméricos se ha llevado a cabo. Los métodos de detección sin contacto de las características de electreto y la espectroscopía infrarroja de transformada de Fourier se han utilizado para estudiar materiales poliméricos de envasado modificados. La conclusión se basa en la investigación realizada. Es posible intensificar el procesamiento cambiando los parámetros tecnológicos de la influencia de descarga de corona. Resulta en la mejora de los parámetros del estado electret de los materiales, por lo que el nivel de oxidación de la superficie será

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by corona discharge. This points to the fact of surface materials oxidation.

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Keywords: physics modifications, corona discharge, electret state, surface structure, polymeric film materials, polypropylene, polyethylene terephthalate

diferente. Se indica que la intensidad de bandas de la absorción del espectro consistente con los grupos OH, C = O, C-O fluctuantes cambia mientras que las películas se procesan mediante descarga en corona. Esto apunta al hecho de la oxidación de los materiales superficiales.

La investigación fue apoyada por el Ministerio de Educación y Ciencia de la Federación de Rusia, el único identificador del proyecto es RFMEFI57418X0191.

Palabras clave: modificaciones físicas, descarga de corona, estado de electreto, estructura superficial, materiales de película polimérica, polipropileno, tereftalato de polietileno.

Resumo

A questão da produção de materiais poliméricos com características operacionais definidas está sob revisão. O estudo tem por objectivo determinar a influência sobre a alteração da estrutura dos materiais no processo tecnológico por descarga em coroa no deslocamento linear particular do material processado, a frequência de tratamento e a quantidade de eléctrodos. Uma técnica de processamento superficial de filmes de polipropileno e polietileno tereftalato é sugerida. A análise das alterações estruturais induzidas pela corona nas amostras de materiais poliméricos foi realizada. Os métodos de detecção sem contato das características dos eletretos e da espectroscopia de infravermelho com transformada de Fourier têm sido utilizados para estudar materiais poliméricos de embalagens modificadas. A conclusão é baseada na pesquisa realizada. É possível intensificar o processamento alterando os parâmetros tecnológicos da influência da descarga corona. Isso resulta na melhoria dos parâmetros do estado de eletreto dos materiais, de modo que o nível de oxidação da superfície será diferente. É indicado que a intensidade de banda da absorção do espectro consistente com os grupos flutuantes OH, C = O, C-O muda enquanto os filmes são processados por descarga de coroa. Isso aponta para o fato da oxidação dos materiais de superfície.
A pesquisa foi apoiada pelo Ministério da Educação e Ciência da Federação Russa, o único identificador do projeto é RFMEFI57418X0191.

Palavras-chave: modificações físicas, descarga de coroa, estado de eletreto, estrutura de superfície, materiais de filme de polímero, polipropileno, polietileno tereftalato

Introduction

Production of polymeric materials with defined operating characteristics in particular electret ones is relevant objective. Electret material is dielectric which maintains poled state after doffing of external influence that has led to polarizing of the dielectric. It also creates electric field (Gorokhovatsky, 1997; Gul et al, 1968). One of the methods that allows to get material in the electret state is physics modification made by corona discharge. It is based on charge transfer from electric discharge region in air-gap clearance to dielectric surface (Kestelman, 1980; Kirsch et al, 2010; Lushcheikin, 1984).

Processing by corona discharge leads to alteration of polymeric material properties and structure (Kestelman, 1980; Kirsch et al, 2010; Lushcheikin, 1984). Efficiency of this processing is influenced by various factors, e.g., electrodes voltage, electric current intensity, gap setting between processed surface and electrode, loading of filler, humidity level and temperature (Borisova et al, 2004; Galikhanov, 2004; Galikhanov, 2005; Galikhanov & Deberdeev, 2005; Galikhanov, 2003; Gul et al. 1983; Ramazanov & Guseynova, 2007). There is still not enough data considering influence on forming of electret state in the materials and their operating characteristics under such technological parameters as linear travel of processed material, processing frequency and number of electrodes.

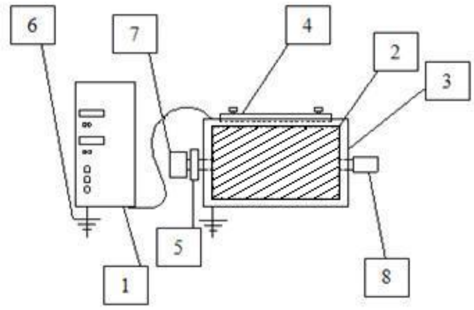
Work objective

Work objective is to define influence on alteration of materials structure under specified processing methods by corona discharge. Objects of the research are polypropylene and polyethylene terephthalate films. Selected polymeric materials fall into the category of polyolefins which are non-polar materials. They possess good dielectric properties despite they are characterized by low values of electric and physicomechanical strength (Maksanova, 2005; Kryzhanovsky et al, 2007). It is known that tertiary atoms of carbon which possess labile hydrogen atoms are involved in polypropylene polarization. C=O linking with moving π-constraint and benzene rings with π-electron atmosphere are involved in polyethylene terephthalate polarization (Lushcheikin, 1984).

Research course

Samples of film materials 25±3 mym thick were made by extrusion technique. Laboratory machine was built to study materials in the electret state. This machine is a research facility which allows to study corona discharge treatment process of film materials (pic. 1). The pilot machine consists of two main units: power supply unit and processing node. Power supply unit is used to generate high voltage power. It creates corona gas discharge in the disruptive distance between the electrode and processed surface of film which is dielectric wherethrough discharge moves to gumming wheel that is the second electrode.

Corona discharge treatment process of film materials made in this machine is periodic. It is equipped by high frequency generator of electric current. Size-defined piece of film material is fixed on the machine roll and while being spinned it passes coronating region. The first electrode is spinned rubber-covered metallic roll and the second is aluminum plate which is put along the roll. Roll diameter used for processing is 0,2 m. Electrodes are made in the form of aluminium plate which size is $0{,}2\times0{,}02\times0{,}003$ m^3.



Pic. 1 – Machine layout: 1) controlling system; 2) gumming wheels with fixed film material; 3) protective cover; 4) electrode; 5) socket joint; 6) ground node; 7, 8) engines

Films surface was processed on this machine. Influence of corona discharge was also of different intensity. Frequency of processing (from single to fivefold) and number of corona electrodes (1, 2, 3 electrodes) were changed. Amperage was 5 A for 1 m of electrode's length, gap setting in the processing zone was 1÷3 mm and tension was 22-24 kW. Diameter of roll which was used to carry out processing is 0,2 m. The possibility of gas environment modification was not used. Moreover, the samples got from 5 to 50 Hz at a pitch of 5 Hz, it depended on various rotation frequencies of the winding device. It corresponds with linear travel of processed material from 5 to 55 meters per minute. Linear travel determines exposure time of corona discharge and it identifies specific concentration of charge carrier in the unit surface area.

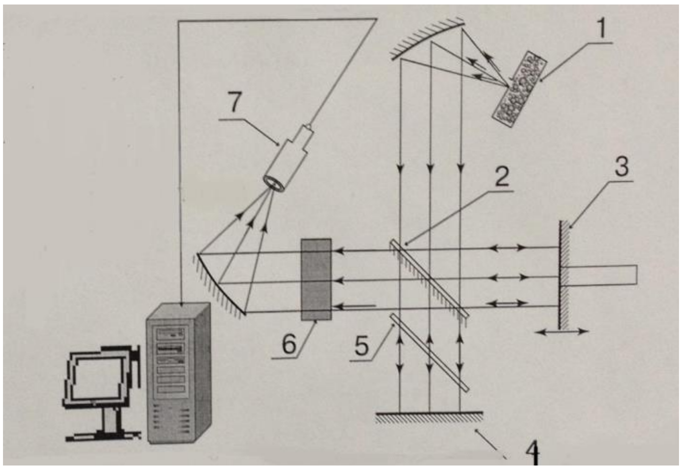
Static field tester was used to study electrostatic parameters of polymeric films in the electret state. This tester is suitable for non-contact sensing of electrostatic-charged objects voltage (U, kW), intensity of electrostatic field nearby charged flat surface (E, kW/m) and surface charge density (σ, $\mu C/m^2$). Operating principle of this device is based on a method of periodic screening of recording electrode. Spinning ground shield (baffle) which closes the recording electrode from the electrostatic field at times is applicable for that purpose. Electrode's voltage is sometimes changed from 0 (when electrode is closed) to the value that is proportional to the potential of this point (when electrode is open). Measuring of surface charge density of samples was made 1 cm off the transmitter near plane to measured surface. Measuring plate (disc) used for creating regular electrostatic field in space between measured object's surface and tester.

First time measurement was less than 1 hour after corona discharge processing. Reported values determine summary surface-bound charge.

Method of Fourier-transform infrared spectroscopy was used to estimate structural alterations in polymeric materials samples after corona discharge. IR spectrophotometer with Fourier-transformer and with adapter of multiple frustrated total internal reflection was used for that purpose. It provides resolution of 1,0 cm^{-1} within the range of following wavenumbers - 400–4800 cm^{-1} (pic. 2). Processing of IR-spectra was made to specify dynamics of polymeric functional groups changing and also changing of absorption bands.

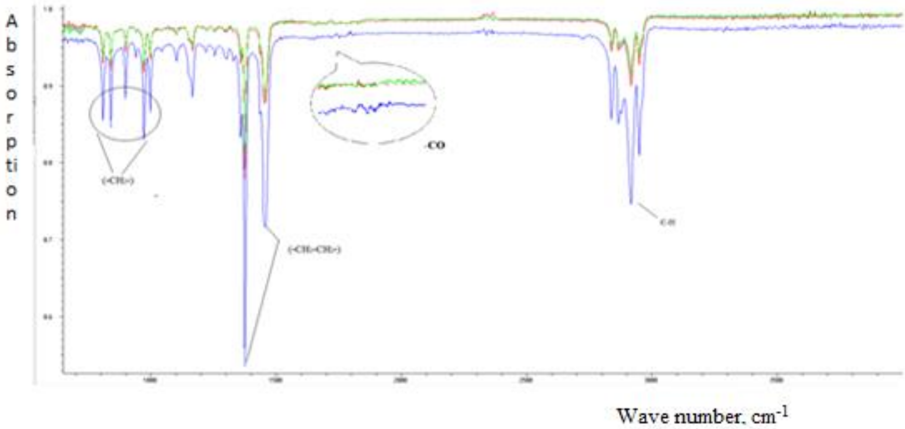
Results and their discussion

Decrease of material rate, increasing of surface processing frequency and installing of additional electrodes lead to magnifying of surface-bound charge as a result of specific concentration build-up in the unit surface area of film.

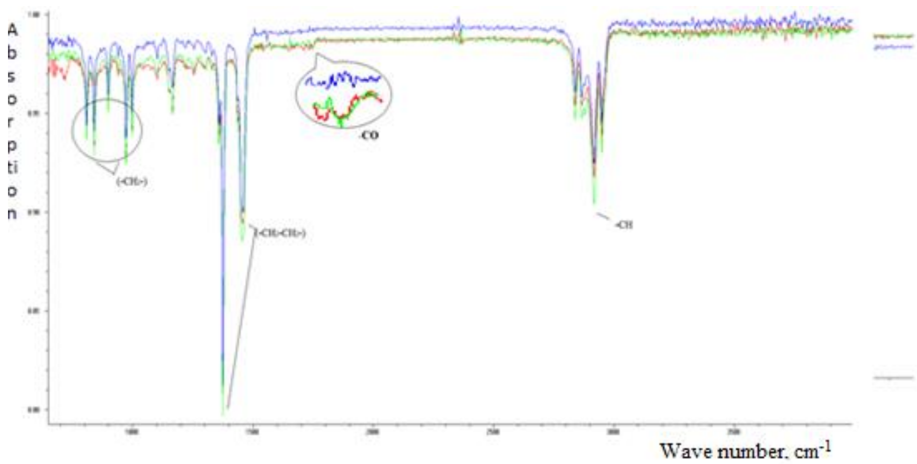


Pic. 2 – IR spectrophotometer with Fourier-transformer and with adapter of multiple frustrated total internal reflection layout: 1 - IR thermal lighter, 2 - beam splitter, 3 - movable mirror, 4 - fixed mirror, 5 - balance plate, 6 - cell holder, 7- photodetector

Spectra of polypropylene films are presented in the pictures 3-10. They appear as spectra of processed and unprocessed films parts under various process conditions. Containing of oxygenated groups (in particular –CO) increases while processing film materials by corona discharge. It indicates surface oxidation process that goes along with corona effect. Ratio rating calculation of absorption bands intensity of polypropylene samples between processed and unprocessed parts was made. The results can be found in Table 1.

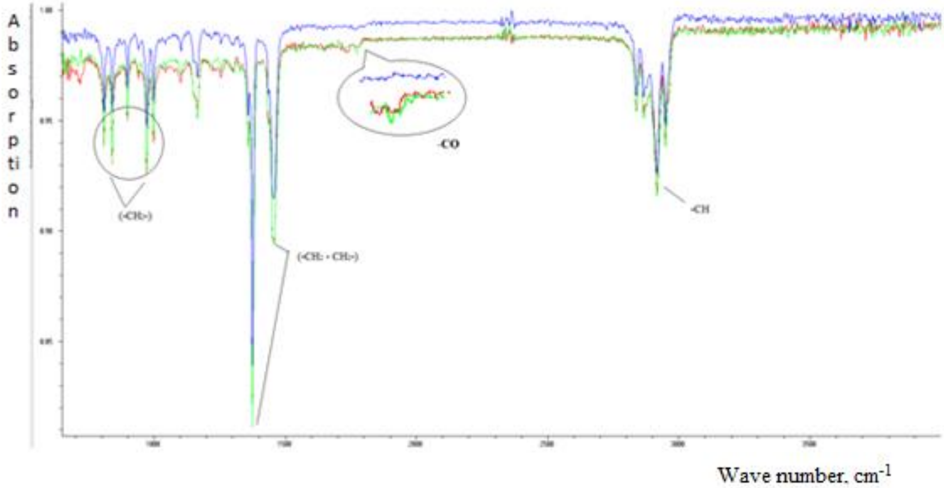


Pic. 3 – IR-spectra of polypropylene film, single processing, V=5 m/min: blue – processed part, red – unprocessed part, green – control

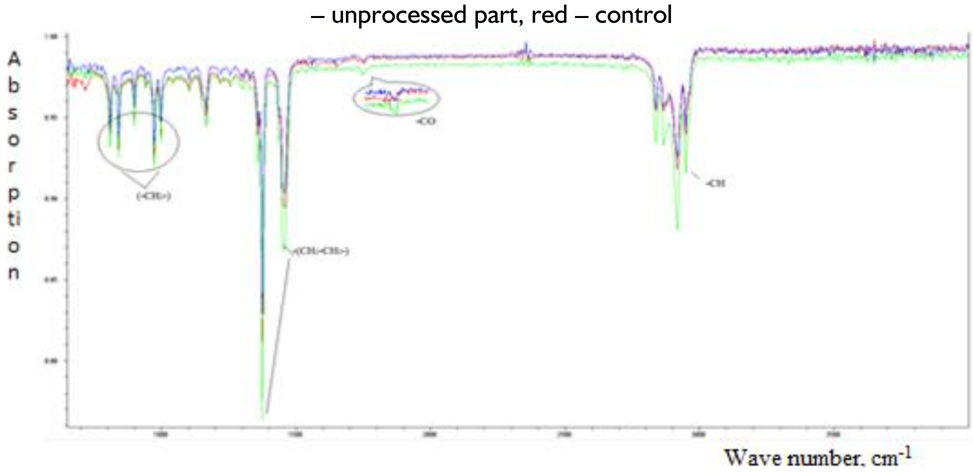


Pic. 4 – IR-spectra of polypropylene film, single processing, V=55 m/min: green – processed part, blue – unprocessed part, red – control

When comparing spectra of processed and unprocessed parts of polypropylene films, it turned out that the absorption bands intensity of samples of single-processed material has practically the same values at V=5 m/min. The difference is very noticeable for others. Also Table 1 shows that the processing frequency affects oxidation level of the unprocessed part.

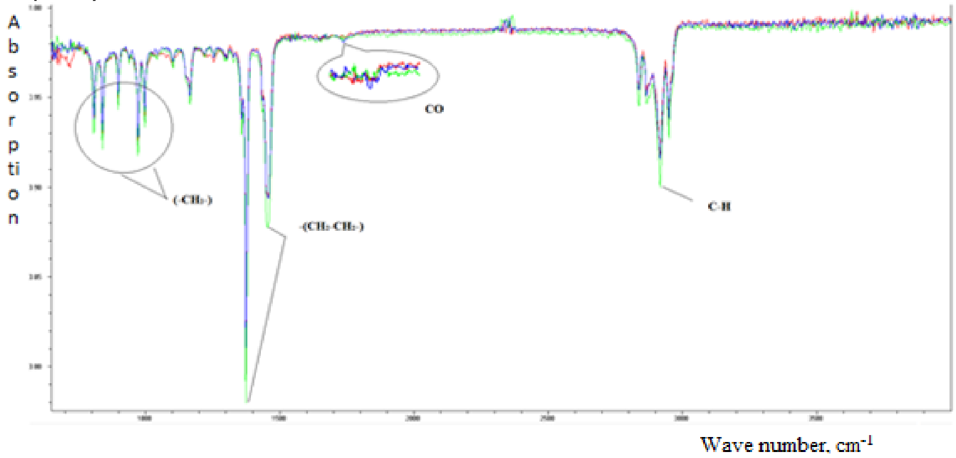


Pic. 5 – IR-spectra of polypropylene film, threefold processing, V=5 m/min: green – processed part, blue – unprocessed part, red – control

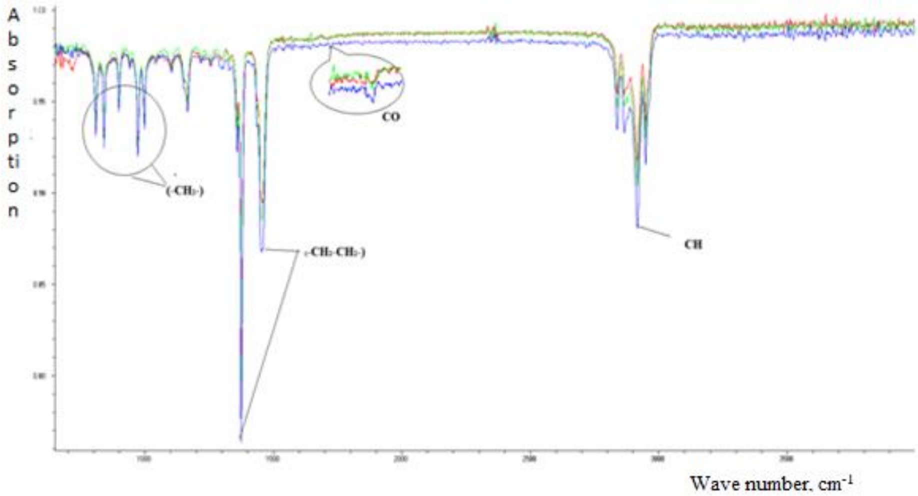


Pic. 6 – Polypropylene film IR-spectra, threefold processing, V=5 m/min: green – processed part, blue – unprocessed part, red – control

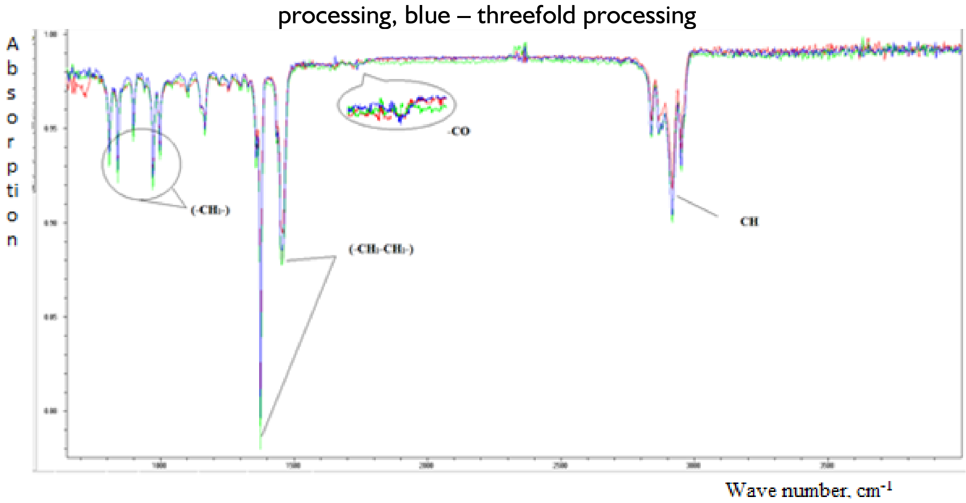
Intensity increasing of corona discharge processing leads to raising oxidation level of polypropylene film's surface (pic. 7-10). Calculation of the intensity of polypropylene samples absorption bands under various technological regimes has been made. Its results are presented in Table 2 from which it follows that an increase in the corona discharge intensity on the material leads to an increase of oxygen-containing groups and consequently to an increase of oxidation level.



Pic. 7 – IR-spectra of polypropylene film's processed part, V=5 m/min: red – control, green – single processing, blue – threefold processing



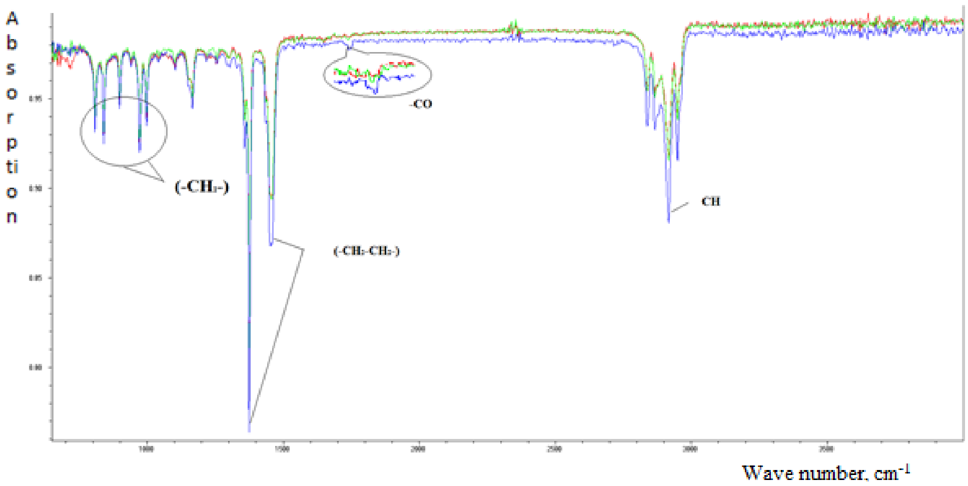
Pic. 8 –IR-spectra of polypropylene film's processed part, V=55 m/min: red – control, green – single processing, blue – threefold processing



Pic. 9 – IR-spectra of polypropylene film's processed part, single processing: red – control, green – at V=5 m/min, blue – at V=55 m/min

Table 1 – Ratio rating of absorption bands intensity of polypropylene samples

Processed part	Process conditions			
	At V=5 m/min, single	At V=55 m/min, single	At V=5 m/min, threefold	At V=55 m/min, threefold
Processed part D*	0,03	0,04	0,03	0,04
Unprocessed part D	0,032	0,006	0,01	0,026
D*/D	0,93	6,67	3	1,73



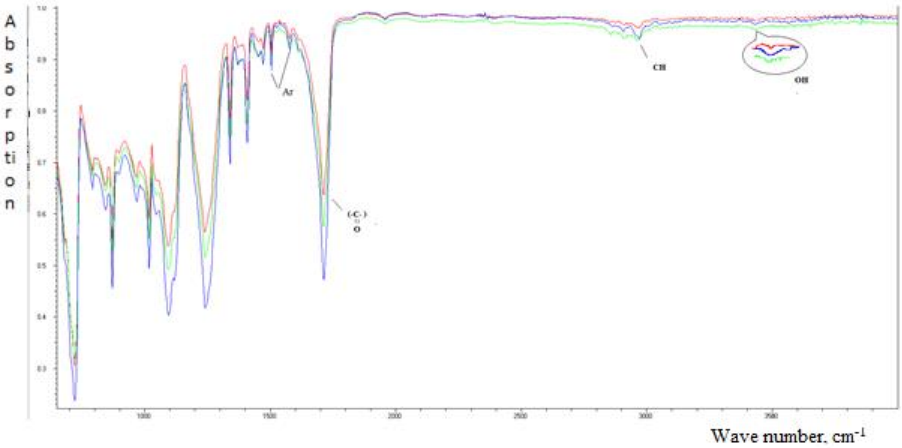
Pic. 10 - IR-spectra of polypropylene film's processed part, threefold processing: red – control, green – at V=5 m/min, blue – at V=55 m/min

Table 2 – Ratio rating of absorption bands intensity of polypropylene samples under various process conditions

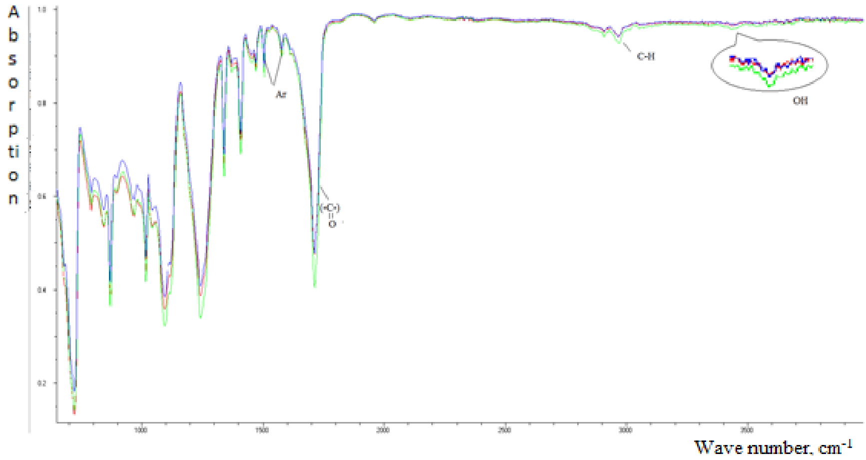
D_1 – single processed part D_3 – threefold processed part D_5 – processed part, V=5 m/min D_{55} – processed part, V=55 m/min	Process conditions			
	D_1/ D_3, V=5 m/min	D_1/D3, V=55 m/min	D_5/D_{55}, single	D_5/D_{55}, threefold
	1	1	0,75	0,75

IR-spectra of polyethylene terephthalate films under different process conditions are presented in the pictures 11-18.

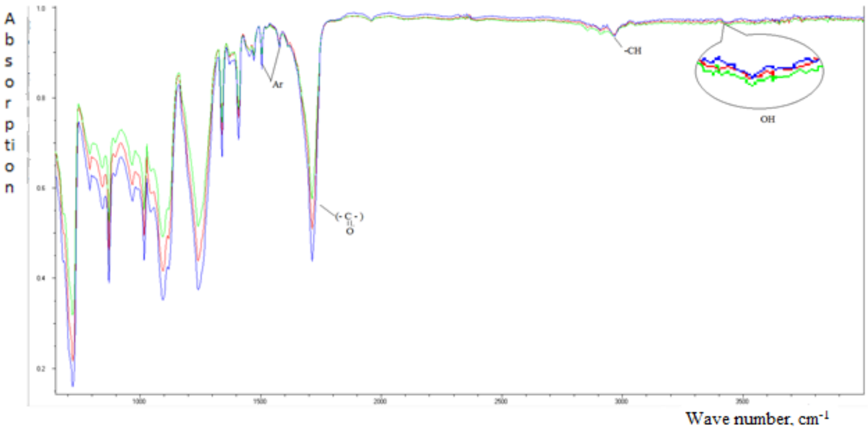
When processing materials by corona discharge, the content of oxygen-containing groups, namely -OH, increases. It indicates the process of surface oxidation as well as the possibility of the appearance of destruction process (pic 11-14). Calculation of absorption bands intensity of polyethylene terephthalate samples of processed and unprocessed parts was made. Its results are presented in Table 3, which shows that corona discharge affects the unprocessed side of the material. Considering polyethylene terephthalate films, frequency does not affect oxidation of the processed part in a single processing at V=5 m/min. When comparing processed and unprocessed parts, it was found that the values differ significantly for all samples, except the sample obtained by threefold processing at V = 5 m/min.



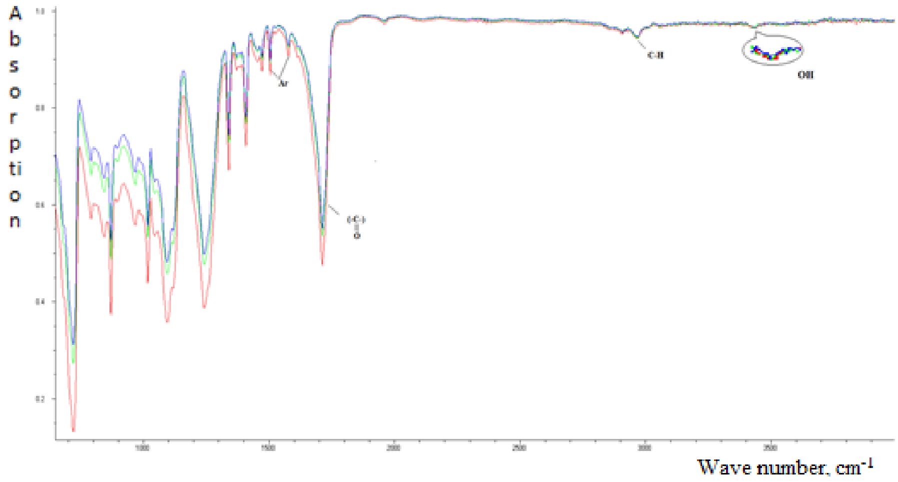
Pic. 11 - IR-spectra of polyethylene terephthalate film, single processing, V=5 m/min: green – control, blue – processed part, red – unprocessed part



Pic. 12 - IR-spectra of polyethylene terephthalate film, single processing, V=55m/min: red – control, green – processed part, blue – unprocessed part



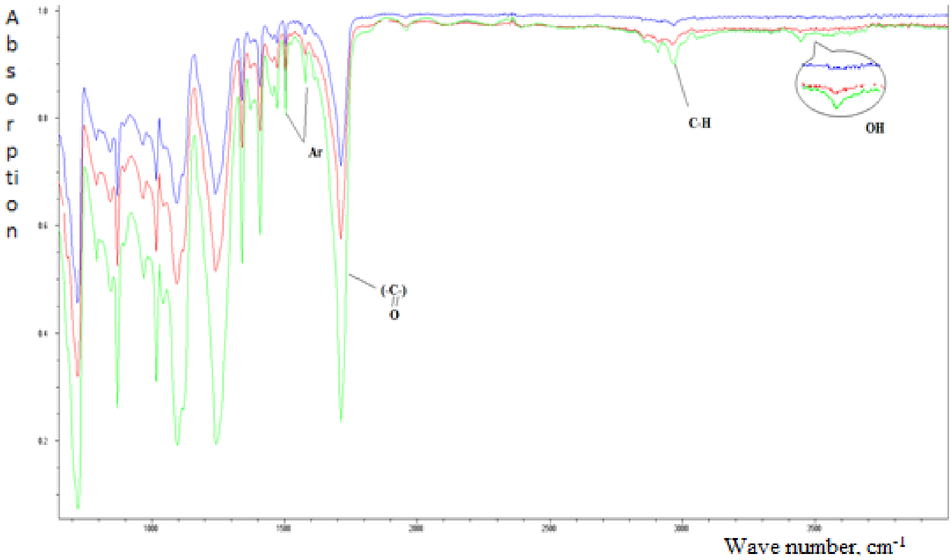
Pic. 13 – IR-spectra of polyethylene terephthalate film, threefold processing, V=5m/min: red – control, green – processed part, blue – unprocessed part



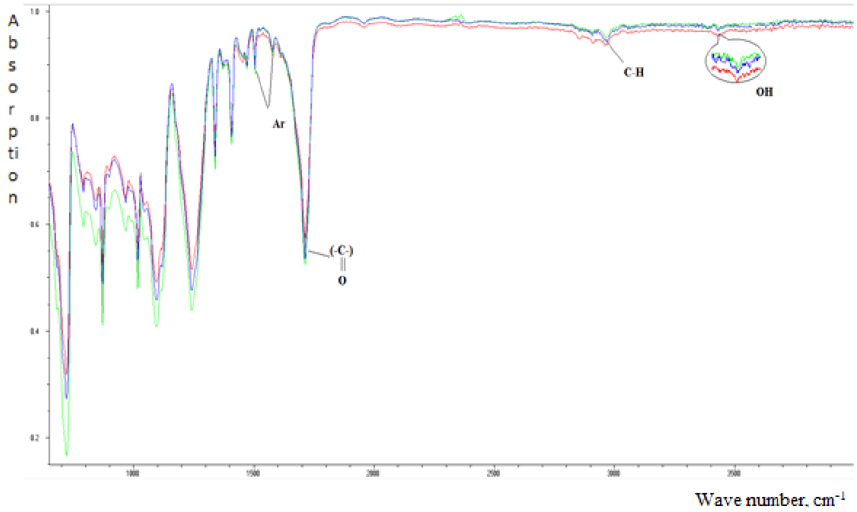
Pic. 14 – IR-spectra of polyethylene terephthalate film, threefold processing, V=55m/min: red – control, green – processed part, blue – unprocessed part

Table 3 – Ratio rating of absorption bands intensity of polyethylene terephthalate samples

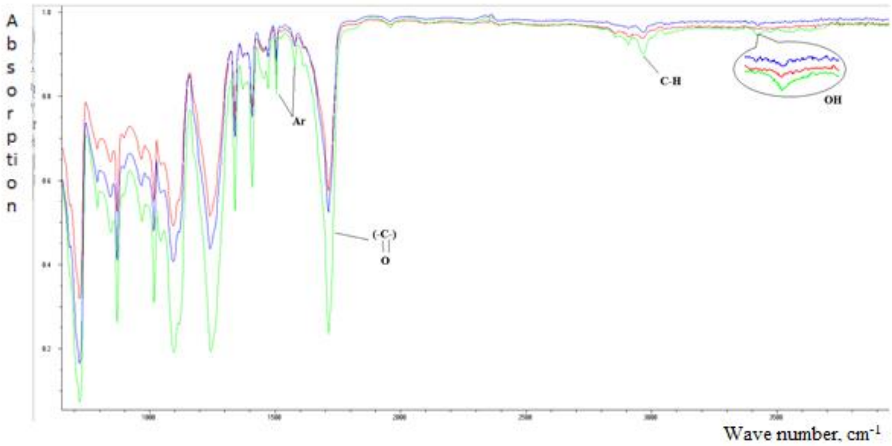
Processed part	Process conditions			
	At V=5 m/min, single	At V=55 m/min, single	At V=5 m/min, threefold	At V=55 m/min, threefold
Processed part D*	0,08	0,083	0,17	0,016
Unprocessed part D	0,2	0,16	0,2	0,08
D*/D	0,4	0,52	0,85	0,2



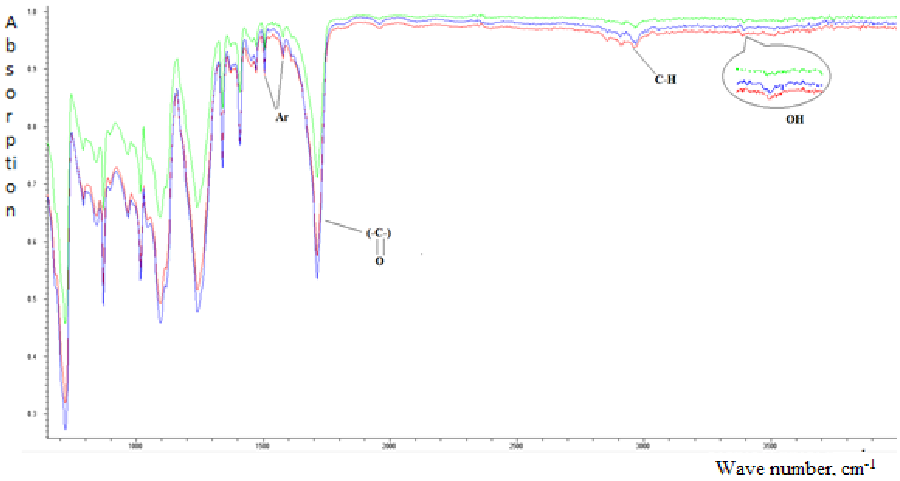
Pic. 15 – IR-spectra of polyethylene terephthalate film's processed part, V=5 m/min: red – control, green – single processing, blue – threefold processing



Pic. 16 – IR-spectra of polyethylene terephthalate film's processed part, V=55 m/min: red – control, green – single processing, blue – threefold processing



Pic. 17 – IR-spectra of polyethylene terephthalate film's processed part, single processing: red - control, green – at V=5 m/min,
blue – at V=55 m/min



Pic. 18 – IR-spectra of polyethylene terephthalate film's processed part, threefold processing: red - control, green – at V=5 m/min,
blue – at V=55 m/min

Intensity increasing of corona discharge processing leads to raising oxidation level of polyethylene terephthalate film's surface (pic. 15-18). Calculation of the intensity of polyethylene terephthalate samples absorption bands under various technological regimes has been made. Its results are presented in Table 4.

Table 4 – Ratio rating of absorption bands intensity of polyethylene terephthalate samples under various process conditions

D_1 – single processed part D_3 – threefold processed part D_5 – processed part, V=5 m/min D_{55} – processed part, V=55 m/min	Process conditions			
	D_1/ D_3, V=5 m/min	D_1/D3, V=55 m/min	D_5/D_{55}, single	D_5/D_{55}, threefold
	0,47	5,2	0,96	10,6

The increase in the intensity of corona discharge effect on the material leads to an increase in the content of oxygen-containing groups and consequently, to an increase in oxidation level of surface. The values are significantly different when comparing all the samples, except the samples obtained three times

Conclusion

It is shown that absorption bands intensity varies with corona discharge processing corresponding to the OH, C=O, and C-O group vibrations. This indicates the oxidation of the material surface.

Thus, changing the technological parameters of the corona discharge effect, it is possible to intensify this kind of processing. It can be seen in the parameters increase of the electret state of the materials, while oxidation level of the surface will be different.

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