

EFFECT OF SHORT – TIME AGING ON HYDROPHILICITY OF DISCHARGE PLASMA PRETREATED BIAXIALLY ORIENTED POLYPROPYLENE

I. Novák and Š. Florián

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9,
842 36 Bratislava, Slovak Republic
E-mail: upolnovi@savba.sk

Abstract. The adhesion of polypropylene and printing with various dyestuffs represents a serious problem which cannot be solved in satisfactory manner without modification. Because of practical usability, simple manipulation, suitability to continuous modification processes and efficiency the modification by plasma produced by electric discharge at atmospheric pressure in the medium of air oxygen was used. The free surface energy value of discharge-plasma pretreated biaxially oriented polypropylene in the course of short-time aging was determined. The free surface energy of modified polypropylene two weeks after modification exceeds the empirically established value $38 \text{ mJ}\cdot\text{m}^{-2}$, that is regarded as a condition of acceptable surface modification of discharge plasma modified polypropylene foils.

Key words: adhesion of polypropylene, free surface energy, surface modification, polar fraction, polar component of free surface energy, corona discharge, hydrophilicity of polypropylene

Introduction

Among the polymers exhibiting a low free surface energy it can rank polyolefins which display the surface energy values of $29\text{--}35 \text{ mJ}\cdot\text{m}^{-2}$. Isotactic polypropylene in non-modified state exhibits the free surface energy value only of $29\text{--}30 \text{ mJ}\cdot\text{m}^{-2}$, because of structure of macromolecules. The bonding and printing of polypropylene with various dyestuffs therefore represents a serious problem which cannot be solved in satisfactory manner without modification. In this respect, the rule according to which a good adhesion of wetting substance to polymer is conditioned by the higher surface energy value of this substance is in force. If this condition is not fulfilled, the adhesion of the substance put on the surface of polymer is low.

There are a great number of methods that cause an increase in surface energy values of polypropylene [1–4]. Some of these methods are based on aggressive oxidizing agents that rapidly deteriorate the mechanical properties, e.g. an oxidation with chromosulfuric acid [3].

Because of practical usability, simple manipulation, suitability to continuous modification processes and efficiency the modification by the use of plasma produced by electric discharge either at reduced pressure (glow discharge) or at atmospheric pressure in the medium of air oxygen [2] (corona discharge) is convenient for surface modification of polypropylene [4]. The effect of aging phenomena in adhesive behavior of corona discharge plasma treated biaxially oriented polypropylene did not yet sufficiently study.

Experimental

The experiments were carried out with biaxially oriented isotactic polypropylene Mosten 59 492 as foil with a thickness 0.02 mm (Chemopetrol, Czech Republic).

The modification of polypropylene foils by corona discharge plasma was performed in a pilot plant (Softal 2005, Germany) in the medium of air oxygen at atmospheric pressure and temperature of 295 K . The measurement of free surface energy of polymers was achieved by using a microscopic Contact Angle Meter (Zeiss, Germany).

Results and Discussion

Figure 1 represents the dependence of free surface energy and its polar component versus the time elapsed after modification for biaxially oriented polypropylene foils modified by discharge plasma. According to Figure 1 free surface energy (curve a) and the polar component of free surface energy (curve b) non-linearly decreased in the course of aging of the modified biaxially oriented polypropylene foils. The decrease of free surface energy

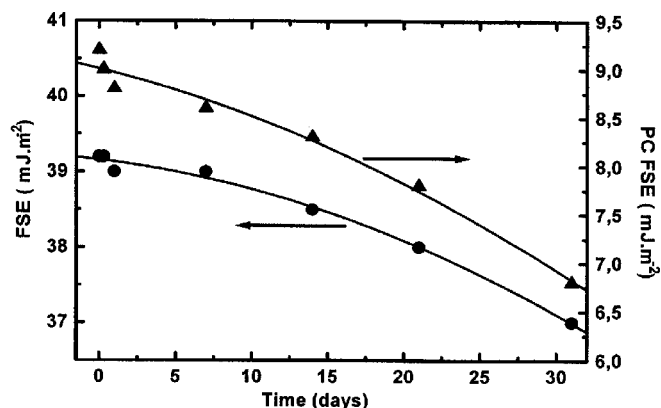


Figure 1. Free surface energy and its polar component of biaxially oriented polypropylene modified by discharge plasma as a function of aging time

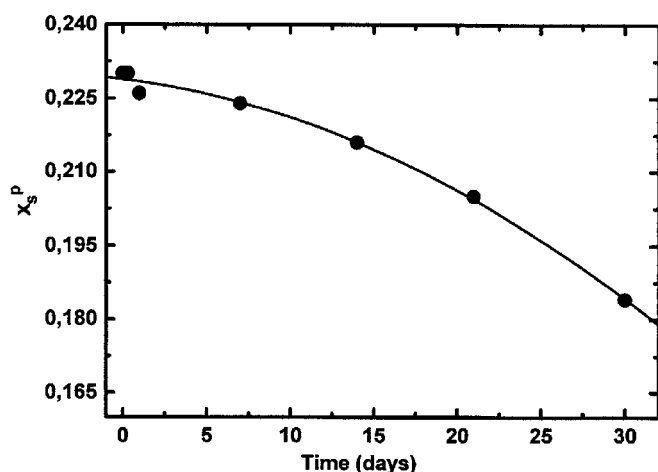


Figure 2. Changes in polar fraction of discharge plasma pretreated biaxially oriented polypropylene in the course of aging

was after 30 days very low and reached the final value of 37.0 mJ.m^{-2} . On the other hand, the decrease in the polar component of free surface energy was greater because its value fell from 9.2 to 6.8 mJ.m^{-2} , i. e. by 24.4% regarding the original value for freshly modified polypropylene. It results from the obtained measurements of free surface energy and its polar component that the total free surface energy of the corona-discharge modified biaxially oriented polypropylene in the course of short-time aging decreased only as a result of the change in polar component of free surface energy, while the value of the dispersion component did not practically change during aging.

Polypropylene has very low value of polar fraction that is equal ca 0.01 . The investigation of the pretreatment stability in the course of aging on polar fraction value of discharge plasma treated polypropylene was observed, as shown in Figure 2. This figure illustrates the non-linear decrease of polar fraction value as a function of the aging time.

The values of polar fraction vales are in the course of aging diminished and while the value of freshly modified polypropylene is 0.235 , after 7 days is lower – 0.221 and after 30 days of aging was equal only 0.184 . This decrease in polar fraction caused by aging was 24.1% in comparison with freshly pre-treated polymer.

The surface energy value of biaxially oriented polypropylene measured 14 days after corona-discharge modification were equal to 38.5 mJ.m^{-2} . This value exceeds the empirically established free surface energy value 38 mJ.m^{-2} that is regarded as a condition of acceptable surface modification of discharge plasma modified polypropylene foils.

Conclusion

The decrease in free surface energy of corona-discharge pre-treated isotactic polypropylene in the course of short-time aging was very low and the final value reached after 30 days of aging was 37.0 mJ. m^{-2} . On the other hand, the decrease in polar component of surface energy was greater and its value fell to 6.8 mJ.m^{-2} , i. e. by 24.4% regarding the original polar component of the surface energy value for freshly modified polymer. The surface energy of modified polypropylene measured after 14 days of aging exceeded the empirically established surface energy that is regarded as a condition of acceptable surface modification of discharge plasma modified polypropylene foils.

Acknowledgements

This research was supported by the Slovak Grand Agency (VEGA) through the grant number 2/5032/98 and 2/5022/98.

References

1. Kruse, A., Kruger, G., Baalman, A., Hennemann, O.D.: Surface pretreatment of plastics for adhesion bonding, *J. Adhes. Sci. Technol.*, Vol. 9, No. 12, pp. 1611–1621, 1995
2. Novák, I., Florián, Š.: Adhesive properties of polypropylene modified by electric discharge, *J. Mater. Sci. Let.*, Vol. 14, pp. 1021–1022, 1995
3. Novák, I.: Surface properties of polypropylene modified by chromosulphuric acid, *J. Mater. Sci. Let.*, Vol. 15, pp. 693–694, 1996
4. Dogué, I. L. J., Forch, R., Mermilliod, N.: Plasma-induced hydrogel grafting of vinyl monomers on polypropylene, *J. Adhes. Sci. Technol.*, Vol. 9, No. 12, pp. 1531–1545, 1995.

EFFECT OF POLYPROPYLENE UV MODIFICATION ON ADHESION TO POLAR POLYMERS

I. Novák and I. Chodák

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9,
842 36 Bratislava, Slovak Republic
E-mail: upolnovi@savba.sk

Abstract: Surface modification of isotactic polypropylene in vapors of phosphoryl chloride under UV irradiation is an effective method for the increase of adhesive properties. Phosphoryl chloride acts as the sensitizer that decomposes under the effect of UV irradiation. The efficiency of the modification was very much dependent on the distance of UV source from the polymer surface. The difference of polar contribution of free surface energy values was found to be low for short times of modification (lower than 5 minutes), while at higher modification times the differences have been more pronounced.

Key words: surface properties of polypropylene, adhesive properties, UV sensitizers, UV-pre-treatment, surface modification, free surface energy, polar component of free surface energy

Introduction

The low hydrophilicity and wettability of isotactic polypropylene are a major drawback, because some components must often be lacquered or glued to fulfill application demands (1–3). To overcome these difficulties various modifications have been suggested consisting in introducing some polar groups on the polymer macromolecules with the aim to increase the free surface energy of polypropylene. The bulk properties of polymer are not affected, because the modification of polypropylene leads to a creation only a very thin modified surface layer having the thickness from 1 to 10 μm . Achieving satisfactory adhesion properties of polymer, however, require an effective modification that can satisfactorily promote bondability.

For higher surface adhesion the surface of polypropylene must be converted to a suitable condition before bonding and this is the main purpose of all surface modifications. The chemical reactions on polypropylene surface lead to a change in the chemical composition of the polymer. In some cases UV irradiation is parallel used resulting in a faster decomposition of the modification compound and direct UV-oxidation of the polymer surface. The effect of halogenization agent is enhanced by such a way.

Surface modification of isotactic polypropylene in vapors of phosphoryl chloride under UV irradiation is an effective method for the increase of adhesive properties. Phosphoryl chloride acts as the sensitizer that decomposes under the effect of UV irradiation.

Experimental

The experiment was performed using a commercial product iPP Tatren TF - 411 (Slovnaft, Slovak Republic). The free surface energies of the polymer were measured by a direct goniometric method using a Contact Angle Meter (Zeiss, Germany). The function $\theta = f(t)$ was extrapolated to

$t = 0$, where θ (is the contact angle (deg) of testing liquid on polymer surface and t (s) is the time of wetting. Total free surface energy was determined as a sum of polar and dispersion component of respective compounds.

Results and Discussion

The dependence of free surface energy and its polar component of UV/ POCl_3 modified isotactic polypropylene on the time of UV irradiation is shown in Figure 1. As seen in Figure 1, the polar component of free surface energy (curve b) is very low for unmodified polypropylene ($0.4 \text{ mJ}\cdot\text{m}^{-2}$). A non-linear rise of the polar component was observed with increasing time of modification and the curve levels off at final value $16.8 \text{ mJ}\cdot\text{m}^{-2}$ which was reached after about 20 minutes of irradiation. A non-linear growth of the total free surface energy (curve a, Figure 1) was observed from $29.4 \text{ mJ}\cdot\text{m}^{-2}$ for unmodified polypropylene up to $45 \text{ mJ}\cdot\text{m}^{-2}$ for the surface – modified material by UV/ POCl_3 for 20 minutes. Thus, the modification

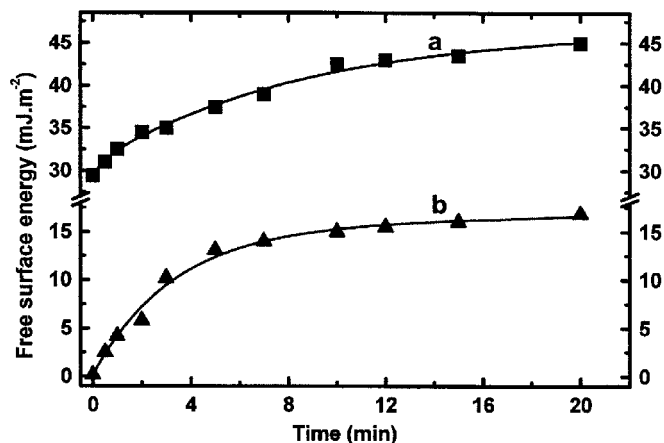


Figure 1. Variation of free surface energy (curve a) and its polar component (curve b) of isotactic polypropylene modified by UV/ POCl_3 with time of UV irradiation

results in an increase of free surface energy by 53% compared to unmodified polymer. By the comparison of curves a and b in Figure 1 the value of polar fraction can be determined. The polar fraction of polymer is defined as a ratio between the polar component of free surface energy and total free surface energy. As the value of polar fraction is depending primarily on the formation of polar groups onto polymeric chain it defines the polarity of modified polymer. It is seen from Figure 1 that the polar ratio is 0.013 for unmodified polypropylene and the value increased up to 0.373 after 20 minutes of UV/ POCl_3 modification.

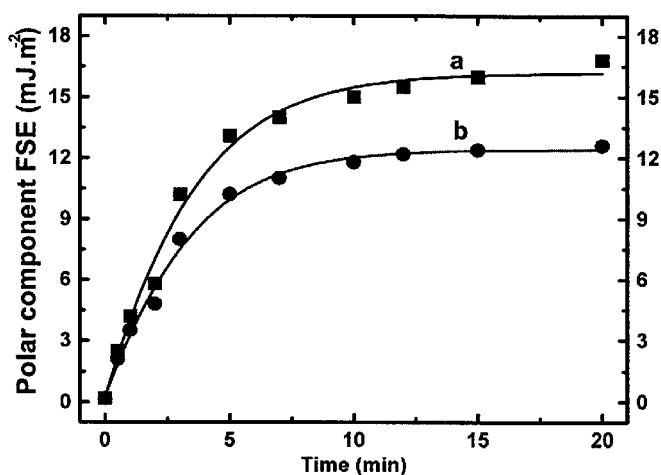


Figure 2. Variation of the polar component of free surface energy of iPP modified by UV/ POCl_3 with time of irradiation at different distance of UV source:

a – d = 50 mm, b – d = 100 mm.

The effect of the distance of UV light source on the polar component of free surface energy of UV/ POCl_3 modified isotactic polypropylene is shown in Figure 2. The efficiency of the modification is very much dependent on the distance of UV source from the polymer surface. An increase of the polar component of free surface energy was observed if shorter distance was used. The efficiency of modification was tested for 50 and 100 mm distance of the UV source from the modified surface. The difference of polar contribution of free surface energy values was found to

be low for short time of modification (lower than 5 minutes), while at higher modification times the differences have been more pronounced (comparison of curves a and b in Figure 2). Levelling off the dependences after certain modification time is obvious for both experimental distances. The observed results can be explained by a saturation of the polymeric surface by polar functional groups when continuing modification can hardly contribute to higher polarity of the surface.

Conclusion

Surface modification of isotactic polypropylene in vapors of phosphoryl chloride under UV irradiation was very much dependent on the distance of UV source from the polymer surface. The difference of polar component of free surface energy values was found to be low for short times of modification (lower than 5 minutes), while at higher modification times the differences have been more pronounced. Levelling off the dependences after certain modification time was obvious for both experimental distances. The obtained result can be explained by a saturation of the surface of polypropylene by polar functional groups and continuing modification has substantially lower influence to higher polarity of the polymer.

Acknowledgements

This research was supported by the Slovak Grand Agency (VEGA) through the grant number 2/5032/98 and 2/5022/98.

References

1. Kinloch, A.J.: Surface pretreatment, In: Adhesion and Adhesives, Science and Technology, Chapman and Hall, London - New York, pp. 103–139, 1987
2. Owen, M.J. : Surface and Interfacial Properties, In: Physical Properties of Polymers, Handbook, Mark, J. E. ed., AIP Press, Woodbury - New York, pp. 669–676, 1996
3. Knaus, S., Nenadal, A.: Surface modification of polypropylene – Hydrophilic finishing with carbohydrates, Macromol. Symp., Vol. 127, pp. 257–263, 1998.