

Polymer Surfaces with Increased Surface Energy and Appropriate Production Method

The invention relates to polymer surfaces with increased surface energy and a method to increase the surface energy of polymer surfaces aiming at an improvement of surface properties, such as the adhesion of varnishes, print paint and adhesive products, and printability, gluability and wettability.

Surface energy can be considered to be a measurable quantity for the linkage forces at surface level; it is the energy which has to be applied to divide an infinitely expanded solid body into two identical, half-infinite parts, keeping them at such a distance which prevents any interaction between the components. In a first step, fission energy should be applied in order to divide the solid body into two components, while a second step serves to keep the two components at a distance to each other allowing them to be shifted to new steady positions.

Subsequent wetting of polyacrylate surfaces by photons using energies of 4 -11 eV is common knowledge and is described, for example, in Patent Specification DE 10 2008 060 906 A1. In this patent, an example (Table 2) is used for the description of the increase of surface energy of a UV-hardened polyacrylate-nano-composite coating from 21 up to 23 mN/m after irradiation with photons from a 172 nm Excimer emitter.

A disadvantage is however the fact that subsequent radiation using a 172 nm Excimer emitter will only increase the surface energy insufficiently; it cannot decisively improve the polymer surface printability, gluability and wettability properties.

In order to achieve this objective, surface energies of more than 45 mN/m and with a polar fraction of more than 10 mN/m are required. The polar fraction of the surface energy is decisive for the adhesion, printability, gluability and wettability.

Increasing the surface energy of e.g. polyacrylate and polymethacrylate surfaces by selecting more polar monomers and oligomer acrylates or methacrylate components is limited and leads to surface energies of the coating being less than 45 mN/m with polar fractions of less than 5 mN/m. Effective additives that can be added to the liquid formulations with the objective of increasing the surface energy are not available.

The effect of corona discharges has been described e.g. in the Softal Report 102d from SOFTAL Corona & Plasma GmbH, Hamburg. Plasma discharges that occur when an adequately high voltage is applied to a gas filled capacitor with asymmetrical electrodes create conductive streamers that lead to a temporary short-circuit. In the discharge channel, positive and negative ions are produced with kinetic energies of up to 100 eV as well as electrons with energies of 12 to 16 eV. Electrons and ions with these energies are in a position to generate atomic oxygen and ozone in the air for example, and radicals and radical ions on the surface of the polymers to be treated. Corona systems with higher exciter frequencies are operated as streamers only have a lifetime of only a few 10 ns and occur with typical frequencies of 10 kHz,

The corona treatment that has been described is however not suitable to achieve effective and, in particular, a long lasting increase in the surface energy of polyacrylates, polymethacrylates and vinyl polymers.

Carbon dioxide, butane, butanol and fragments of the polymer chain are created through the thermal degradation of e.g. poly(n butyl acrylate) in the presence of oxygen. Monomers such as butyl acrylate, low molecular weight alkanes and alkenes, carbon monoxide and hydrogen are produced with a lower yield.

/ V.V.Krongauz, M.T.K.Ling, Photo-cross linked acrylate degradation kinetics, J.Ther.Anal.Calorim. (2009) 96: 715-725/ *Analoge Prozesse der oxidativen Degradation der Polymeroberfläche erwartet man bei Elektronen- und Ionenbeschuss des Polymeren bei Anwesenheit von Sauerstoff* (Analogous processes of the oxidative degradation of the polymer surface expected on the electron and ion bombardment of polymers in the presence of oxygen). Although the corona treatment results in the polar fraction of the surface energy of polyacrylates and polymethacrylates being increased immediately after the treatment, the effect decreases sharply within a few days, so no long lasting effect is achieved. The reason for this effect can be the migration of low molecular weight polar bonds on the surface and their transition into the ambient air.

Migration is however hindered when the polar chemical groups on the polymer chains or on the polymer fragments are bound. Then, one achieves a long lasting increase in the polar fraction of the surface energy.

The objective of this invention is thus, to find solutions that create a long lasting increase in the surface energy of polyacrylate and polymethacrylate surfaces of equal to or greater than 45 mN/m with polar fractions of greater than 10 mN/m.

This objective is achieved by this solution according to the invention as described in the Patent Claims 1 to 8.

According to the invention, an irradiation of the polymer surface is carried out with photons by a Xe₂ Excimer radiation source in a nitrogen-oxygen atmosphere with oxygen concentrations of 0.1 to 1 vol. %.

The solution according to the invention is explained in further detail based on illustrative embodiments and two diagrams.

According to the invention, the polymer surface is irradiated with photons that have energies of 6.5 to 7.8 eV. The source of the photons is placed as close as possible to the polymer surface.

There is a nitrogen-oxygen mix with an oxygen concentration of between 0.1 and 1 vol. % between the source of the photons and the polymer surface. A part of the photons is absorbed by the oxygen. The rest of the photons reach the polymer surface. Fig. 1 shows the depth to which the photons penetrate into the nitrogen-oxygen mix with an oxygen concentration of between 0.1 and 1 vol. %.

Photons with energies of between 6.5 and 7.8 eV that are absorbed by oxygen produce atomic oxygen through electronic excitation of the oxygen molecule. This atomic oxygen is converted to ozone in a reaction with molecular oxygen. It is known that ozone reacts with polymers and can form peroxy radicals that can initiate the degradation of polymers on the surface. / S.D.Razumovskl, A.A. Kefeli, G.E.Zaikov: European Polymer Journal Volume 7 (1971) p. 275-286/

The degradation products on the surface of the polymers contain oxygen in the form of polar chemical groups. These help to increase the polar fraction of the surface energy.

Of the photons with energies of between 6.5 and 7.8 eV that reach the polymer surface, some penetrate 10 to 100 nm into the polymer. Primary processes are initiated by the electronic excitation of molecular states in polymers that finally lead to the production of polymer radicals.

Polymer radicals react with the oxygen from the nitrogen-oxygen mix to form peroxy radicals that initiate the process of degradation on the polymer surface and thus also contribute to the formation of polar chemical groups and so to the increase in the polar fraction of the surface energy.

Excimer emitters are the preferred source of photons; for reasons of design, they are manufactured as line sources with lengths of up to 2.5 m. A source that covers an area is obtained by switching more than one line source together.

The following Excimer emitters are available as sources for photons

Excimer Emission wavelength Photon energy
Typical penetration depth in polymers

	(nm)	(eV)	(nm)
Xe ₂	Maximum	from 6.5	Maximum
< 100	at 172	to 7.8	at 7.2

Preference is given to the use of Xe₂ Excimer emitters as these have a broad emission spectrum of 160 to 185 nm. By selecting the oxygen concentration in the emission zone, one can ensure that adequate ozone is produced and also that adequate photons reach the surface of the polymer. The spectrum of the Xe₂ Excimer emitter and the penetration depth of the Xe₂ Excimer photons in a nitrogen-oxygen mix are shown in Fig. 1 as an example.

The physical active principle, the construction and the use of Excimer emitters are described e.g. in:

1. B. Eliasson, U. Kogelschatz: Appl. Phys. B 46, p.229 (1988)
2. U. Kogelschatz: Pure] Appl. Chem. Vol 62, p. 1667 (1990)
3. U. Kogelschatz. Proceedings Tenth Int. Conf. Gas Discharges and their Applications, Vol. II, p. 972 (1992)
4. R. Mehnert, I. Janovsky, A. Pincus: UV & EB Curing Technology and Equipment, Wiley- SITA, London

As Fig. 1 shows, at an oxygen concentration of 1 % e.g., the short wavelength fraction of the Excimer emission spectrum is absorbed to a large extent. For photons in the maximum of the spectrum of 172 nm, the penetration depth is approx. 5.5 cm and increases for photons with a wavelength of greater than 175 nm to above 10 cm. Therefore, according to the invention, the polymer surface is irradiated with photons from a Xe₂ Excimer emitter in a nitrogen-oxygen atmosphere.

Surprisingly, it was determined that the surface energy was increased the most, when the photons were absorbed to an equal extent by the oxygen in the gaseous phase as well as on the polymer surface.

In the process according to the invention, the polymer surface is bombarded by photons from a Xe₂ Excimer emitter in a radiation chamber that is flushed with a nitrogen-oxygen mix.

The duration of the irradiation can be between 0.01 and 300 sec, preferably between 0.1 and 5 sec. The oxygen concentration can be between 0.1 and 2 vol. %, preferably between 0.2 and 0.5 vol. %.

The invention generally relates to polymers of acrylate, methacrylate and vinyl compounds.

Examples

Example 1

An acrylate nano-composite paint (manufactured by Cetelon Nanotechnik GmbH, Eilenburg, Sa.) that can be hardened by ultra-violet radiation is applied to a 12 µm foil of bi-axially oriented polypropylene (BOPP) in gravure printing. The application weight is 3 to 4 g/m². The BOPP foil so printed is run through a UV hardening system at a speed of 30 m/min and hardened there in the presence of oxygen. The hardening is measured by an infrared (ATR) spectroscope through the conversion of the olefinic double bonds. The measured conversion of 93% of the double bonds means that the UV hardening can be considered to be complete. The surface energy of the coating is determined by a contact angle measuring instrument manufactured by Krüss GmbH Hamburg.

The following values are obtained:

Surface energy in mN/m 41.9

Dispersible fraction 37.9 Polar fraction 3.9

After that, the coated foil is irradiated in a pilot plant manufactured by IOT GmbH, Leipzig, that consists of a processing fraction, an irradiation chamber with a Xe₂ Excimer emitter and a winding fraction. The radiation chamber is flushed with a nitrogen-oxygen mix that contains 0.4 vol. % of oxygen. The oxygen concentration is adjusted in a stable way by means of a needle valve and is measured using a GSM device manufactured by Metrotec GmbH, Kirchheim. The web speed is set at 30 m/min. After the irradiation, the surface energy is measured again.

The following values are obtained:

Surface energy in mN/m 51

Dispersible fraction 39 Polar fraction 12

Observations regarding the results of Example 1:

After irradiation with a Xe₂ Excimer emitter in a nitrogen-oxygen mix, the surface energy increases to 51 mN/m. The polar fraction increases significantly from 3.9 to 12 mN/m and so exceeds the required 10 mN/m.

Example 2

The irradiated sample from Example 1 is stored under laboratory conditions. The surface energy is measured as a function of time. The results are given in Table 1.

Observations regarding the results of Example 2:

After 85 days of storage, the polar fraction of the surface energy has fallen to 11 mN/m. The surface energy is, at 48 mN/m, however clearly higher than the required value of 45 mN/m. The polar portion exceeds the required 10 mN/m.

Example 3

The irradiated foil with increased surface energy is laminated on a printed sheet. Folded boxes are made from the printed sheets. The parts of the folded boxes are coated with dispersion adhesive on the irradiated foil in strips and glued using a machine with a production speed of up to 200 m/min. Pre-treatment such as plasma

treatment is not carried out. After a storage time of 30 sec, a peel resistance of >200 N/m is achieved.

Result of Example 3:

The required adhesive seam resistance of the folded box samples is achieved with the foil that has been irradiated according to the invention. Thus, technologically common pre-treatment such as plasma or corona treatment can be done away with in the folding box machine.

Example 4

In a coating system manufactured by finitec Performance films GmbH, Berlin, an irradiation chamber with a Xe₂ Excimer emitter manufactured by IOT GmbH Leipzig is installed. The dose rate of the Xe₂ Excimer emitter is 25 mJ/cm² max. Optionally, a double Xe₂ Excimer emitter is also used. With that, a dose rate of 45 mJ/cm² is achieved, Fig. 2).

The oxygen concentration in the irradiation chamber is set at 0.5%. A BOPP foil with a polyacrylate nano-composite coating corresponding to Example 1 is irradiated.

The coating system is designed for web speeds of up to 200 m/min. The relationship between the surface energy of the coating and the web speed at dose rates of 25 and 45 mJ/cm² of the Excimer source are examined.

The consolidated values are given in Table 2.

Observations regarding the results of Example 4:

Polar fractions of the surface energy of greater than 10 mN/m can be achieved at web speeds of up to 110 m/min under specific technical conditions and the use of a double Xe₂ Excimer emitter with a dose rate of 45 mJ/cm²

Patent claims

Claim 1:

Polymer surface, characterised in that it displays an increased surface energy.

Claim 2:

Polymer surface according to Claim 1, characterised in that the increased surface energy remains stable over a period of time of at least three months.

Claim 3:

Process for the creation of polymer surfaces with increased surface energy, characterised in that the polymer surface is irradiated with photons from a Xe₂ Excimer emitter in a nitrogen-oxygen mix.

Claim 4:

Process according to Claim 3, characterised in that the irradiation takes place in a chamber that is flushed with a nitrogen-oxygen mixture.

Claim 5:

Process according to Claim 3, characterised in that the oxygen concentration is between 0.1 and 2 vol. %, preferably between 0.2 and 0.5 vol. %.

Claim 6:

Process according to Claim 3, characterised in that the irradiation by photons from the Xe₂ Excimer emitter has irradiation time periods of 0.01 to 300 sec, preferably between 0.05 to 50 sec and in particular, most preferably of 0.05 to 5 sec.

Claim 7:

Process according to Claims 4 to 7, characterised in that acrylates, methacrylates and vinyl compounds are used as the polymer substrates.

Claim 8:

Application of a process for treating polymer surfaces with irradiation by photons from an Xe₂ Excimer emitter in a nitrogen-oxygen atmosphere to increase the surface energy of the polymer surface.

Claim 9:

Use of acrylates, methacrylates and vinyl compounds as polymer substrates.

Claim 10:

Use of a Xe₂ Excimer emitter to increase the surface energy of polymer surfaces in a process for treating polymer surfaces.