Surface energy of corona treated PP, PE and PET films, its alteration as function of storage time and the effect of various corona dosages on their bond strength after lamination

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ABSTRACT: The aim of this study was to analyze how corona dosages above recommended levels affect film surface energy and hydrophobic recovery of such treated film surfaces as well as laminate bond strength of laminates made of these films. The adhesive for lamination was a polyurethane-adhesive with a dry film thickness of ∼5 μm. Polar and dispersive parts of the surface energy were measured frequently according to DIN 55660-2 (Owens–Wendt–Rabel-and-Kaelble method) for up to 140 days after corona treatment. The corona dosage had a value of up to 280 W min/m^2. Laminate bond strength was measured according to DIN 55543-5. The effect of corona treatment was highest for low-density polyethylene (PE-LD) films, mean for biaxial-oriented polypropylene (PP-BO) films, and lowest for biaxial-oriented poly(ethylene terephthalate) (PET-BO) films. With increasing storage time, surface energy decreased, as expected. The higher the effect of corona treatment, the faster the polar part of surface energy decreased. At PE-LD, laminate bond strength increased with a higher corona dosage from 0.05 to 8.87 mN/15 mm, whereas at PET-BO and PP-BO laminate bond strength was so high that samples teared before delamination during bond strength testing. By our results is shown that corona dosages above recommended levels resulted in higher laminate bond strength. Only at PP-BO a reduction of laminate bond strength due to "overtreatment" was be observed. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2018**, *135*, 45842.

INTRODUCTION

The laminate bond strength of laminates is one of their most relevant mechanical properties and it can be increased by surface treatment. Therefore, in industry, film surfaces are corona treated prior to lamination. Alternative methods are flame, various chemical and plasma treatments. They have in common, that these treatments increase the surface energy of these films. This leads to a better wettability and also to a higher bond strength.[1]

Corona treatment is an established method in industry to achieve higher polarity of surfaces.[2–6] It is based on corona discharge which forms plasma—a highly reactive gas that contains ions, radicals, and also reactive ozone.[2,7] This gas reacts with polymer surfaces primarily by breakage of H—C bonds. Thereby, polar groups, i.e. carbonyl and carboxyl groups, form on nonpolar polymer surfaces.[3,7–16] Polar groups increase

the polar part of surface energy and thus also the overall surface energy. A high energy impact during corona treatment causes a higher surface energy.[17] However, at a certain level of corona treatment, the surface reaches its maximum radical concentration so that saturation occurs and a higher corona dosage does not increase surface energy furthermore.[17,18] A side effect of corona treatment can be polymer chain scission (C—C bonds) in the polymer surface.[2,8] Thus, short-chain molecular substances are formed in this process.[2,8] These substances are one reason for laminate failure even at high surface energy. On the other hand, also the opposite effect is discussed. A higher corona dosage can increase the molecular weight because polymer molecules crosslink.[2,7]

Although the surface energy increases by corona treatment, it is reduced with increasing storage time.[3,19] The reasons are

restructuring of the surface and reaction of functional groups on the surface formed by oxidation. Worth to mention is that corona treatment can remove particles from film surfaces and it can cause microroughness there.[2]

The impact of corona treatment on the laminate bond strength of laminated films depends on several parameters: corona dosage, substrate (kind of polymer), adhesive, storage time after treatment and before lamination as well as the concentration, and kind of additives in the matrix polymers of the film.[2,20,21]

In the literature, following corona dosages are recommended: 0.6–0.8 kJ/m^2 (10–13 W min/m^2) for poly(ethylene terephthalate) (PET) films; 0.6–2.0 kJ/m^2 (10–33 W min/m^2) for low-density polyethylene (PE-LD) films; and 1.6–2.0 kJ/m^2 (27–33 W min/m^2) for polypropylene (PP) films.[2] A reason for the difference in the recommended corona dosages is the different initial polarity and initial chemistry of the polymers.

For industrial converters, wetting properties and laminate bond strength—which are both related to surface energy—majorly affect process stability and material quality. Many industrial converters own corona treatment units and can treat the material just before converting. However, some converters or packaging companies are dependent on the corona treatment applied by the film producer—which might take place some weeks before further processing steps such as sealing, printing, or laminating. Therefore, questions of major interest are, whether hydrophobic recovery can be delayed by overtreatment, and whether overtreatment affects the laminate bond strength.

The decrease of surface energy over storage time has been observed at various polymer surfaces by other research groups by measuring contact angles, wettability, and surface energy. However, to the authors' knowledge, for no study, films made of the three polymers of the present study (PP, PE, PET) have been corona treated and subsequently laminated with the same equipment, using such a wide range of corona dosages as in this study (from 0 to 280 W min/m^2), nor have the dispersive and polar parts been evaluated over such a long storage time.

Therefore, the aim of this study was to test the impact of corona treatment more extensively than currently reported in literature. This is why not only the contact angles, but also the polar and dispersive parts of the surface energy were frequently measured over a storage time of up to 140 days after corona treatment. As this behavior seems to be material dependent, it has additionally been studied for three different base polymers, namely PE-LD, biaxial-oriented PP (PP-BO), and biaxial-oriented PET (PET-BO).

According to literature, a too intensive corona treatment might cause a weak-boundary-layer and therefore a lower laminate bond strength.[7,20] This is why in the second part, the scientific question shall be answered, whether and to which extent an "overtreatment" (i.e., dosage above the recommended value) affects the laminate bond strength.

EXPERIMENTAL

Films and Adhesive

For trials, following films and adhesives were used. (1) The PE-LD film was "Puv 60" from Südpack (Ochsenhausen, Germany)

with a thickness of 60 μm. PE-LD has a tensile strength of about 10 N/mm^2 (ca. 9 N/15 mm).[22] It was not corona treated by the producer. (2) The biaxial oriented PET-BO film was "Hostaphan RN 12" supplied by Mitsubishi (Wiesbaden, Germany) with a thickness of 12 μm and a tensile strength of 230–260 N/mm^2 at 23 °C (ca. 41–47 N/15 mm, 50% rel.h. measured according to ISO 527-1-2, information from product data sheet). It was not corona treated by the producer. (3) The PP-BO film was "TNS" from Taghleef Industries (San Giorgio di Nogaro, Italy), the thickness was 40 μm with a tensile strength of 150–280 N/mm^2 (ca. 90–170 N/15 mm) measured according to ASTM D882 (product data sheet). This film was corona treated on one side by the producer, but the non-treated side was used for our trials. (4) The polyurethane (PU)-adhesive was "Novacote NC 120 ASL" with the hardener "NC-111-B" from Coim (Settimo Milanese, Italy). The applied dry film thickness was ∼5 μm.

Corona Treatment and Lamination

The films were in-line corona treated directly before lamination at Fraunhofer IVV, Freising at a corona station (Type "CLNE") from Softal (Hamburg, Germany). The corona dosage E was calculated from the generator power P (0, 150, 300, 600, and 800 W) divided by the web velocity v (5 m/min), the corona electrode width l (570 mm) [eq. (1)][2,23] and the number of treated sides (2), as the discharge appears on both sides of the film. The corona dosages were 52, 105, 210, and 280 W min/m^2 (3.1, 6.3, 12.6, and 16.8 kJ/m^2). The relative humidity during the trials was 50% and the temperature was 23 °C. The film reels were stored after corona treatment at 50% relative humidity and 23 °C. Following laminates were produced:

- PE-LD (60 μm)/PU (5 μm)/PE-LD (60 μm);
- PET-BO (12 μm)/PU (5 μm)/PET-BO (12 μm);
- PP-BO (40 μm)/PU (5 μm)/PP-BO (40 μm).

$$E = \frac{P}{l \cdot v} \tag{1}$$

Determination of Surface Energy

The surface energy was measured according to DIN 55660-2 (DSA 100-system, Krüss, Hamburg, Germany). The polar and dispersive parts of the surface energy were determined using the statistical method and the Owens–Wendt–Rabel-and-Kaelble (OWRK) data evaluation method.[24–27] This method is an extension of the Fowkes method.[28] In the OWRK method, it is additionally assumed that surface energy is composed of dispersive and polar forces. Therefore, it is necessary to measure the contact angles with at least two liquids of known surface tensions, in order to calculate the dispersive and polar part of interfacial tension between liquid and solid. Test liquids were water, diiodomethane, and ethylene glycol. The contact angles were measured in equilibrium. Testing was done fivefold. The decrease of the polar part of the surface energy was fitted to Cassies equation [eq. (2)] with the software "OriginPro" with a Levenberg Marquardt iteration algorithm. This equation divides the polar part (f_p) of the surface energy into two parts: an immobile (f_{im}) and a mobile (f_m) polar part. The mobile polar part decreases over time (t) exponentially. The parameter (τ) is included as
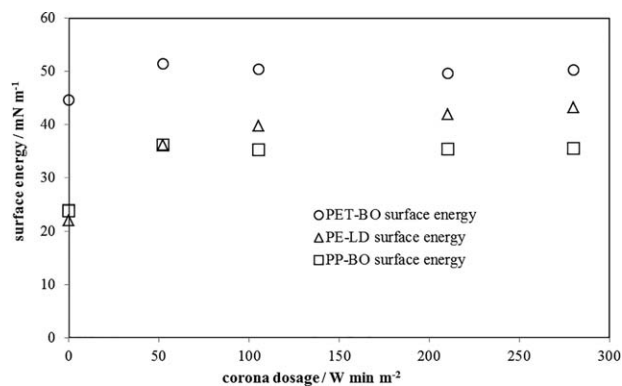
Figure 1. Surface energy of different films for different corona dosages; treated films analyzed directly after corona treatment (as standard deviation is too small as to be visible in that graph, data is available in the Appendix).

the exponent to e, describing the time dependency of the decrease of the mobile polar part.[29]

$$f_p(t) = f_{im} + f_m \cdot e^{-\frac{t}{\tau}} \qquad (2)$$

Determination of Laminate Bond Strength
Average laminate bond strength was measured according to the DIN 55543-5 using a 90°-T-Peel-Off test with a universal testing machine Schenck-Trebel RM 50 at a crosshead speed of 100 mm/min. Specimens were tested in machine and transverse direction. The test samples were clamped with 50 mm clamping length in the clamps of a tensile test machine. The width of the samples was 15 mm. The crosshead distance was 60 mm. Samples were stored before testing at 23 °C and 50% relative humidity. Testing took place 16 days after lamination on PP-BO and after 28 days on PE-LD and PET-BO and was executed tenfold. Mean values and standard deviations were calculated.

RESULTS AND DISCUSSION
Surface Energy
Effect of Corona Dosage on Surface Energy. In Figure 1 the surface energy is shown for the three different substrate materials (PE-LD, PP-BO, PET-BO) at different corona dosages (52, 105, 210, and 280 W min/m²). The surface energy was determined directly after corona treatment.

The initial surface energy, before corona treatment, with values of 24 mN/m on PP-BO (Figure 1) was lower than the values reported in literature with 29–32 mN/m.[2,23,30] The same was observed for PE-LD. The initial surface energy with a value of 22 mN/m was lower than the literature value with 30–32 mN/m for non-modified PE-LD-films.[2,23,30] This might be due to different testing methods and different substrate material additives. The initial surface energy of the PET-BO film with a value of 44 mN/m was similar to the values reported in literature with 42–43 mN/m.[2,30]

As expected, the corona treatment increased the surface energy (Figure 1). The main effect was observed at PE-LD films. At PET-BO films, the overall surface energy was increased by up to 7 mN/m, at PP-BO films by up to 11 mN/m, and at PE-LD films by up to 21 mN/m. This might be due to the chemical

nature of the polymers. As polyolefins have few or no surface energy increasing polar groups available before the treatment, the treatment shows the most pronounced effect there in comparison to more polar polymers.

For all films made of the different polymers, the maximum values (Figure 1), after corona treatment, are compared to the following values reported in literature. At PP-BO, the value in the present case is 35 mN/m, whereas Guimond et al.[31] reported a value of 40 mN/m. The maximum value of PE-LD film with 43 mN/m is below the value of 46 mN/m stated by Földes et al.[32] Similarly, the maximum surface energy of 52 mN/m for PET-BO is below the value of 57 mN/m reported for PET.[33] The values for PE-LD are higher than for PP-BO. This is in line with Tuominen et al.[23] who observed that PE-LD was more oxidized than PP at the same corona dosage. In contrast to that, Zenkiewicz[9] determined a stronger oxidation of PP-BO compared to PE-LD above a dosage of 83.3 W min/m² (5 kJ/m²).

For PP-BO, a saturation effect appears at a corona dosage of <35 mN/m and 50 W min/m² (Figure 1). Guimond et al.[31] reported a saturation already at 1.6 W min/m² (0.1 J/cm²) and Guimond and Wertheimer[8] at 0.83 W min/m² (0.05 J/cm²). For PP, Izdebska[2] reported a dosage of 20 W min/m² (1.2 kJ) to increase the surface energy. At dosages higher than 66 W min/m² (4 kJ) the breakage of chemical bonds appears and above 83 W min/m² (5 kJ) the surface roughens. Therefore, a dosage of 27–33 W min/m² was recommended for PP. Consequently, the 50 W min/m² applied in this study might already exceed the real saturation point.

Similarly for PET-BO, dosages above 50 W min/m² show no further rising in surface energy. In contrast to that, Brzezinski et al.[33] report increasing values up to a dosage of 324 W min/m² (21.4 J/cm²). This is surprising, as the recommended dosage for PET films is 10–13 W·min/m².[2]

Only for PE-LD, a continuous increase in surface energy is observable. Pascual et al.[5] also show continuously increasing surface energies up to 48.8 mN/m. (However, the dosage is not provided, and information about machine width is missing.) Kim et al.[34] reached saturation at about 44.5 mN/m. (However, the dosage is not provided here either.) Iwata et al.[35] observed saturation at about 833 W min/m² (50 J/cm²), i.e. at a much higher corona dosage than applied in this study. This might explain why the saturation point is not reached yet within this study.

In Figure 2 a closer look on the dispersive and polar part of the surface energies is presented. For all three materials, the polar part is slightly lower and the dispersive part slightly higher than literature values. Generally, both the dispersive and the polar part increase (apart from PET-BO). Whereas dispersive forces have their origin in London, Casimir, and van-der-Waals forces, the polar forces originate from all other interactions due to polar molecular groups. Correspondingly, Matthews[36] and Novák et al.[37] showed a linear correlation between the surface energy and the concentration of oxygen containing hydroxyl and carboxyl groups. Moreover, Guimond and Wertheimer[8] showed that by rinsing corona-treated PP film with water, the amount of oxygen as well as the polar part of surface energy
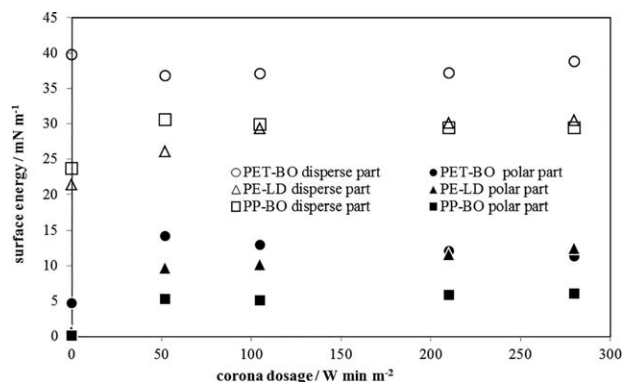
Figure 2. Polar and dispersive part of surface energy of different films for different corona dosages; treated films analyzed directly after corona treatment (as standard deviation is too small as to be visible in that graph, data is available in the Appendix).

Figure 3. Total surface energy of PP-BO film at different corona dosages (whiskers indicate standard deviation).

was significantly reduced, whereas the dispersive part stayed unchanged. This is again an indication that only the polar part of the surface energy changes due to the introduction of oxygen containing groups. Moreover, the increase of the polar forces was extensively investigated [i.e., by Fourier transform infrared (FTIR)] and explained by several authors.[33,36,38–40] (Therefore, the authors of this study decided not to apply these tests again and replicate prior findings.) In our study we surprisingly observed that even the disperse part increases, which was not described before. This observation was not further experimentally evaluated for this study (as it was not in the focus of this investigation). However, it can be explained with the following reasons:

a. In the case of micro roughening (not analyzed in this study), this effect might lead to a misinterpretation of the dispersive forces.[41]
b. Although the breakage of C—C bonds generally leads to smaller molecules, crosslinking might appear at higher corona dosages. Our hypothesis is that this in turn leads to higher molecular weights. Molecules with higher molecular weights generally have more electrons available for polarization and have therefore higher dispersive forces.[42–45]

Whereas at PE-LD and PP-BO surface energy increases, PET-BO is an exception here (Figure 2). Interestingly, the dispersive part of PET-BO decreases slightly, before it then converges again toward its initial value. Similarly, Tuominen et al.[23] observed a decrease of the dispersive energy of corona-treated PE-LD and PP-BO films. However, the reason for this discrepancy is unknown. In comparison to that, a continuous increase of surface energy on PET is observed by other authors.[38,46]

At PE-LD a slight but continuous ascend of both polar and dispersive part at increasing corona dosages was measured. This might be due to the high availability of hydrogen carbons on the polymer surface. In a study by Guimond and Wertheimer,[8] a polar part of 20 mN/m and a dispersive part of 25 mN/m was reached.

In the case of PP-BO, both polar and dispersive parts stay constant at corona dosages higher than 50 W min/m². In a study
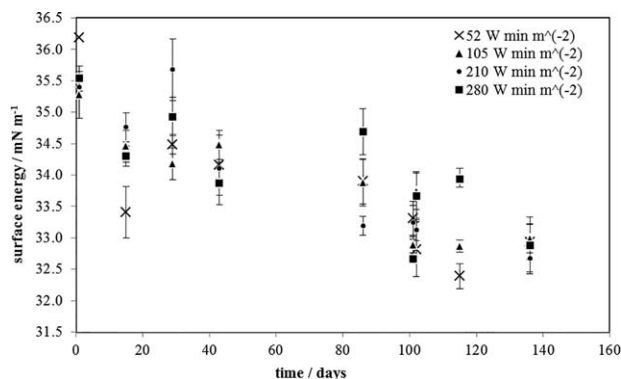
by Guimond and Wertheimer,[8] the polar part reached about 10 mN/m and the dispersive part 25 mN/m.

Alteration of the Total Surface Energy as a Function of Storage Time. At all samples (Figures 3–5) surface energy decreased as function of time as observed by other groups.[2,19,23] The substrates with the lowest initial surface energy also had the lowest surface energy after storage time. This process is commonly described as "hydrophobic recovery." It is explained by the re-orientation and creep of the chemical groups introduced by corona treatment into the bulk polymer (inward-diffusion) or sublimation of low-molecular weight oxidized materials (LMWOM).[19,31]

Comparing the rate of hydrophobic recovery, there is a difference for the different polymer substrates. In order to estimate the rate of recovery, a linear function was fitted for each combination of material and corona dosage. Like this, a rate of decrease in mN/m per day can be found for the three materials. The minimum and maximum values for the rate of recovery are (R^2: coefficient of determination):

- PP-BO: 0.02 mN/m/day (R^2: 0.87)
- PE-LD: 0.03–0.07 mN/m/day (R^2: 0.66; 0.19)
- PET-BO: 0.08–0.10 mN/m/day (R^2: 0.79; 0.95)

When having a look at the surface energies after treatment on day 1, it becomes clear that the film with the highest surface
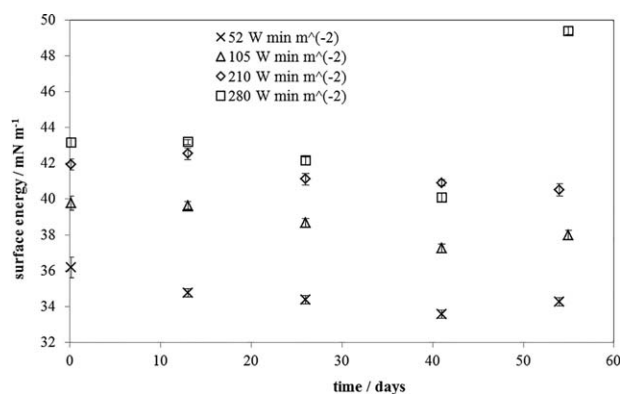

Figure 4. Total surface energy of PE-LD film at different corona dosages (whiskers indicate standard deviation).
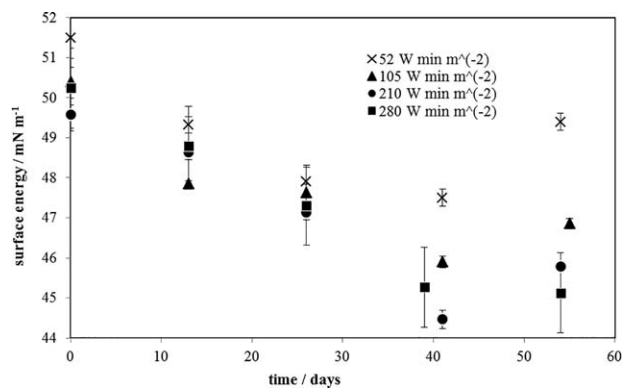
Figure 5. Total surface energy of PET-BO film at different corona dosages (whiskers indicate standard deviation).

Figure 7. Polar and dispersive part of surface energy of PE-LD film at different corona dosages over storage time (for better readability, the standard deviation is not shown in this graph but can be found in the Appendix).

energy (PET-BO) has the fastest decrease of surface energy. The film with the lowest surface energy after treatment (PP-BO) has the slowest decrease in surface energy. Similarly, Strobel et al.[10] found a stronger decrease in surface wettability of PET-BO compared to PP-BO. This was related to a stronger reorientation of oxidized groups and migration of oxidized species out of the surface region. Additionally, the rate of hydrophobic recovery also depends on the crystallinity of the polymer and is therefore lower for oriented polymers like PP-BO.[47] No clear correlation between the rate of recovery and the corona dosage was found (compare with Ref. 31).

Apart from the rate, the point of time when hydrophobic recovery is practically completed shall be compared. In a study by Guimond et al.,[31] the hydrophobic recovery is more or less finished after a storage time of 10 days on PP-BO films. In the present study, there is a continuous decrease up to a storage time of 140 days (Figure 3) which is rather in line with the findings in of other research groups.[37,39] For PE-LD a continuous decrease up to a storage time of 160 days[32] and even more than 360 days[37] was reported in literature. This is in line with our findings (Figure 4). For PET-BO films, the surface energy seems to decrease up to a time of 41 days with a slight increase afterwards (Figure 5). Comparatively, it was also reported that the recovery stagnated after 20 days[48]; that after 20 days no stagnation could yet

be seen[38,49] and also that a stagnation seems to appear at 60–120 days, depending on the intensity of treatment.[50]

Alteration of the Polar and Dispersive Part of Surface Energy as a Function of Storage Time. Both, the polar and the dispersive part decrease over storage time (Figures 6–8). This can be explained by two effects. The first effect is the reorientation of molecules, which appears due to the natural driven tendency of surfaces to lower their surface energy.[8] This re-orientation step mainly takes place for polar molecules.[51,52] The second effect is the migration of low-molecular-mass components to the surface. Such components can be additives, oligomers, and oxidized polymer fractions.[32] Especially the forming of oxidized polymer fractions is triggered by the corona process, where C—C bonds in the polymer chain are cleaved due to the similarity of bond dissociation energies for C—C (370 kJ/mol, polyethylene) and C—H (397 kJ/mol, polyethylene).[23] With further treatment, the polymers might even be cleaved to very small molecules, often referred to as LMWOM.[8] Additionally, smaller molecules have a lower surface energy due to their lower ability to be polarized.[44] As a consequence, the migration of these molecules again fulfils the intrinsic tendency to reduce the surface energy.
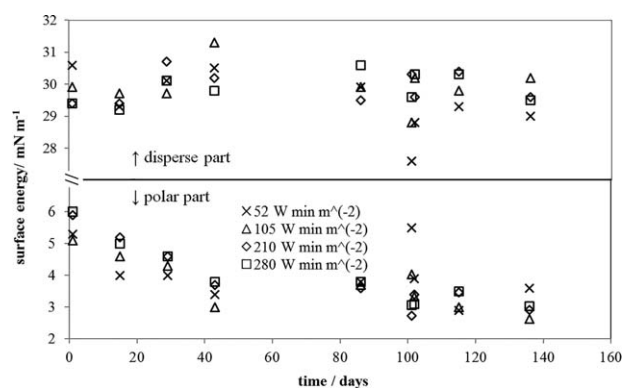

Figure 6. Polar and dispersive part of surface energy of PP-BO film at different corona dosages over storage time (for better readability, the standard deviations are not shown in this graph but can be found in the Appendix).
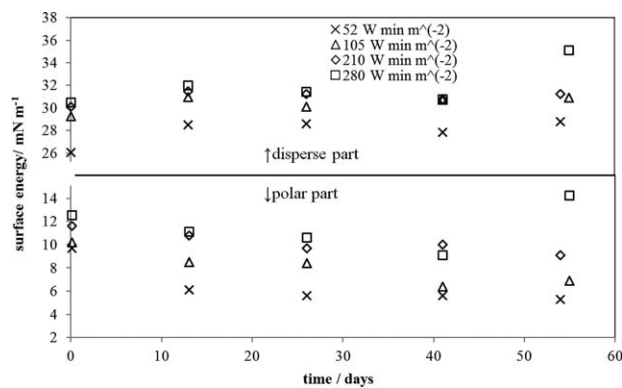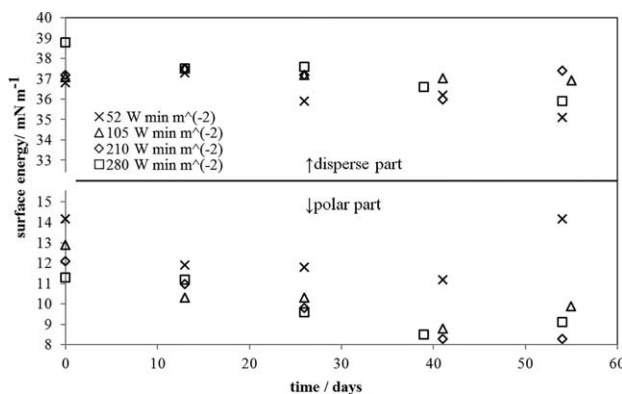

Figure 8. Polar and dispersive part of surface energy of PET-BO film at different corona dosages over storage time (for better readability, the standard deviation is not shown in this graph but can be found in the annex).
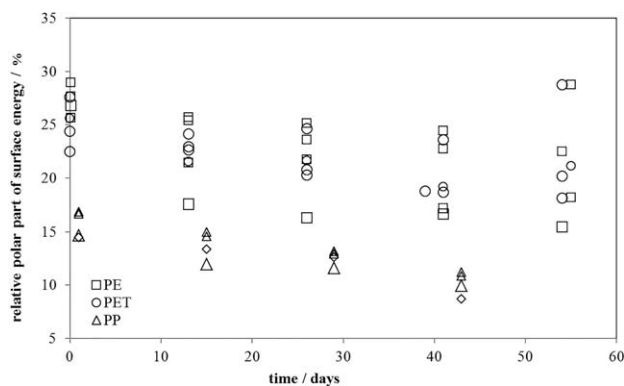
Figure 9. Relative polar part as a percentage of overall surface energy over storage time on different substrates (for better readability, the standard deviation is not shown in this graph but can be found in the annex).

The decrease of the polar part resembles the development of the surface energy (compare Figures 3–5). Similar results were found by Novák and Florián.[53] The polar part of the surface energy decreases over storage time for all substrates (Figures 6–8). The decrease is about 32% for PET-BO, 45% PE-LD, and 54% for PP-BO (maximum values). Compared to that, the decrease in the dispersive part is much lower: 7% for PET-BO, 15% for PE-LD, 13% for PP-BO (maximum values). Thus, it can be followed that the rearrangement of polar molecules occurs faster than the migration of LMWOM to the surface. All in all, the relative amount of the polar part as percentage of the overall surface energy decreases over storage time on all substrates (Figure 9). Correspondingly, the relative dispersive part increases. The adhesion between surfaces depends on chemical interactions between adhesive and polymer which are in turn affected by the strength and number of bonds.[54,55] Based on the energy additivity concept,[56] it can thus be concluded that not only the absolute values of surface energy, but also the ratio of polar and dispersive forces alters the adhesion.

In the next step, the decrease of the polar part over time was fitted according to the Cassie equation (2) (see section "Determination of Surface Energy").[29] Although the fitting function did not converge in each case, relatively higher τ were found for PET-BO ($\tau = 10–50$ days) than for PP-BO ($\tau = 12–40$ days) and PE-LD ($\tau = 7$ days). Low values for τ mean that the decrease is relatively fast. Assuming that this process appears mainly due to the re-orientation of polar groups, this means that materials with a low τ let the polar molecules reorient easily and fastly.

Laminate Bond Strength for Different Corona Dosages
The laminate bond strength was measured in transverse and machine direction after corona treatment with dosages of 52, 105, 210, and 280 W min/m². The measurements were executed on the 16th day after lamination on PP-BO, and on the 28th day on PE-LD and PET-BO.

For the PET-BO film, the laminate bond strength had a mean value of 1.27 N/15 mm in machine direction and 1.80 N/15 mm in transverse direction at non-corona treated films. However, laminate bond strength of films after corona treatment could not be measured. This was because the bond

strength was higher than the tensile strength of these films which caused tearing of the films. This is interesting as apparently the overtreatment did not lead, as expected, to bond strength reducing effects such as the development of LMWOM which are reported to build a loosely bound layer and compromise good adhesion.[8] Neither did the surface energy increase for dosages > 52 W min/m². Therefore, one explanation for this laminate bond strength might be the increased surface roughness (not analyzed in this study), which rises with increasing dosages[31,32,38,40,57] and is reported to increase the adhesion to e.g. scotch tapes and spray coatings.[38,43,46,54] This is explained with the relative increase in surface area which leads to an improvement in wettability and adhesion.

Similar results were observed for PP-BO. At dosages of 52 and 105 W min/m², the laminate bond strength was higher than the tensile strength of the film so that the film teared. For higher corona dosages of 210 and 280 W min/m² apparently the adhesion was reduced again, so that the laminate bond strength in machine direction was possible to be determined (Figure 10). This effect might be explained with the appearance of the aforementioned LMWOM, which reduces the adhesion. By visual evaluation, it was observed that the laminate teared mainly due to adhesive failure with only little cohesive failure.

Only in the case of PE-LD the laminate bond strength could be measured. It has to be taken into account that the absolute values presented in the graph might be influenced by a certain degree due to the elastic deformation of the PE-LD as it has a very low Young's modulus (200–600 $\times$ 10^{-3} N/cm² [58]). The laminate bond strength clearly increased with a more intensive corona treatment. Apparently, an overtreatment did not appear. With increasing corona dosage, the polar and dispersive part of the surface energy increase, so that they can interact with the functional groups of the PU-based adhesive.

When comparing the values in transverse and machine direction, it can be observed that the laminate bond strength transverse to machine direction was up to a factor of 1.2 higher than the bond strength in machine direction on PE. For PP, the laminate bond strength in transverse direction was also too high so that it was not measureable, whereas in machine direction at least two data points were recordable. In Figure 11 it can be seen that the adhesive shows a non-isotropic coverage, with a
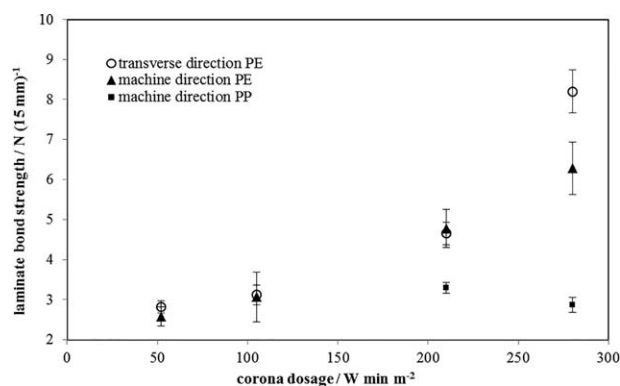

Figure 10. Laminate bond strength of PP-BO film in machine direction and of PE-LD film in transverse and machine direction.
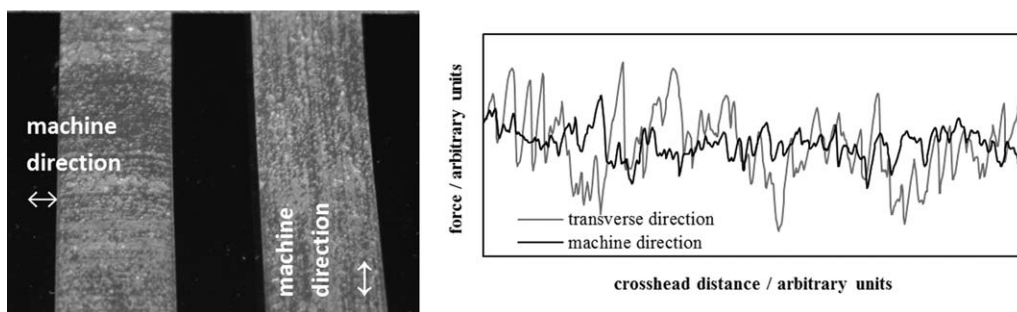
Figure 11. Specimen for laminate bond strength measurement in transverse direction and machine direction (left), exemplary force–distance curves (right).

predominant direction in machine direction. This might be a relic from the coating process, which was executed by gravure coating. In the case of measurement in transverse direction, a very high force is needed to peel apart an area, where the adhesive is thicker and a very low force, where the adhesive is thinner. This leads to high amplitudes and long "wavelengths" in the force–distance curve during peel testing. In machine direction, the force is rather constant with shorter wavelengths. This leads to lower mean laminate bond strengths.

CONCLUSIONS

It is often recommended that the corona dosage applied on film surfaces during corona treatment should be as high as needed to reach the maximum surface energy but as low as possible in order to save energy. However, and as not expected, in the present study it is shown that an "overtreatment" increases bond strength of laminated films, even though the surface energy does not rise further at higher corona dosages. (Only at PP-BO a reduction of laminate bond strength due to "overtreatment" was observed.) Therefore, the surface energy cannot be correlated to laminate bond strength.

Additionally, it was found that the speed of hydrophobic recovery is different for different polymer substrates. This needs to be taken into account, when a film is already treated by a film producer and then stored at a subsequent converter before lamination.

Moreover, bond strength depends on the amount of polar and dispersive bonds on the surface. This is because bond strength, i.e. adhesion, is supported by disperse and polar bonds between substrate film and coating. The amount of bonds between substrate and coating or between both substrates is highest, when the ratio between the polar and disperse part are similar for the substrate and the coating. In such a case, the statistical probability is as high as possible for matching as many dispersive and polar interactions, respectively. However, as it was shown, this ratio changes over storage time and the relative amount of the dispersive part rises on the polymer substrate. This means that coatings with a low polarity will spread more and adhere stronger on the substrate surface after longer storage time. Therefore, it is recommended to quantify this ratio between disperse and polar part, when wetting and adhesion problems occur. The speed of hydrophobic recovery was not reduced by increased corona dosages. Thus, the effect of storage time cannot be reduced by a more intense treatment.

As these observations were partially not expected, the authors of this study recommend to determine and better explain why "overtreatment" does not necessarily result in a negative effect on laminate bond strength. The interaction between corona ("over-") treated surfaces and its effects (surface roughness, LMWOM, chain scission, forming of weak boundary layer) and the interaction with adhesives should be analyzed in more detail, i.e., by surface analysis (i.e., with atomic force microscopy (AFM), Raman spectroscopy, FTIR, electron microscopy, and gas chromatography–mass spectrometry (GC-MS) for LMWOM determination).

ACKNOWLEDGMENTS

APPENDIX

Table AI. Standard Deviations for All Surface Energy Measurements

Dosage (W min/m^2)	Storage time (days)	Standard deviation disperse part (mN/m)	Standard deviation polar part (mN/m)	Standard deviation surface energy (mN/m)
PET-BO 0	≤1	0.14	0.09	0.24
52	≤1	0.49	0.25	0.74
	13	0.12	0.09	0.21
	26	0.21	0.14	0.36
	41	0.1	0.11	0.21
	54	0.1	0.11	0.21
105	≤1	0.4	0.18	0.58
	13	0.05	0.03	0.08
	26	0.13	0.08	0.2
	41	0.1	0.05	0.15
	55	0.06	0.07	0.12

Table AI. *Continued*

Dosage (W min/m²)	Storage time (days)	Standard deviation disperse part (mN/m)	Standard deviation polar part (mN/m)	Standard deviation surface energy (mN/m)
210	≤1	0.28	0.13	0.41
	13	0.14	0.05	0.19
	26	0.14	0.05	0.19
	41	0.17	0.06	0.23
	54	0.08	0.05	0.12
280	≤1	0.14	0.07	0.22
	13	0.09	0.05	0.14
	26	0.11	0.04	0.16
	39	0.17	0.06	0.22
	54	0.13	0.07	0.21
PE-LD 0	≤1	0.19	0.03	0.21
52	≤1	0.4	0.18	0.58
	13	0.17	0.07	0.24
	26	0.17	0.08	0.24
	41	0.16	0.06	0.22
	54	0.16	0.08	0.24
105	≤1	0.27	0.11	0.38
	13	0.13	0.07	0.2
	26	0.17	0.08	0.25
	41	0.16	0.08	0.24
	55	0.2	0.07	0.27
210	≤1	0.22	0.11	0.32
	13	0.22	0.12	0.34
	26	0.2	0.12	0.32
	41	0.1	0.09	0.19
	54	0.21	0.13	0.34
280	≤1	0.15	0.08	0.23
	13	0.08	0.06	0.14
	26	0.14	0.07	0.22
	41	0.16	0.08	0.24
	55	0.1	0.11	0.21
PP-BO 0	≤1	0.12	0	0.13
52	≤1	0.29	0.12	0.41
	15	0.11	0.04	0.16
	29	0.39	0.1	0.48
	43	0.26	0.1	0.36
	86	0.2	0.07	0.27
	101	0.23	0.21	0.44
	102	0.13	0.07	0.2
	115	0.2	0.08	0.28
	136	0.33	0.16	0.49
105	≤1	0.28	0.09	0.37
	15	0.16	0.08	0.25
	29	0.18	0.08	0.25
	43	0.18	0.05	0.23

Table AI. *Continued*

Dosage (W min/m²)	Storage time (days)	Standard deviation disperse part (mN/m)	Standard deviation polar part (mN/m)	Standard deviation surface energy (mN/m)
	86	0.28	0.09	0.37
	101	0.06	0.07	0.13
	102	0.2	0.09	0.29
	115	0.06	0.03	0.1
	136	0.17	0.05	0.23
210	≤1	0.1	0.05	0.15
	15	0.16	0.07	0.23
	29	0.38	0.11	0.49
	43	0.21	0.09	0.3
	86	0.09	0.05	0.15
	101	0.22	0.05	0.27
	102	0.14	0.05	0.18
	115	0.1	0.05	0.15
	136	0.16	0.05	0.21
280	≤1	0.14	0.06	0.2
	15	0.1	0.06	0.16
	29	0.23	0.08	0.31
	43	0.27	0.07	0.34
	86	0.29	0.08	0.37
	102	0.29	0.09	0.38
	115	0.16	0.21	0.05
	136	0.35	0.09	0.45

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