Polymeric substrate properties tailored by irradiation

Roll-to-roll adaptation of mechanical and thermo-mechanical properties of substrates by means of electron beam irradiation at atmospheric pressure

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Source: Fraunhofer FEP

Roll-to-roll processes are well-known for its high throughput, low cost, high quality and high yield potentials. They are commonly used if flexible substrates like paper, metal foils or polymer films have to be processed. Focusing on the latter, it is common to tailor their surface properties to certain needs. The polymeric material becomes conductive to act as a flexible electrode in circuit board or display applications. They receive an optical layer stack to reduce reflection in window films or they will be equipped with a permeation barrier layer to protect electronic devices or food against oxygen and humidity. All these examples may use chemical (CVD) or physical vapor deposition (PVD) processes to achieve the needed properties. The processing is combined very often with stress like thermal load or mechanical strain. This stress is limiting the productivity due to physical limitations of the material itself. Their thermal stability is too low. Or the elastic modulus is so small that simple winding through a roll-to-roll winding system is restricted to very low winding forces to prevent wrinkling or undesired material stretching. As the mentioned processes are very often concomitant with a temperature increase mechanical properties has to be considered not only at room temperature but also at higher temperatures. An example is given for PLA's elastic modulus over temperature in **Fig. 1**. There is a steep decrease in the elastic modulus around 48 °C, the so-called glass transition temperature, there the polymer changes from a glassy state to a more viscous or rubbery state. A second exemplary diagram is to be seen in **Fig. 2** for a 25 µm thick, 1000 mm wide film made out of PLA. The elongation of the film at room temperature is fairly low (0,2 %) but increases to 1.7 % at elevated temperature above the glass transition. Wrinkling of this film is very likely to occur within processes with higher temperature like metallization.

The problems described above may be solved by changing the process conditions but typically, this decreases productivity or raises other issues. Alternatively, a change of certain substrate properties may be done. Therefore, electron beam irradiation can be used to alter the molecular structure of polymeric substrates and this changes mechanical and thermo-mechanical properties.

SUMMARY

Roll-to-roll processes are well-known for its high throughput, low cost, high quality and high yield potentials. They are commonly used if flexible substrates like paper, metal foils or polymer films have to be processed. Focusing on the latter, it is common to tailor their surface properties to certain needs. Therefore, technologies like chemical (CVD) or physical vapor deposition (PVD) processes are used. Such processing is very often combined with stress like thermal load or mechanical strain. This stress is limiting the productivity due to physical limitations of the material itself, like low thermal stability or very small elastic modulus and especially in its combination. The treatment of such polymers by electron beam at atmospheric pressure may alter the mentioned properties. Respective investigations of polyester, polyethylene and different kinds of bio-based polymers with respect to elastic modulus, puncture resistance and thermal stability will be shown.

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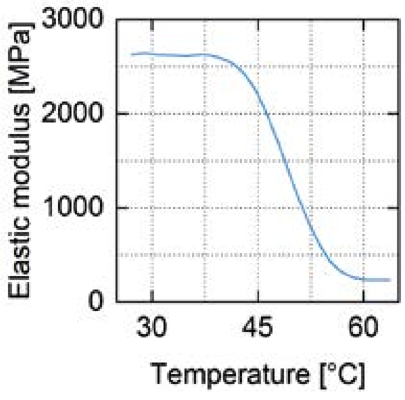

FIGURE 1: **Exemplary trend of PLA's elastic modulus over temperature**

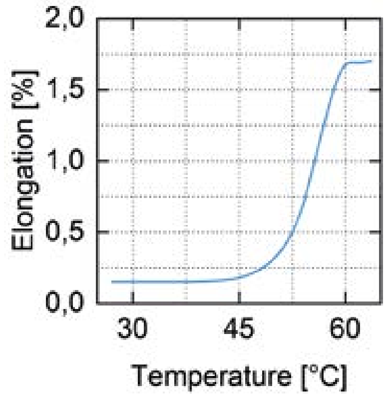

FIGURE 2: **Exemplary elongation of 25 µm thick, 1000 mm wide PLA film at web tension of 100 N over temperature**

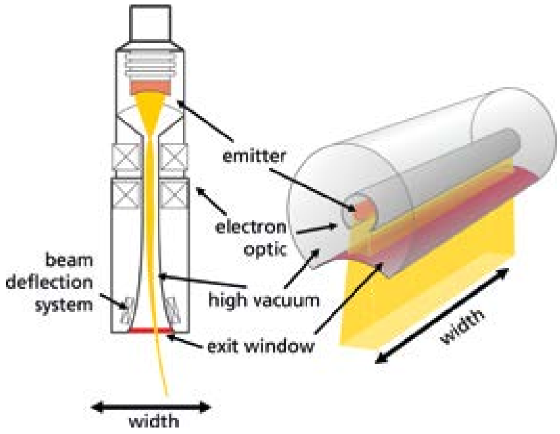

FIGURE 3: **Setup of industrially used electron beam systems to be used at atmospheric pressure, scanner (left side) and curtain type (right side)**

Electron beam technology at atmospheric pressure

Electron beam irradiation systems produce their free electrons within a small high vacuum chamber by glow discharge or by means of a plasma. The electrons will be accelerated by high voltage (> 50 kV) and guided by an electron optic to an electron beam transparent window. Such window consists typically of a thin titanium foil (approx. 10 to 20 µm) and separate the high vacuum from the atmosphere. The electrons penetrate the window and enter the atmosphere, where they may be used for irradiation processes like sterilization, curing or change of polymeric networks. There are two types of electron beam units industrially used worldwide. The scanner type system uses electrons generated by a point source. Their acceleration voltage might be very high but this limits the irradiation width. In contradiction, the linear or curtain type system emits electrons from a line source and this allows nearly unlimited irradiation widths. **Fig. 3** shows the setup of these two types. Their main differences are listed in **table 1**.

Scanner type	Linear or curtain type
electron emission from "point source"	electron emission from "line source"
acceleration voltage up to 10 MeV	acceleration voltage mostly limited to 300 kV
high uniformity	limited uniformity
treatment width technically limited	nearly unlimited treatment width possible

TABLE 1: **Comparison of scanner and curtain type electron beam system regarding their typical properties.**

Interaction of electrons with matter

If (highly accelerated) electrons hit matter, they will lose energy through scattering and ionization processes. Dependent from the electron energy and the density of the matter, the electrons are able to penetrate the matter by some extend until all of its energy is transferred to the matter. **Fig. 4** shows an example of electrons penetrating water. The penetration depth increases with electron energy. This energy is related to the irradiated mass and gives the irradiation dose with its unit gray (Gy). In typical industrial applications the unit kGy (1 kGy = 1 J/g) is used.

Irradiating organic materials like polymers with electrons lead to several effects. First, bond breaks and radicals are generated. Dependent from radiation intensity, molecular structure and chemical nature the radicals may cross-link to each other to build a new network. This is the preferred effect to tailor the mechanical and thermo-mechanical properties of polymers. But

ZUSAMMENFASSUNG

Strahleninduzierte Anpassung der Eigenschaften von Kunststoffsubstraten – Rolle-zu-Rolle-Anpassung der mechanischen und thermo-mechanischen Eigenschaften von Substratmaterialien mittels Elektronenbehandlung unter Atmosphärendruck

Rolle-zu-Rolle-Prozesse sind für ihren hohen Durchsatz, niedrige Kosten, hohe Qualitität und niedrige Ausschussquoten bekannt. Zum Einsatz kommen sie immer dann, wenn flexible Substrate wie Papier, Metallfolien oder Kunststofffolien prozessiert werden sollen. Insbesondere bei letzteren werden häufig die Oberflächeneigenschaften angepasst, wobei chemische (CVD) oder physikalische (PVD) Beschichtungsverfahren benutzt werden. Entsprechende Prozesse sind meist mit thermischen oder mechanischen Belastungen verbunden. Diese reduzieren die Produktivität der Prozesse durch entsprechende Limitierungen der Substratmaterialien, wie z. B. niedrige Temperaturstabilität oder niedriger E-Modul und besonders deren Kombination. Die Behandlung der Kunststoffsubstrate mittels Elektronen kann diese Eigenschaften anpassen. Entsprechende Untersuchungen wurden an Polyester, Polyethylene und verschiedenen Arten von biobasierten Kunststoffen vorgenommen. Ergebnisse in Bezug auf E-Modul, Durchstoßverhalten und thermische Stabilität werden vorgestellt.

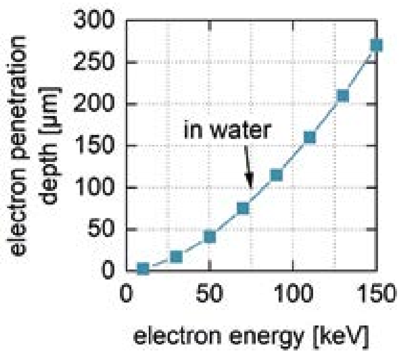

FIGURE 4: **Penetration depth of electrons in water dependent from the electron energy**

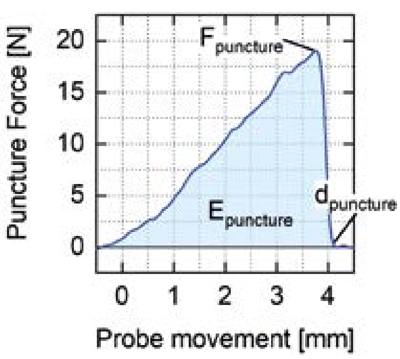

FIGURE 5: **Diagram showing puncture force measured continuously over probe movement penetrating a polymer film until tearing appears**

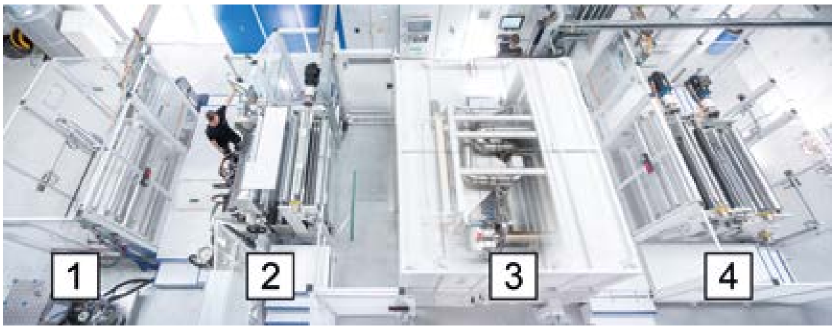

FIGURE 6: **Roll-to-roll converting machine for handling of 1250 mm wide flexible materials like paper, polymer films or thin metal foils, consisting of 4 process modules: module 1 - unwinding and liner removal; module 2 - pre-treatment, cleaning, coating and laminating; module 3 - e-beam treatment & curing; module 4 - rewinding, slitting and laminating**

the radicals may be also saturated by ions or smaller radicals like ozone. This will lead to chain scissions that may be recognized by reduced tear resistance. Especially, at very high doses a complete de-polymerization may take place as it is used to produce PTFE powder.

Property measurement

The characterisation of the irradiated and pristine polymers was done using self-made equipment to simply measure elastic modulus at room temperature and elevated temperature. Additionally, the temperature dependent elastic modulus was measured by using dynamic measurement at increasing temperature (DMA). A self-made penetration testing unit was used to measure the puncture resistance similar to ASTM F1306-21 using a Ø 2.5 mm penetrating needle at sample size of Ø 20 mm. **Fig. 5** shows a typical measurement and respective measurement values $F_{puncture}$ (maximum penetration force), $d_{puncture}$ (penetration depth at tearing occurs) and $E_{puncture}$ (integral below curve – overall energy of penetration).

To limit the number of figures only graphs for $E_{puncture}$ will be presented. Graphs for $F_{puncture}$ and $d_{puncture}$ may be requested from the author.

Irradiation trials

Several polymer films were irradiated by electron beams at different doses using the roll-to-roll converting machine atmoFlex 1250 at Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP to be seen in **Fig. 6**. The machine is equipped with a slot-die-unit for coating, surface cleaning unit, corona system for surface treatment and an electron beam unit of curtain type for curing and treatment. The web could be 1250 mm in width and is wounded at 150 m/min maximum speed.

There were several types of PE irradiated, additionally PLA, PET and a cellulose based thermoplastic film were also investigated. An overview is given in **table 2**.

Results

PE films

The several types of PE show different behavior with respect to electron irradiation. HDPE shows nearly no changes as to be seen in **Fig. 7** for elastic modulus at room temperature but also in view of the elastic modulus with respect to temperature as to be seen in **Fig. 8** comparing pristine and irradiated samples.

There is some small decrease in the penetration force to be seen for irradiated samples but this is not reflected by

Material classification	Type of material	Thickness
PE	HDPE	30 µm
	LDPE	100 µm
	LLDPE	100 µm
Polyester	PET	50 µm
Biopolymer	PLA	30 µm
	Cellulose based thermoplastic	100 µm

TABLE 2: **Overview of irradiated polymeric films**

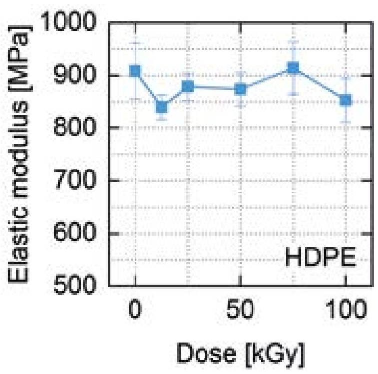

FIGURE 7: **Elastic modulus vs. irradiation dose of HDPE at room temperature**

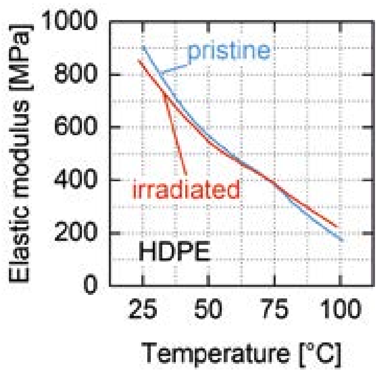

FIGURE 8: **Elastic modulus vs. temperature of pristine and irradiated HDPE**

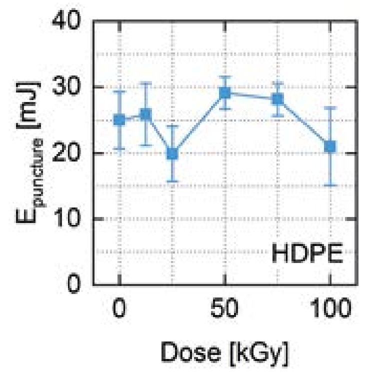

FIGURE 9: **Puncture energy vs. irradiation dose of HDPE**

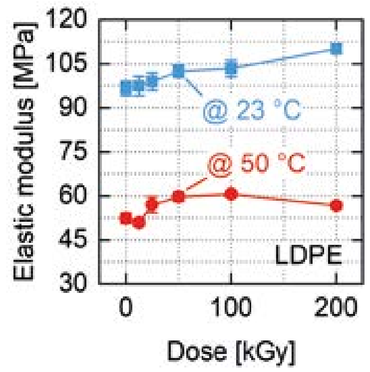

FIGURE 10: **Elastic modulus vs. irradiation dose of LDPE at different temperatures**

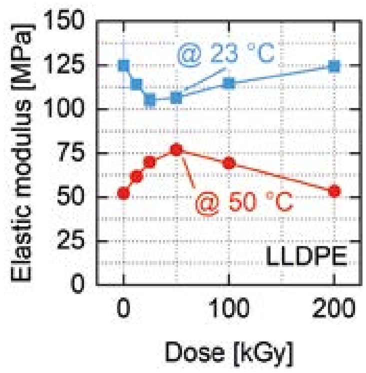

FIGURE 11: **Elastic modulus vs. irradiation dose of LLDPE at different temperatures**

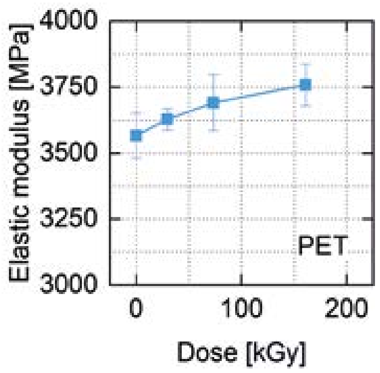

FIGURE 12: **Elastic modulus vs. irradiation dose of PET at room temperature**

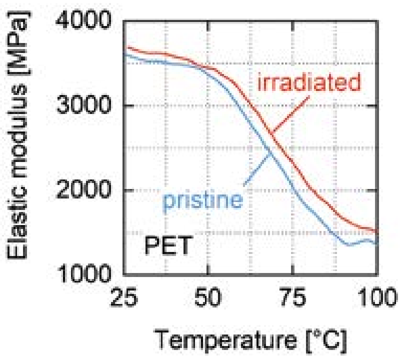

FIGURE 13: **Elastic modulus vs. temperature of pristine and irradiated PET**

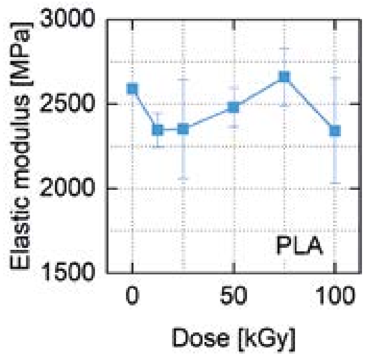

FIGURE 14: **Elastic modulus vs. irradiation dose of PLA at room temperature**

puncture depth nor puncture energy in **Fig. 9.**

LDPE shows slight increase in elastic modulus both at room temperature but also at elevated temperature in **Fig. 10.** This behaviour is in contradiction to LLDPE. As to be seen in **Fig. 11** elastic modulus of LLDPE at room temperature decreases first for increased irradiation dose up to 25 kGy but becomes higher for more increased doses up to 200 kGy. Surprisingly, at elevated temperature a mirrored trend is to be seen with maximum of the elastic modulus at 25 kGy.

Polyester

The polyester shows slight increase of elastic modulus at room temperature with increasing irradiation dose as to be seen in **Fig. 12.** A change in the glass transition temperature was not observed. This is to be seen by comparing the two curves for elastic modulus versus temperature in **Fig. 13.**

Biopolymers

The biopolymer PLA shows slight decrease of elastic modulus for low doses but an increase for higher doses in **Fig. 14.** As the measurement deviation was fairly high for this material, a clear trend cannot be deduced. But there was a remarkable increase of the glass transition temperature by irradiating the PLA as to be seen in **Fig. 15.** Approximately 10 K increase in T_G was observed for the irradiated sample.

The puncture measurements show huge impact of irradiation, if dose becomes 50 kGy or more. All these samples show very low penetration force, depth and energy as shown in **Fig. 16.**

The thermoplastic cellulose based film shows some decrease in elastic modulus if irradiated independent from the irradiation dose as shown in **Fig. 17.** The thermal stability is slightly increased as the curve for the irradiated sample is shifted to higher temperatures in **Fig. 18.**

The puncture test gave only some slight increase in puncture depth if samples are irradiated but no influence in view of the penetration force. This behaviour is also reflected by the puncture energy in **Fig. 19.**

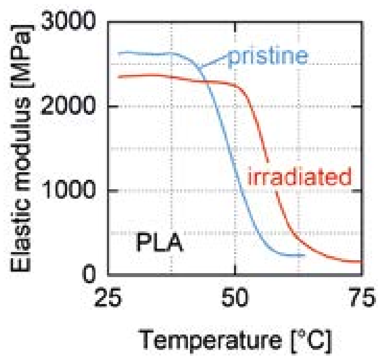

FIGURE 15: **Elastic modulus vs. temperature of pristine and irradiated PLA**

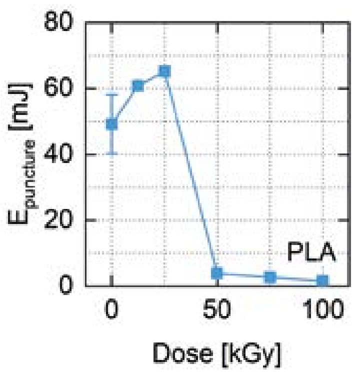

FIGURE 16: **Puncture energy vs. irradiation dose of PLA**

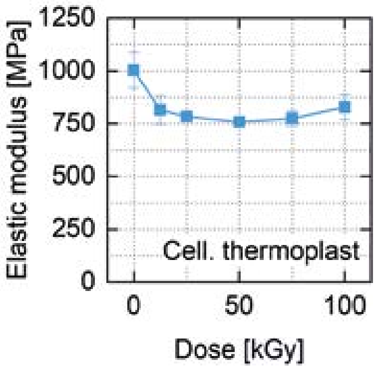

FIGURE 17: **Elastic modulus vs. irradiation dose of cellulose based thermoplastic material at room temperature**

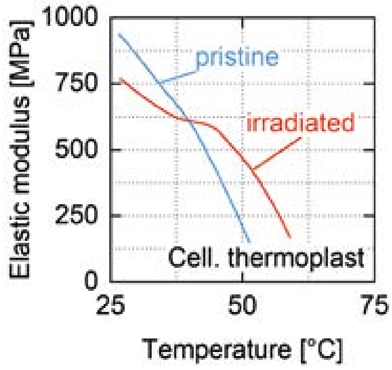

FIGURE 18: **Elastic modulus vs. temperature of pristine and irradiated cellulose based thermoplastic material**

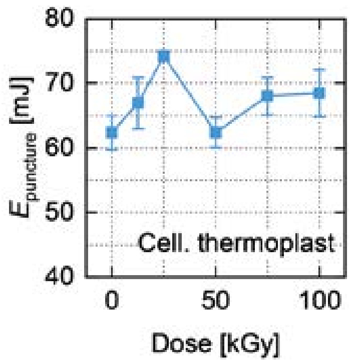

FIGURE 19: **Puncture energy vs. irradiation dose of cellulose based thermoplastic material**

Conclusions

Polymeric materials are widely used in the roll-to-roll business. An improvement of its thermal stability in view of mechanical properties is still requested. Dependent from the polymer, its chemical nature but also its morphology the irradiation by means of highly accelerated electrons is an option to achieve for instance increase in glass transition temperature or an increased elastic modulus. The tailoring of tear resistance is also possible but belongs more to application-related properties.

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