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Development perspectives of selected technologies of polymer surface layers modification

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ABSTRACT

Purpose: The purpose of the paper is to present the results of a comparative analysis of the five selected technologies of modification of polymer surface layers based on the outcomes of own materials science and foresight research. A criterion of dividing is represented by physical processes the result of which is polymer material surface layer modification.

Design/methodology/approach: This paper presents the results of own materials science research of surface modification for selected polymer materials subjected to the activity of corona discharges, laser light and high-temperature electron-beam irradiation. The technologies analysed include also modification with low-temperature plasma generated in the air by a generator situated outside the material modification zone and with low-temperature plasma in the conditions of low pressure (0.05-5 hPa). The value of the individual technologies as well as the type and intensity of environment influence was assessed in the course of foresight works. The results of the research are provided graphically with a bar chart, pool of context matrices, strategic development tracks and technology roadmaps.

Findings: An important role of polymer surface layers modification technologies for the development of overall materials surface engineering was pointed out.

Research limitations/implications: The research pursued represents part of a larger project aimed at identifying and characterising the priority, innovative materials surface engineering technologies.

Originality/value: The value of this paper is represented by an original contribution consisting of objectivised assessment of the selected polymer materials surface layers modification technologies and presenting the directions of their strategic development against the overall materials surface engineering based on the results of foresight- materials science research.

Keywords: Manufacturing and processing; Surface treatment; Polymers; Foresight; Technology Roadmapping

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RESEARCH MONOGRAPH

1. Introduction

The European Union's priority strategy set out in the recent years called Europe 2020 assumes that the development of the continent should be intelligent, supportive to social inclusion and sustainable [1]. For this to be feasible, it is necessary to take extensive actions at the European, national and regional level, to support a more effective, competitive and low-emission economy based on knowledge and innovation, ensuring high employment and social and territorial cohesion, which is expressed by five strategic objectives (Fig. 1). Such objectives should also be achieved under a project on establishing the innovation Union, promoting innovation understood as precious, innovative ideas [2]. A stream of investments, therefore, should be channelled into those fields of science and industries bringing the highest added value. Special consideration should be given to small- and medium-sized enterprises encompassing 99.8% of all domestic companies and generating 68% of GDP. The aim of the foresight research conducted broadly in the recent decade in Europe and Poland, also in the field of materials science [3-9], is a quest for innovative areas deserving financial support. Technology foresight serving to identify the priority, innovative technologies and the directions of their strategic development was pursued also for materials surface engineering [10]. One of the 14 thematic areas analysed under such foresight research is the surface engineering of polymer surface layers.

The properties of surface layers (SL) of polymer materials including composites [11-14]are gaining increasing importance as the rapid growth of diverse applications of such materials has been seen [15, 16]. The formation of properties of materials' SL is the task of technology design, which, together with structural design and material design, represent three equivalent and inseparable elements of engineering design [17, 18]. The majority of polymer materials exhibit low reactivity, are hydrophobic by their nature and are characterised by low surface free energy (SFE) [19, 20]. Such characteristics to a large extent are limiting the adhesive properties of such materials and of polymeric and metallic layers deposited. Different physical methods of modifying such materials' SL are used to improve the adhesive properties of polymer materials, notably such as corona discharges, plasma method, laser method and electron-beam irradiation. The methods consist primarily in initiating reactions causing the formation of polar functional groups in this layer and in changing the geometric structure of the modified material's surface [21, 22]. The polymer materials SL modification methods analysed in this paper permit to eliminate chemical products hazardous for the environment used in the methods of chemical modification of such layer.

2. Research scope and subject matter

The research efforts focussed on the selected technologies of modifying polymeric surface layers are of an interdisciplinary

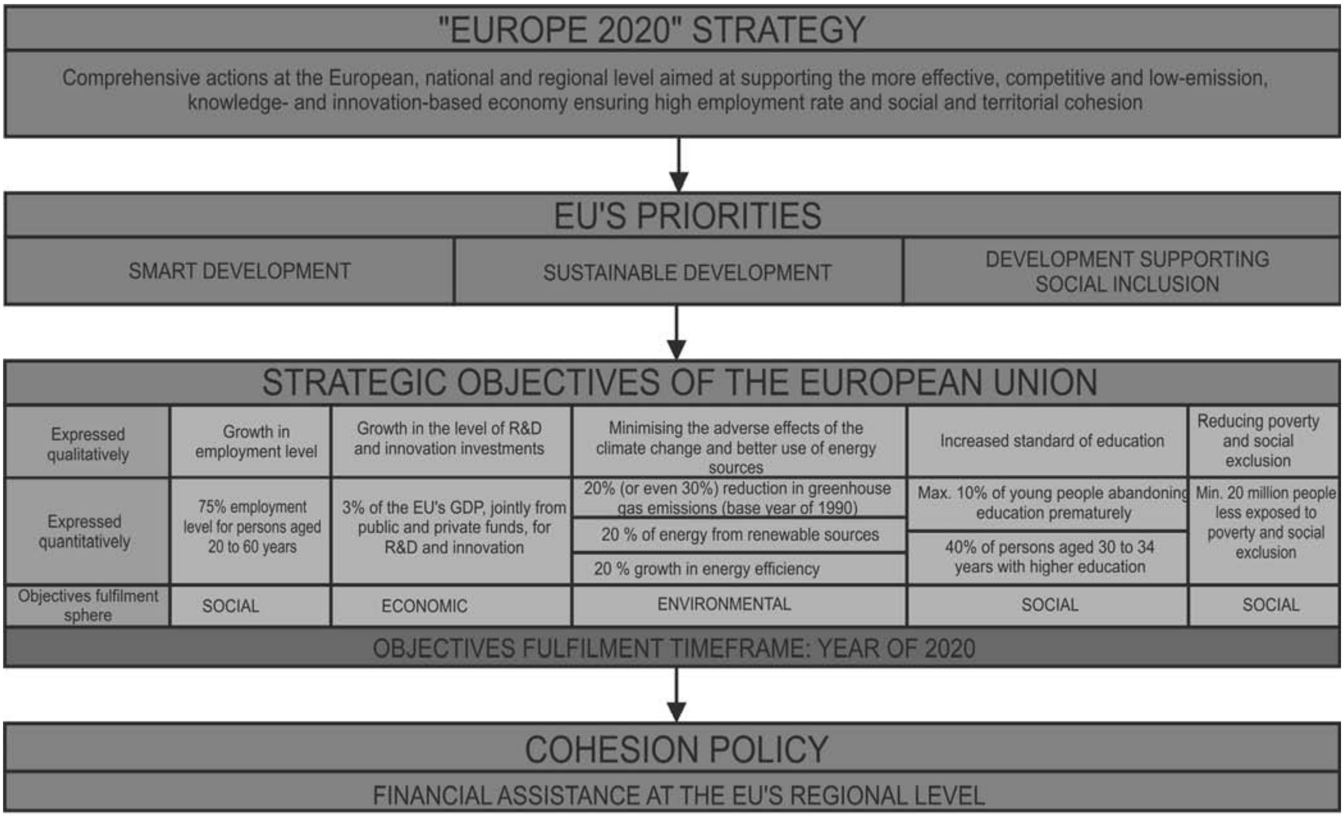


Fig. 1. EU main strategy, priorities and objectives. Custom presentation prepared on the basis of [1]

character. The foresight-materials science research methodology [23, 24] applied concerns technology foresight being part of the field of knowledge called organisation and management and of surface engineering forming part of the widely-understood materials science. A much broader prospective into the issues investigated had to be used at some stages, however. For this reason, methods and approaches deriving from other areas of specific knowledge had to be employed, i.e. computer science including information technology [25] and artificial intelligence [26] (neural networks joining with Monte Carlo methods); statistics; econometrics; operational studies; machine construction and operation; automation and robotisation of industrial processes; strategic, tactical and operational management; quality and environment management; accounting and finance. The following five homogenous groups were distinguished between for the purpose of the foresight and materials science investigations carried out under this task by adopting, as a criterion of grouping, physical processes the result of which is polymer material surface layer modification, i.e. respectively:

(A) Corona Treatment (CT);
(B) Remote Plasma Treatment (RPT);
(C) Low Pressure Plasma Treatment (LPTT);
(D) Laser Treatment (LT);
(E) Electron-Beam Irradiation (EBI).

3. Technologies descriptions, adopted methodology and materials science research results

This paper provides an overview of five, selected technologies of polymeric surface layers modification induced by various physical processes. The methodology adopted and the results of own research in this area by means of corona discharges, laser light and electron-beam irradiation are also presented in relation to modification.

3.1. Corona Treatment

The corona treatment (CT) methods were described for the first time in patents [27-29], and the first industrial applications, primarily for modifying the SL of polyolefine foils, date back to the 60’s of the last century. The current applications of the method are much more extensive and encompass not only flat plastic products such as foils and plates but also products with complex shapes (e.g. tubes and bottles) [30]. For this reason the CT method has become the most popular method of industrial SL modification of plastics.

Corona discharges occur due to differential potentials created between two activator electrodes, i.e. an HV discharge electrode and an earthed electrode in a space filled with gas (typically air) under atmospheric pressure [31]. The production of plasma is initiated by electrons staying within an interelectrode space. The electrodes are highly accelerated under the influence of an electromagnetic field. The electrons, while moving in an interelectrode space, collide with air molecules, causing their ionisation and hence an increase in the number of electrons and ions. Electric current starts to flow in the interelectrode space as a result of such phenomena. A stream of plasma falling on the SL of a product removes contaminations and changes the geometric structure of the surface. The molecules within plasma have a different kinetic energy. The most of the electrons in the interelectrode space of the activator have their kinetic energy of approx. 10 eV. The kinetic energy of electrons is higher than the energy of the basic bonds occurring in the macromolecules of polymer chains (e.g. energy of C - C, C - H, C - N bonds is smaller than 5 eV). The impact of molecules, atoms and ions on changes to the SL of the modified material is much smaller in the plasma generated during corona discharges than the impact of electrons [32]. Some chemical bonds of polymer chains are knocked out due to the kinetic energy of the electrons hitting against polymer chains. Radicals are formed that initiate chemical reactions modifying the SL of products (oxidisation processes are mainly at play). The radicals react with, in particular, oxygen, ozone, OH groups, water molecules, by forming polar compounds. The polar compounds forming in the SL as a result of chemical reactions, during which oxygen decomposition occurs, change the surface properties of the products modified, including the growth of SFE [33-34].

The subject matter of the own research was concerned with polyactide (PLA) 2002 D by Cargill Down LLC with the melt flow index of 4.2 g per 10 min. (2.16 kg, 190^oC) and density of d = 1.24 g/cm^3, in form of approx. 100 µm thick foil. An AF2 foil activator (Metalchem, Toruń) was used for modifying the surface layer of the PLA. The tested PLA samples were subjected to the activity of CT at ambient temperature (approx. 23ºC) under atmospheric pressure in the air. The surface layer of PLA was modified using a 0.25 m long, HV, single-point electrode. The parameters of the modification process are shown in Table 1.

Table 1.
Modification process parameters of the PLA surface layer, (E_j – unit energy of modification, P – capacity of corona discharges, v – foil displacement rate)

E_j, kJ/m^2	P, W	v, m/min
0.5	200	96
1	400	96
1.5	400	64
2	400	48
3.5	400	27.4
5	400	19.2
7	400	13.7
10	400	9.6
20	400	4.8

The values of water (Akchem, Poland) and diiodomethane wetting angle (Sigma - Aldrich, Germany) for the PLA samples modified with the CT method in the air are shown in Fig. 2. As E_j is growing, the values of water or diiodomethane wetting angles are declining, whereas larger changes are seen for water. This is caused by the fact that polar forces take part in intermolecular interactions more intensively. Much higher growth in the interactions of polar liquid than dispersion liquid with modified PLA foil derives from the fact that polar groups are created in the surface layer of PLA that strongly interact with water molecules as a consequence of the modification process. Interactions of a dispersive character are of smaller importance here.

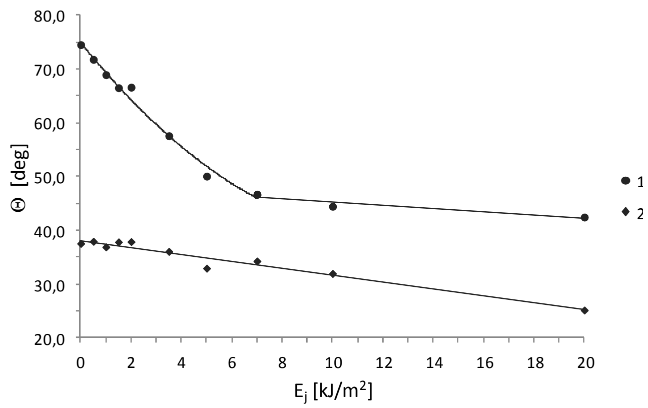


Fig. 2. Impact of unit value of modification energy (E_j) on water (θ_w) (1) or diiodomethane (2) wetting angle (θ_d) of samples modified in air

The surface free energy (SFE) of the tested samples was calculated with the Owens – Wendt method. Fig. 3 shows the values of a polar component (γ_s^p) and dispersive component (γ_s^d) of SFE and the result of SFE calculations for the samples modified in the air. The growth of the E_j value is accompanied by the growth of SFE of the PLA samples modified in the air. Growth in SFE is caused mainly by an increase in the polar component as polar groups are created strongly interacting with water molecules and improving wettability.

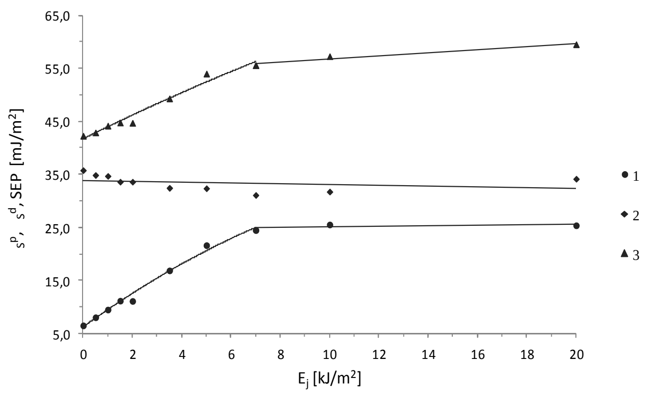


Fig. 3. Effect of unit value of modification energy (E_j) in the air of samples tested according to: (1) a polar component of surface free energy (SFE), (2) a dispersive component of SFE and (3) SFE values

Investigations into the oxidisation degree of the surface layer of PLA were performed with X-ray photoelectron spectroscopy (XPS) using the Escalab 210 electron spectrophotometer (VG Scientific, UK). An oxidisation degree (O/C) determined as a quotient of the number of oxygen and carbon atoms present in the tested SL (in percents) is shown in Fig. 4. As E_j increases, so increase the O/C values of the surface layer of PLA during modification in the air. Growth in O/C is a result of the higher share of oxygen groups the creation of which is initiated by free radicals reacting with oxygen from the environment and generated under the influence of energy of electrons colliding with the material being modified.

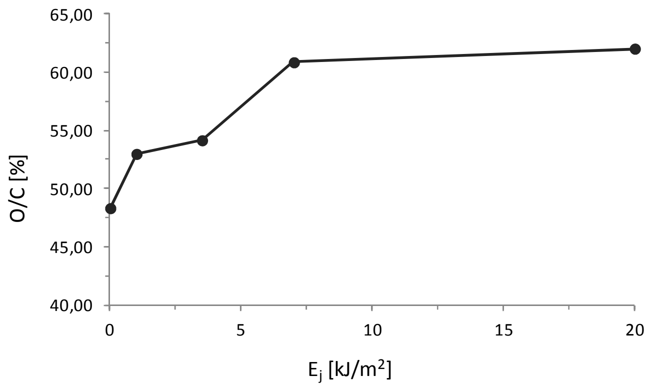


Fig. 4. Oxidisation degree (O/C) of the SL of the PLA samples modified in the air

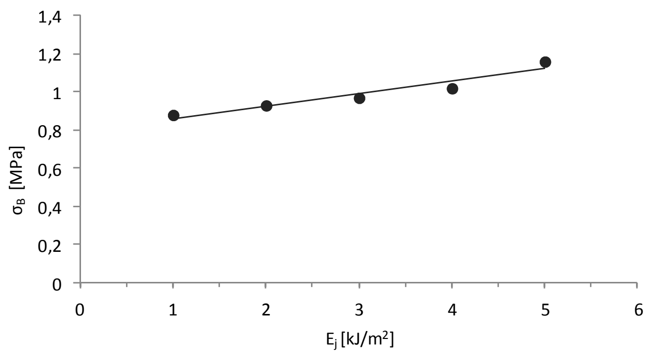


Fig. 5. Peel stress (σ_B) for joints of the PLA sample - Rapida F50RP paint modified in the air

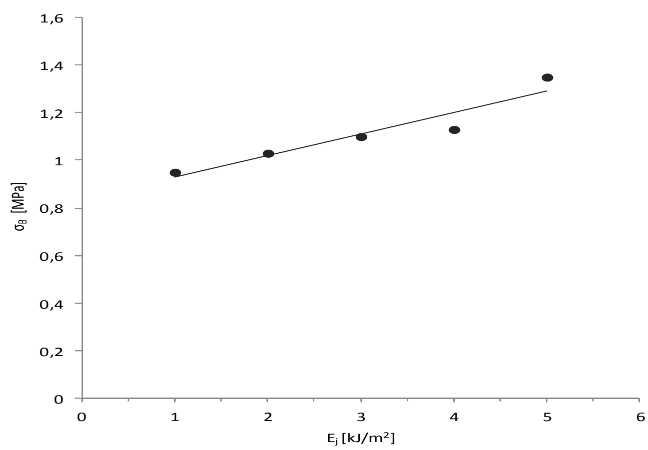


Fig. 6. Peel stress (σ_B) for joints of the PLA sample - Acrylic Enamel 2750 paint modified in the air

Adhesion investigations were carried out with the method of detaching an adhesive joint by means of the PosiTest AT device and with the method of detaching with adhesive tape. Rapida F50RP paint (Michael Huber, Poland) and Acrylic Enamel 2750 (Bondex, Poland) paint and Araldite 2011 epoxy glue (Huntsman, Switzerland) were used for the test. The results of the investigations are presented in Figs. 5 and 6. Twelve peel stress measurements were made for each E_j value. Two extreme values were rejected and the arithmetic mean of the other ten results were used as the result. Paint was completely peeled off the tested samples at the entire area of the glued measuring stamp during the tests in both cases. The adhesive joints were fracturing between the paint and the tested substrate in all the tested samples. The strength tests of the PLA–paint joint with a method of peeling off with adhesive tapes did not exhibit any damaged printing after detaching the tape, nor any traces of paint on such tapes. This indicates that the adhesion of the tested samples and paint meets the requirements for printing technology and that the strength of their adhesive joints improves under the influence of CT.

3.2. Remote Plasma Treatment

The method of generating plasma outside the modification zone, as opposed to the corona treatment method, consists in modifying a polymer material outside a plasma generation zone. A device for modification with this method is shown in Fig. 7.

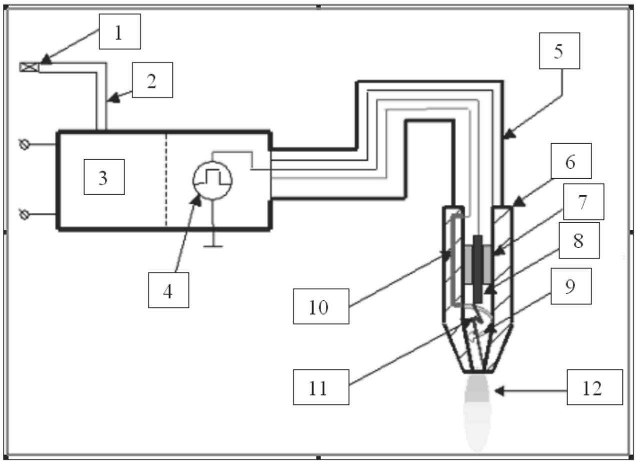


Fig. 7. Diagram of a plasma generating device outside the modification zone (1 - gas connection, 2 - gas supply, 3 - electricity and gas supply device, 4 - voltage generating set for supplying electrodes, 5 - flexible sheathing, 6 - earthed electrode, 7 - dielectric insulation, 8 - high voltage electrode, 9 - gas outlet, 10 - gas inlet, 11 - partial discharges, 12 - stream of plasma)

High voltage and process gas are supplied to a unit of discharge electrodes with flexible conduits, whereas air may also be used as the gas. A stream of gas removes active plasma molecules produced during partial discharges and diverts the molecules onto the surface of the material being modified through a specially shaped nozzle. A special advantage of such devices is the ease of generating plasma with different properties, using different gases. The devices can also be constructed as small portable devices (used mainly for modifying items with complex shapes), including hand-held devices, and also devices mounted in the holders of robots. There are many constructional variants of such devices.

3.3. Low Pressure Plasma Treatment

Plasma is a partially ionised gas or a mixture of gases composed of the equal (approximately) number of electrons and neutral atoms and particles of relevant gases, as well as photons of electromagnetic radiation. Ions, atoms and neutral particles can occur in excited and/or basic conditions. In the natural conditions of the Earth plasma is produced during atmospheric discharges, and it is the most common state of matter in the universe, distinct, however, from the low-temperature plasma discussed here by its composition and temperature. The plasma existing there is called high-temperature (hot) plasma as its temperature is around 10^6 K, and its particles are completely ionised. On the other hand, the temperature of cold, low-temperature plasma discussed in this paper is lower than 10^4 K and is generated during electrical discharges in gas [32, 35-39].

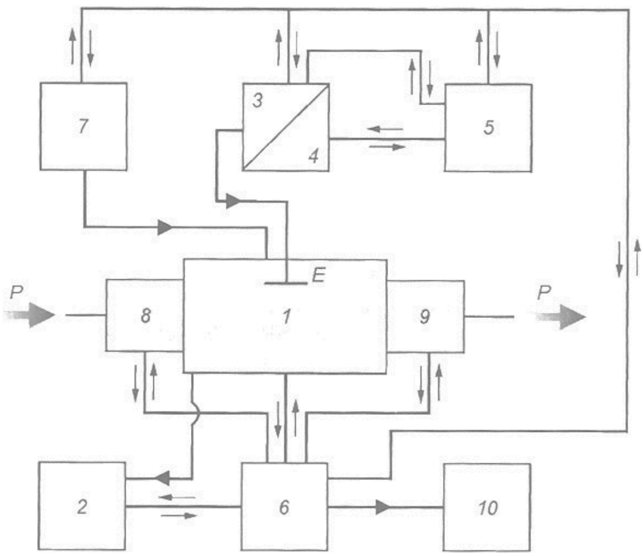


Fig. 8. Block diagram of a device for modifying the SL of materials: 1 – discharge chamber, 2 – unit generating lower pressure, 3 – generating set supplying discharge electrodes, 4 – impedance adjusting device, 5 – power control unit, 6 – automatic monitoring and control circuit, 7 – gas tank, 8 – supply unit, 9 – discharge unit, 10 – screen and printer, E – discharge electrode, P – stream of modified material [42]

Low-temperature plasma is formed under the influence of partial discharges taking place in a vacuum chamber where two electrodes are provided. The discharges are generated by a rapidly changing magnetic field in gas, most often in oxygen, nitrogen, helium, argon, chlorine and in the air [40, 41]. Low-temperature plasma, with its temperature lower than 10^4 K, interacts with the product being modified between several dozens of seconds to more than ten minutes. The pressure of gas in a vacuum chamber, called a discharge chamber, is low and is between 0.05 to 5 hPa. The average temperature does not exceed ambient temperature, whereas a concentration of electrons in plasma is between 10^{16} to 10^{18} electrons per cubic cm. A diagram of a device for modifying the SL of materials with plasma under a lower pressure is shown in Fig. 8.

Plasma is generated according to the following principle: a rapidly changing electromagnetic field generated between two electrodes placed in a vacuum chamber induces the vibrations of the molecules present in the inter-electrode area. The vibrations are accompanied by such processes as: ionisation, dissociation and excitation of molecules and atoms of gas. Electrons in an electromagnetic field gain much higher speeds than ions, atoms or gas molecules (as their mass is much lower) and, therefore, their kinetic energy is higher. The kinetic energy of the molecules of gas, atoms and ions reaches the values of around 10^{-2} eV and is between 10^2 to 10^4 times lower than the kinetic energy of electrons. For this reason such energy is not of any major significance in the plasma generation process and does not cause marked changes to the SL of materials. A kinetic energy of electrons is usually between several to more than ten electronovolts and is sufficient for breaking convalescent bonds in polymer micromolecules. This leads to changes in the SL of the material and to the development of partial discharges [43]. The following processes occur while modifying the SL of materials with low-temperature plasma [44]:

- impurities are removed from the surface and SL of the material. The operating time necessary for plasma to clean the surface of material is tens of seconds, and unit power required for this purpose is several dozens of W/m^2;
- SL etching to remove part of the material (so-called weak boundary layer) and pieces of the amorphous phase. This process is especially important when glued joints are made, as surface roughness is increased as a result, thus the contact surface area between the material and paint or glue. A system with high adhesive strength is next created after anchoring them in the substrate;
- netting of macromolecules in the SL contributing to improved adhesive strength of two-phase systems. A structure strongly attached to the substrate is then formed and resistant to the activity of thermal energy, featuring high mechanical strength and inhibiting the breaking of adhesive joints;
- new chemical structures are created, in particular ketone, aldehyde, hydroxyl and carboxyl groups, under the influence of free radicals, oxygen and water steam. The groups change the chemical properties of the SL. In addition, plasma polymerisation can occur as a result of which a thin, insoluble, strongly netted layer of polymer is produced, acting as a good barrier for gases and liquids. The properties of the layer depend to a large extent on the type of gas in a discharge chamber.

The essential conditions of the SL modification process of materials by means of low-temperature plasma: (1) the time plasma acts on the material, (2) unit energy of partial discharges (J/m^2) and unit power of partial discharges (W/m^2), (3) temperature, pressure and type of gas in a discharge chamber, (4) electric voltage and frequency of partial discharges, (5) temperature of the modified material, (6) discharge chamber dimensions.

3.4. Laser Treatment

A group of the latest devices enabling to modify the SL of polymer materials is represented by lasers. Their special advantages can be used for the very accurate modification of small areas with complex shapes occurring for example when producing modern electronic circuits. A separate area of applications for laser modification can be polymer materials used in medicine, where sterilisation is also needed apart from changing the properties of the SL. As opposed to the methods of modifying the SL of polymer materials known to date, however, laser modification is a new method, still in the phase of basic research [45]. The laser modification of the SL of polymer materials allows to change precisely different properties of this layer, mainly such as: wettability and SFE (by implementing polar function groups, chiefly in the oxidisation process), degree of polymer netting and the type of the geometric structure of the surface, without changing at the same time the properties of the material underneath this layer [46]. The laser modification process is simple, easy to control and environmentally secure. The physiochemical phenomena associated with the process are not fully identified, yet and intensive scientific research into this area is continued [47-50]. Considering the many types of lasers available at the market, excimer lasers are characterised by advantageous properties due to modification to the SL of polymers [51]. Excimer lasers operate within the range of ultraviolet radiation with short-lived impulses. This radiation is strongly absorbed by the majority of polymers. Ultraviolet radiation with the short duration of impulses is able to initiate photochemical reactions in a polymer material without causing heat damage to the material. Laser irradiation can be carried out using an energy higher or smaller than the energy of the ablation threshold of a polymer material. Radiation with an energy not causing material ablation is used to improve adhesive properties [52-54]. Table 2 presents our tests of wettability and free surface energy of samples made of PC (Lexan 143 R, GE Plastics, USA), PET (Elpet-A, Boryszew SA, Poland) and PS (Owispol 945 E, Dwory S.A. Oświęcim, Poland), whereas Fig. 9 presents changes to their geometric structure caused by radiation with the different number of ArF laser impulses.

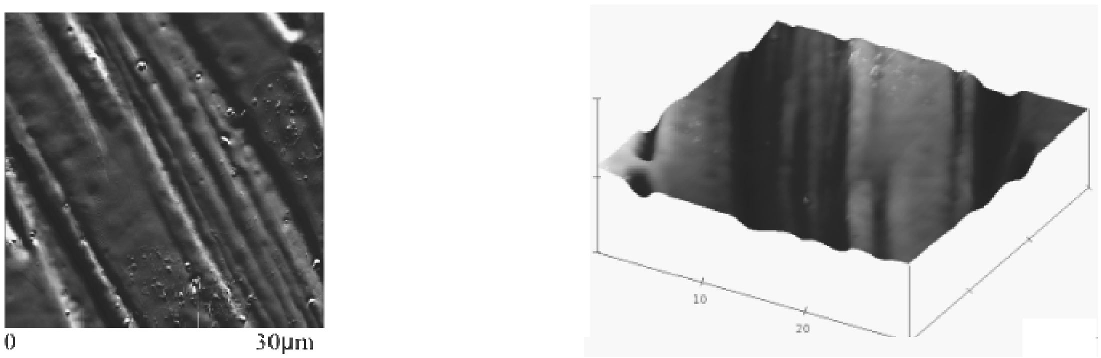
Table 2.
Angle values of wetting with water ($\square_w$), with diiodomethane ($\square_d$), and surface free energy (SFE) of polycarbonate PC, poly(ethyl terephthalate) PET and polyesterine PS irradiated with the different number (N) of laser impulses with Ej = 6 mJ/cm^2

N	$\square_w$	$\square_d$	SEP	Material
0	91.2	43.0	38.2	PC
10	90.1	42.1	38.7	
100	77.9	40.9	40.1	
500	74.1	34.2	43.8	
1000	73.3	33.5	44.4	
2000	67.1	33.1	46.2	
0	79.1	50.3	35.8	PET
10	78.6	50.0	36.0	
100	78.0	47.1	37.8	
500	74.4	43.3	40.3	
1000	70.1	36.1	44.2	
2000	66.9	32.9	46.2	
0	104.0	77.2	19.1	PS
10	101.1	71.0	22.3	
100	100.3	66.9	24.6	
500	103.9	33.2	46.8	
1000	103.3	33.0	46.8	
2000	107.0	29.4	50.9	

An oxidisation degree (O/C) of the surface layer of polycarbonate (PC), poly(ethyl terephthalate) (PET) and polyesterine (PS) irradiated with the different number (N) of laser impulses is presented in Fig. 10. The degree of oxidisation is growing in all the tested samples. The character of such changes is similar in PET and PC, which can be described with exponential dependencies. Increase of O/C in PC is higher than in PET and the saturation level is reached faster. Increase in the value of O/C in PS is approximately linear.

Very intensive changes to the chemical and geometric structure of the irradiated polymer materials can be induced with an energy of laser impulses higher than the ablation threshold, and chemical reactions of additional components occurring in such materials can be initiated. Such method of laser modification is used for electroless metallisation of polymer materials and enables to create differently shaped conductor tracks. Thermal degradation of polymer material is seen as a result of laser radiation acting on the surface and surface layer of the polymer material containing an appropriate precursor and metal clusters are produced (the source of which is the precursor), initiating and catalysing the autocatalytic process of such material's metallisation [55,56].

a)



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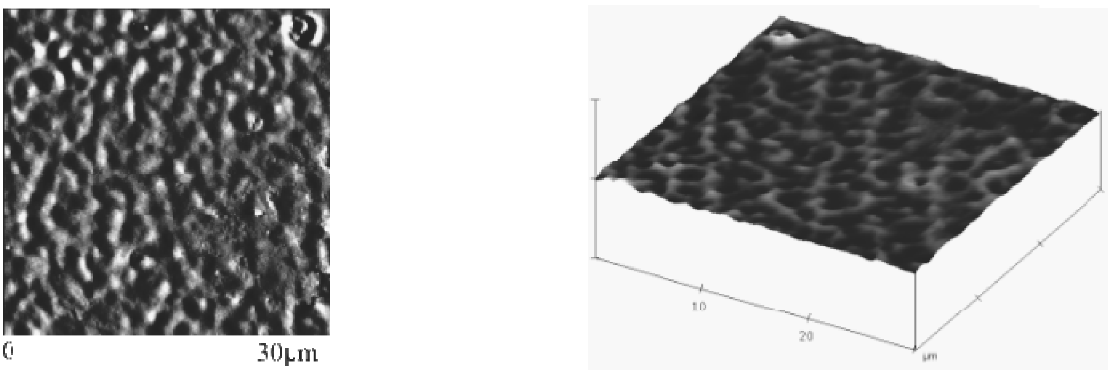


c)

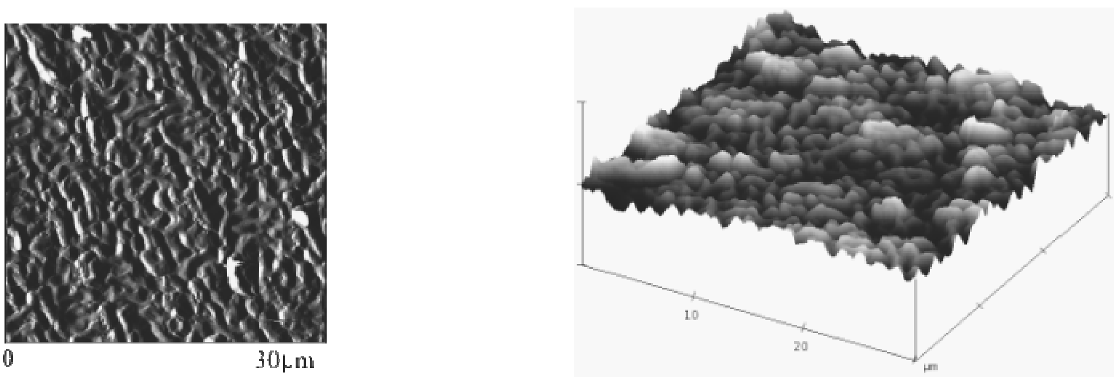


Fig. 9. Two- and three-dimensional images of samples surface: a) PC; b) PET; c) PS, irradiated with 2000 impulses of laser (E_j=6 mJ/cm^2)

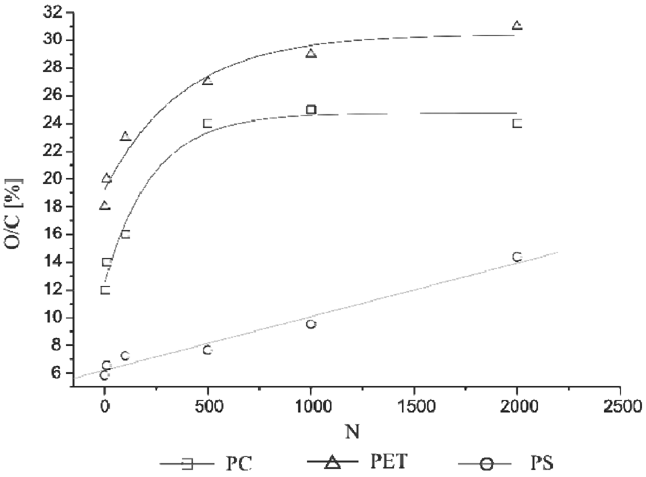


Fig. 10. O/C dependence of the surface layer of PC, PET and PS samples irradiated using the different number of laser impulses (E_j = 6 mJ/cm^2)

While seeking new polymer materials for the autocatalytic metallisation, metallisation precursors (other than used so far) were introduced as part of own works at the stage of polymer material processing. A new polymer composite has been established as a result of the research with a polyamide 6 matrix containing two metallisation precursors: copper acetylacetonate (II) $Cu(acac)_2$ and copper oxide (II) CuO. Excimer laser ArF (λ = 193 nm) was used to modify the SL and activate the surface of a new composite. Impulses with the unit energy (E_j) of irradiation of, respectively, E_{j1} = 40 mJ/cm^2 or E_{j2} = 120 mJ/cm^2 were used when modifying such composite. The composite was modified with the different number of impulses of: 5, 10, 50, 100 and 500.

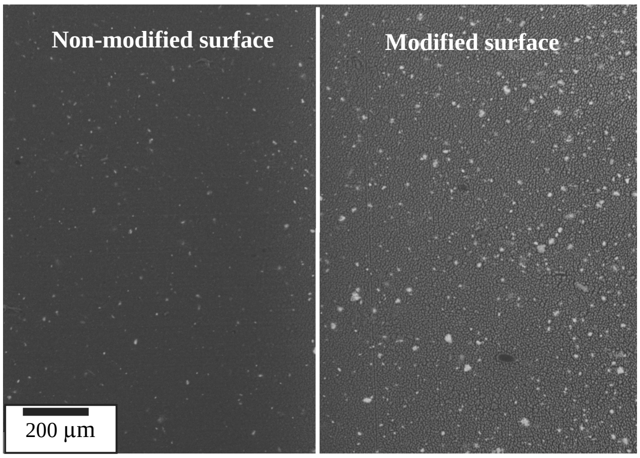
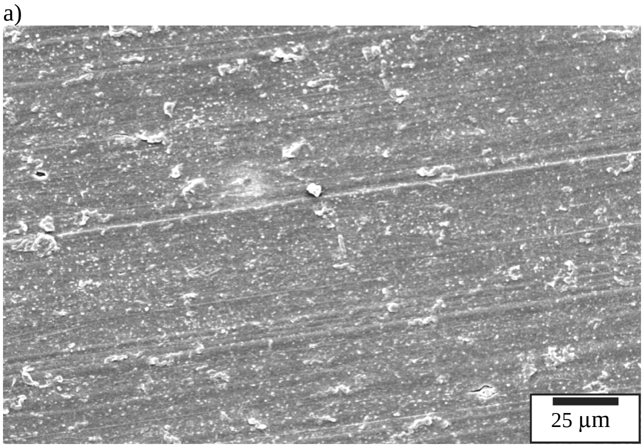


Fig. 11. SEM image of the surface of the new composite not irradiated and irradiated with 500 impulses of laser with the energy of 120 mJ/cm^2

SEM investigations revealed that the surface of the composite is undergoing marked changes as a result of laser modification. Fig. 11 shows a clear boundary of laser impulses activity. An unmodified surface of the sample is characterised by small roughness with visible scratches being a replica of the injection moulding walls (Fig. 12a). The surface of the irradiated sample is largely modified. Any surface irregularities being a replica of the injection moulding surface disappear and new cone-like structures typical for the ablation process are formed (Fig. 12b).

a)



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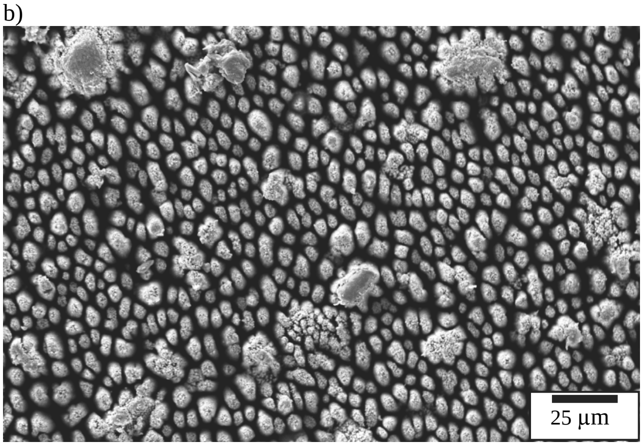


Fig. 12. SEM image of a) unmodified and b) modified surface of new composite

A thickness of the modified SL depends on the number of laser impulses (Fig. 13). Growth in the number of impulses is leading to the deeper ablation of the SL of a new composite. A thickness of the modified layer can be estimated based on the images of fractures of the samples. The thickness for 50 laser impulses is approx. 4 μm, whereas for 500 impulses it is approx. 25 μm. The comparison shows that if the number of impulses is increased, this has a decisive effect on increasing the thickness of the modified layer and on increasing surface roughness.

The laser irradiation of a composite developed contributes to the decomposition of metallisation precursors and metallic copper clusters are produced. An image of a quantitative EDS analysis of the new composite (Fig. 14) confirms this process. Copper atoms contained in the SL of the new composite initiate and catalyse its metallisation process. This enables to deposit a layer of metallic copper on the surface of this composite, and such layer is deposited already after 5 laser impulses (Fig. 15).

a)

b)

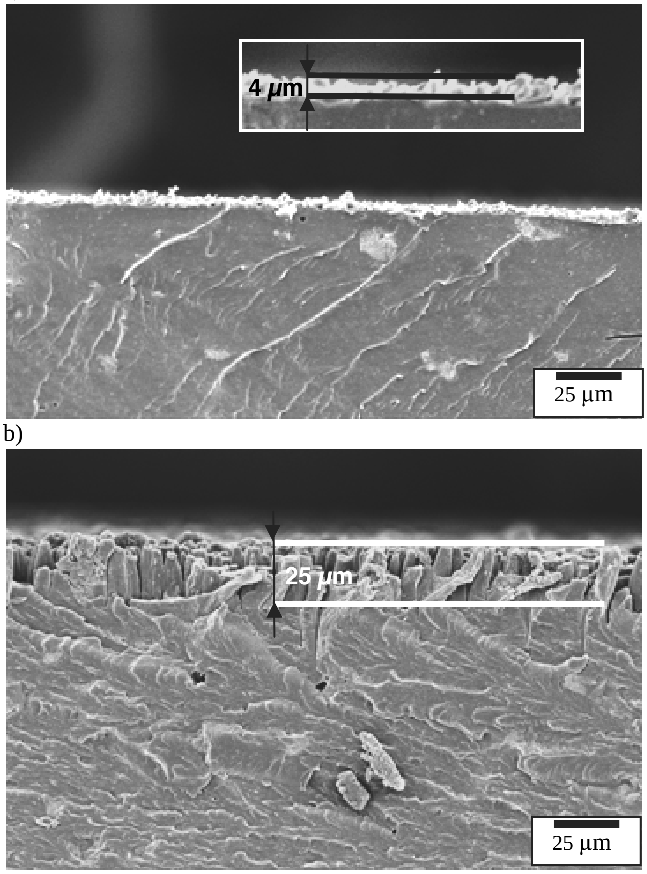


Fig. 13. SEM images of fractures of the new modified composite: a) 50 or b) 500 laser impulses with the energy of 120 mJ/cm^2

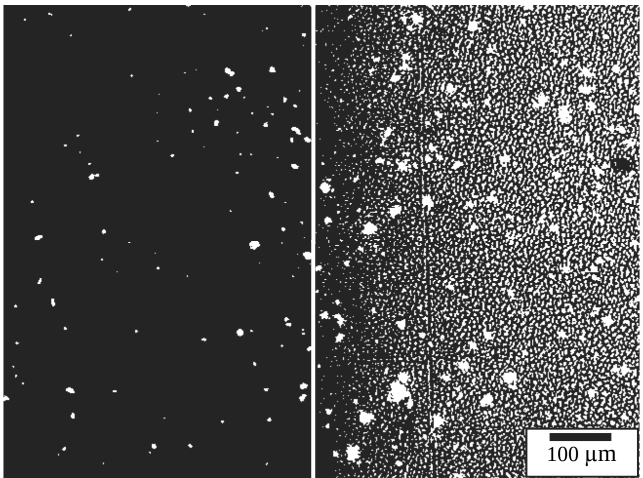


Fig. 14. Image of a quantitative analysis of Cu atoms content in the surface layer of a new composite partially irradiated with 500 laser impulses with energy of 120 mJ/cm^2 (line marks a laser impulses activity boundary)

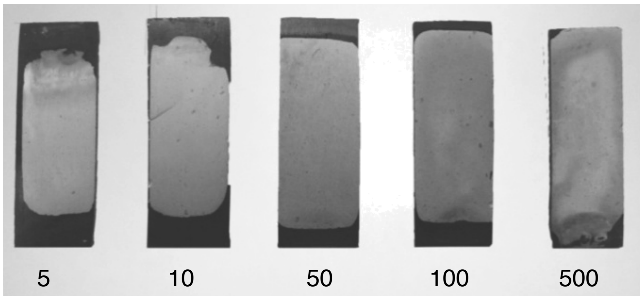


Fig. 15. Effects of metallising a new composite irradiated with the unit energy of 120 mJ/cm^2 and with the different number of impulses (the number of impulses is identified with a digit under each of the samples presented). Scale 1:1

The further advancement of laser SL modification methods for the purpose of polymer materials metallisation will contribute to the miniaturisation of electronic components. Functional components that may be designed and produced using laser methods will reduce the number of individual parts and shorten their manufacturing process.

3.5. Electron-Beam Irradiation

Irradiation has been used for over 50 years for modifying the volumetric and surface properties of polymer materials [57-60]. The impact of irradiation, mainly electron-beam one, on changes to the surface properties of polymer materials was a subject of extensive scientific research [61, 62]. When a polymer material is irradiated, its SL is oxidised in the air and this increases wettability and growth of the SFE, thus improving the adhesive properties of this material. Such irradiation can also be performed in the atmosphere of reactive gases, in particular such as O_2 or NH_3, to produce polar functional groups in the surface layer of the modified material.

The subject of the research presented in [62] were composites differing both, in the composition of polymers used for manufacturing them as well as in mass fraction of compatibilisers. Low density polyethylene (LDPE) Malen-E FABS 23-D0022 (Basell Orlen Polyolefins Płock, Poland), high density polyethylene (HDPE) Hostalen ACP 5831 D (Basell Orlen Polyolefins Płock, Poland), isotactic polypropylene (PP) Malen P F 401 (Basell Orlen Polyolefins Płock, Poland), polystyrene (PS) Owispol 945 E (Dwory S.A. Oświęcim, Poland), amorphous poly(ethylene terephthalate), (PET) Elpet-A, (Boryszew SA, Oddział Elana Toruń, Poland) and a compatibiliser in form of trimethylolpropane triacrylate (TMPTA) (Sigma Aldrich, Germany) were used for producing them. 2 types of composites were obtained by extruding such polymers: (a) a three-component composite, mass fraction of 33.4% LDPE, 33.3% HDPE and 33.3% PP, hereinafter called composite A, containing, respectively, 1% (A1), 2% (A2) or 3% (A3) by weight of TMPTA and (b) a five-component composite, mass fraction of 24% of LDPE, 23% HDPE, 21% PP 15% PS and 17% PET, hereinafter called a composite B containing, respectively, 1% (B1), 2% (B2) or 3% (B3) by weight of TMPTA.

The tested samples were irradiated at the Institute of Nuclear Chemistry and Technology, Warsaw, using an UELW-101-10 accelerator (NPO TORYJ, Russia). The samples of the mixtures produced were placed on a conveyor moving with a finely adjusted speed. A dose of electron irradiation absorbed by the samples was dependent on such speed. The samples were radiated with the doses of 25, 50, 100 and 300 kGy. The values of the doses were controlled with the calorimetric method. The average values of wetting angles for particular components are presented in Table 3. The data presented shows that that a wetting angle is decreasing monotonically as the irradiation doses of the tested components are growing. The effect of an electron irradiation dose on changes to the SFE of particular components is shown in Table 4. SFE changes occurring under the influence of electron irradiation are similar for all components. The dose is growing monotonically within the whole range of the doses applied, with the highest increase seen within the range of doses up to 50 kGy, and the slowest increase within the range of 50 to 100 kGy, and much slower for doses above 100 kGy. An increase in wettability and SFE occurring due to electron irradiation is caused mainly by the implementation of polar oxygen groups in the surface layer of the radiated composites. Table 5 provides the oxidisation degree values of the investigated composites, irradiated with the different doses of energy. The data shown in Table 5 provides that the TMPTA compatibiliser is substantially influencing the growth of the oxidisation degree of the SL of the irradiated composites. This influence derives from the chemical structure of TMPTA containing double bonds that are breaking under the influence of electron irradiation. The radicals produced as a result react with the oxygen present in the SL and increase the oxidisation degree of this layer.

Table 3.
Value of wetting angle with water of composites irradiated with different doses of energy

Type of composite	Irradiation dose, kGy				
	0	25	50	100	300
A	106.6	102.4	97.3	90.8	87.3
A1	105.7	95.2	85.1	80.9	78.1
A2	104.2	86.8	84.0	80.8	77.4
A3	101.2	84.0	82.2	71.1	66.9
B	104.0	101.3			
B1	108.5	94.1	92.2	87.6	82.5
B2	105.3	91.5	85.8	86.5	83.4
B3	104.5	96.0	89.1	84.4	80.2

Table 4.
SFE values (mJ/m^2) of composites irradiated with different doses of energy

Type of composite	Irradiation dose, kGy				
	0	25	50	100	300
A	19.1	21.4	24.5	28.4	30.4
A1	20.2	30.6	32.1	34.0	36.0
A2	19.6	30.6	31.8	34.3	36.3
A3	22.6	32.3	33.7	40.2	42.5
B	20.7	22.3	26.4	27.6	29.7
B1	17.8	26.4	27.7	30.4	33.6
B2	19.9	28.3	31.7	31.3	33.1
B3	20.2	25.2	29.4	32.7	35.1

Table 5.
O/C (%) values of composites irradiated with different doses of energy

Type of composite	Irradiation dose, kGy				
	0	25	50	100	300
A	0.3	1.6	2.0	4.3	7.3
B	1.9	3.9	4.3	5.2	6.4
A2	1.7	5.1	10.1	11.6	19.0
B2	3.9	5.7	7.1	8.4	11.2

4. Development perspectives of polymer surface layers modification

4.1. Polymer surface layers modification versus surface engineering development

The anticipated development and strategic position of polymer surface layers modification technologies against surface materials engineering was determined using the reference data acquired whilst performing technology foresight for materials surface engineering [23, 10]. Over 300 independent domestic and foreign experts representing scientific, business and public administration circles have taken part in the foresight at different stages of the efforts. The experts have completed approx. 650 multi-question surveys and held thematic discussions during 10 expert panels. An analysis of development prospects has been performed in the initial phase of research for approx. 500 groups of detailed technologies including a state-of-the-art review, technological review and a strategic analysis with integrated methods. The following scientific and research methods were used for this purpose: trends extrapolation, environment scanning, STEEP analysis, SWOT analysis, expert panels, brainstorming, benchmarking, multi-criteria analysis, computer simulations and modelling, econometric and statistical analysis. 10 critical technologies were selected in 14 thematic areas as a result of the works performed. A group of 140 critical technologies were analysed in detail for three iterations of the e-Delphix method according to the e-foresight concept [25]. The polymer surface layers modification technologies were one of 14 thematic areas analysed under this foresight research.

Investigations with the e-Delphix method with the sample size of 198 have revealed the robust strategic position of polymer surface layers modification technologies among other materials surface engineering technologies. 38% of the surveyed claim that the technologies have good prospects of industrial applications. 41% of the respondents maintain that numerous scientific and research works will be devoted to such technologies in the nearest 20 years. 43% of the surveyed point out that the thematic area of “Surface engineering of polymers” is crucial and its significance should be absolutely on the rise so that an optimistic scenario of the country's/Europe/World development – "Race won" – can come true. The scenario provides that the potential available is exploited adequately for fulfilling the strategic development objectives; people are, statistically, better off; social attitudes are optimistic and prospects for the coming years bright. 63% of the surveyed think that the importance of laser technologies in relation to other

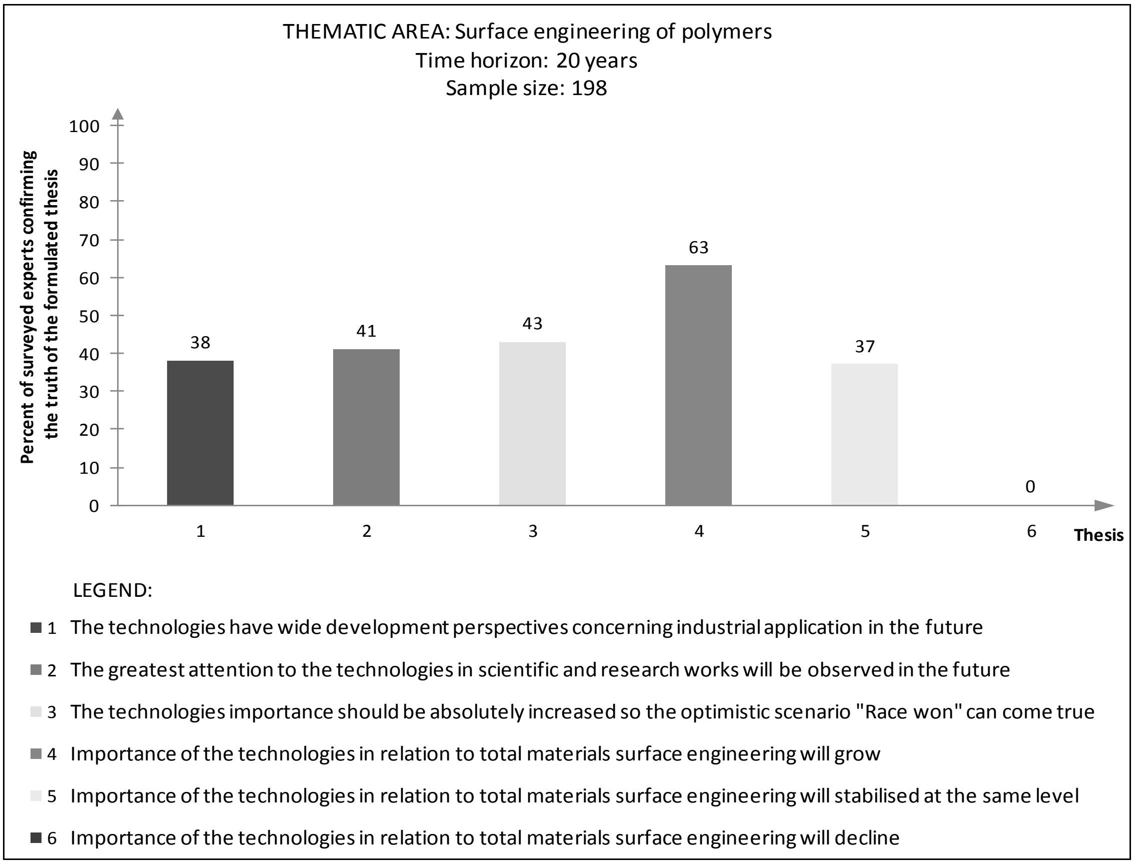


Fig. 16. Strategic position of polymer surface layers modification technologies versus other materials surface engineering technologies

materials surface engineering technologies will be growing, whereas 37% maintain it will remain on the same level, and no one said that this role would diminish over the nearest 20 years. The promising outcomes of technology foresight, elaborated based on the reference data, point, therefore, to the predicted important role of polymer surface layers modification technologies for the development of materials surface engineering overall (mezo scale) and for the development of the entire national/European/global economy (macro scale). The discussed results of technology foresight, established according to the opinions of the experts expressed during investigations with the e-Delphix method, presenting the position of polymer surface layers modification technologies versus overall materials surface engineering, is shown in Fig. 16.

4.2. Strategic position of the selected polymer surface layers modification technologies

The results of the foresight research described in this paper include the assessment of the potential and attractiveness of the analysed technologies against a micro- and macro-environment. The assessment was performed based on key experts' opinions expressed with a universal scale of relative states consisting of ten points and a recommended strategy of managing a relevant technology together with the predicted strategic development tracks resulting from such assessment.

The individual technologies have been evaluated by the experts for their: business, economic, humane, natural and system attractiveness as well as for their: creational, applicational, qualitative, developmental and technical potential. A weighted average for the criteria considered (attractiveness and potential) was calculated using a multi-criteria analysis, and a result obtained for the individual groups of technologies was entered into the dendrological matrix of technologies value (Fig. 17). The base technology of corona discharges (A) and the mature technology of polymer surface layer modification by means of low-temperature plasma in the conditions of lower pressure (C) were found in the field of rooted dwarf mountain pine representing a high potential and limited attractiveness. A prototype technology of laser modification of polymer surface layers (D) with very promising development prospects, especially in the electronic and computer industry, the evolving technology of polymer materials surface layer modification with plasma generated outside the modification zone (B) and a prototype technology of modification of a polymer materials surface layer with a high-energy electron beam (E) was found in the soaring cypress field corresponding to attractive technologies with a limited potential, so additional investigations strengthening such technologies and representing groundwork for future, broad industrial applications are necessary.

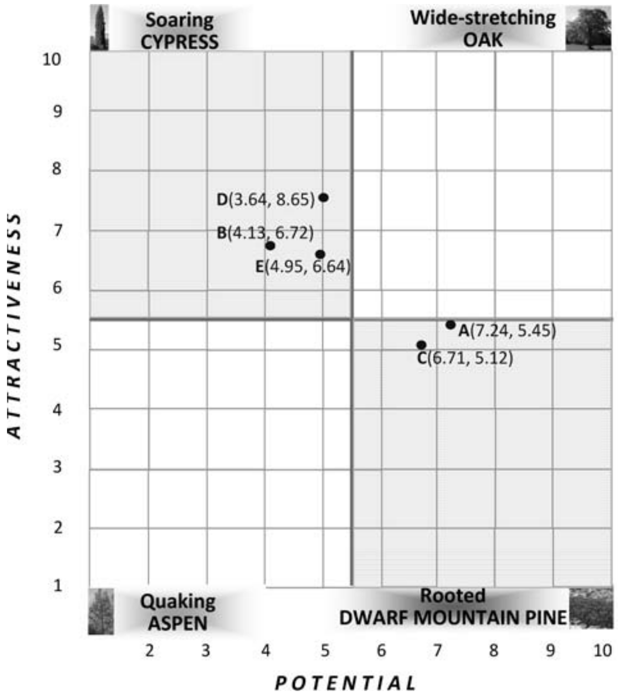


Fig. 17. The dendrological matrix of technology value prepared for, respectively: (A) Corona Treatment, (B) Remote Plasma Treatment, (C) Low Pressure Plasma Treatment, (D) Laser Treatment, (E) Electron-Beam Irradiation

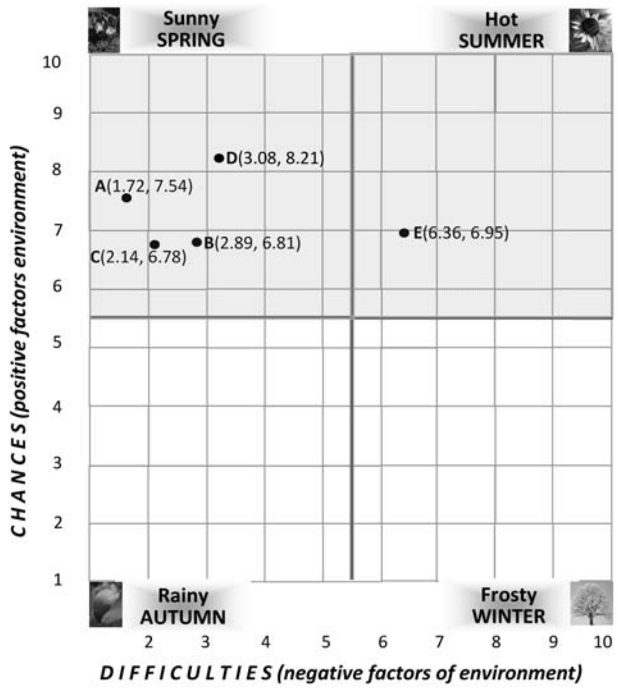


Fig. 18. The meteorological matrix of environment influence prepared for, respectively: (A) Corona Treatment, (B) Remote Plasma Treatment, (C) Low Pressure Plasma Treatment, (D) Laser Treatment, (E) Electron-Beam Irradiation

Positive and negative environment influence on the relevant groups of technologies is presented graphically with a meteorological matrix of environment influence. The results of a multi-criteria analysis of the experts' scores acquired in the survey-taking process were entered into the matrix, as shown in Fig. 18. The environment of most of the investigated technologies (A-D) is unusually supportive and provides ample opportunities and very few difficulties, therefore was placed in the sunny spring field. The technology (E) consisting in the modification of the polymers surface layer with a high-energy electron beam is in a stormy environment, as it is accompanied by numerous opportunities such as new applications and opportunities to enter new markets, as well as by difficulties related to high investment costs, necessity to employ highly qualified staff, a strong position of buyers and suppliers in the supply chain, as well as a high level of specialisation and applicability in relation to a narrow group of products.

Using the pre-defined mathematical relationships, the specific numerical values provided in the dendrological and meteorological matrix [2x2] were moved to the technology strategy matrix dimensioned [4x4]. The matrix presents graphically the position of the investigated polymer surface layers modification technologies according to their values and intensiveness of environment influence, by indicating the appropriate action strategy (Fig. 19). The development prospects of the technology of (A) corona discharge and (C) polymers surface layer modification by means of low-temperature plasma in the conditions of lower pressure was rated 9 points in a universal scale of relative states consisting of 10 points and were found in the field of dwarf mountain pine in spring. It is recommended in relation to these technologies to exploit good market conditions while enhancing the attractiveness of a high potential technology, especially in terms of modernising, automating, computerising and promoting it intensively to maintain competitive edge. The technology D (4.7, 8.8) of laser modification of polymer surface layers was rated equally high (9 points), and 8 points were assigned to the technology B (4.3, 8.6) corresponding to the modification of the polymers surface layer with plasma generated outside the modification zone. Both technologies were found in the cypress in spring field, with the development strategy envisaging investigations, improvements and additional investments for an attractive technology taking advantage of the robust market circumstances. The development prospects of the technology (E) of modifying the surface layer of polymer materials by means of a beam of high-energy electrons were rated as moderate (6 points) due to a stormy environment bringing both, many opportunities but also difficulties. The cypress in summer strategy, appropriate for the technology (E), consists of strengthening the potential of an attractive technology in uncertain environment conditions, of individual risk assessment and, depending on the outcome, fighting fiercely for customers or phasing out the technology slowly from the market if difficulties outpace opportunities offered by the environment.

Strategic development tracks for the individual specific technologies representing a forecast of their development for the years of 2015, 2020, 2025 and 2030 according to the three variants: optimistic, pessimistic and the most probable one, were next entered into the matrix of strategies for technologies. Simplified charts presenting the results of all the investigations carried out for the five analysed groups of technologies corresponding to polymer surface layers modification using different physical processes are shown in Figs. 20a-e.

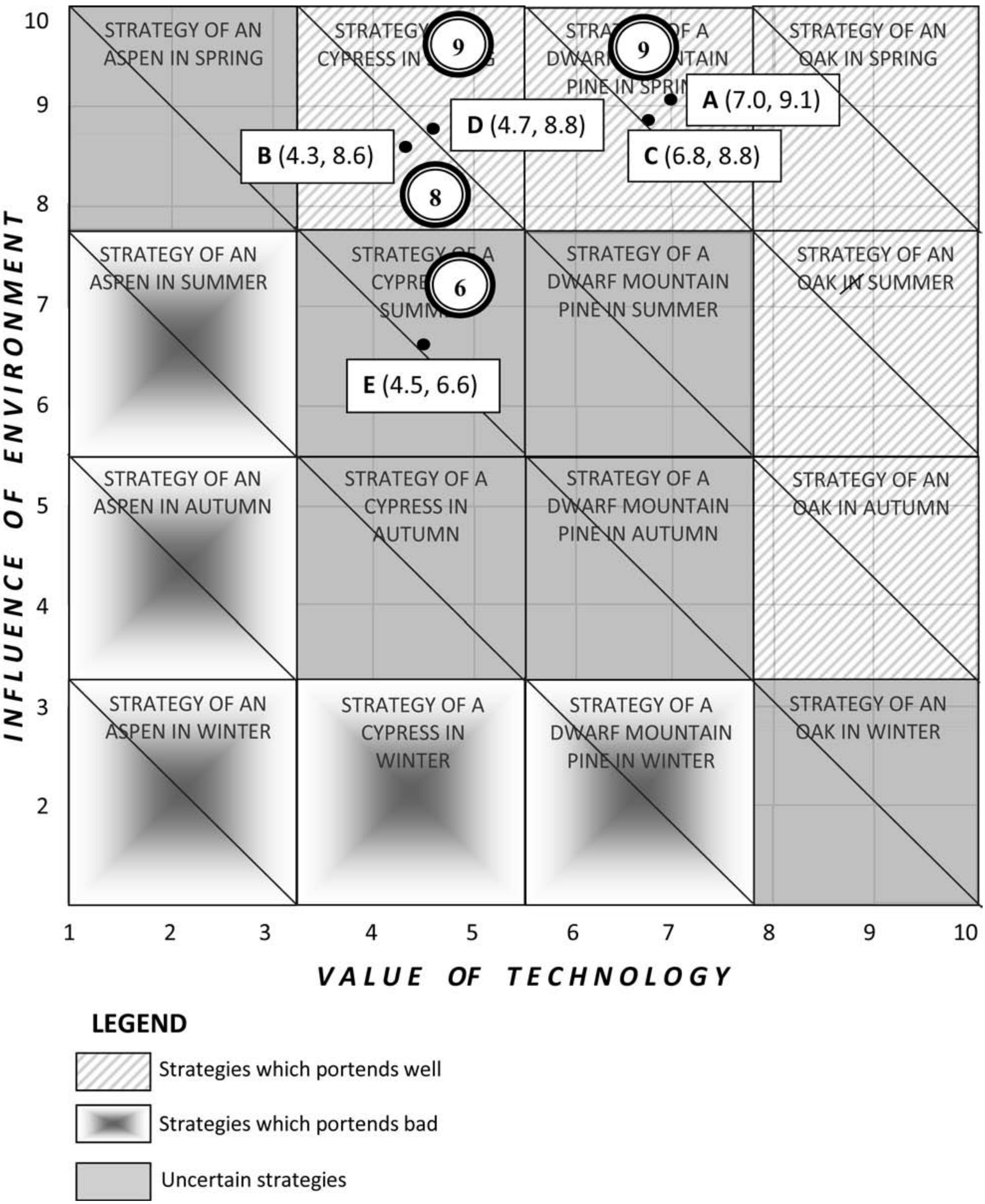
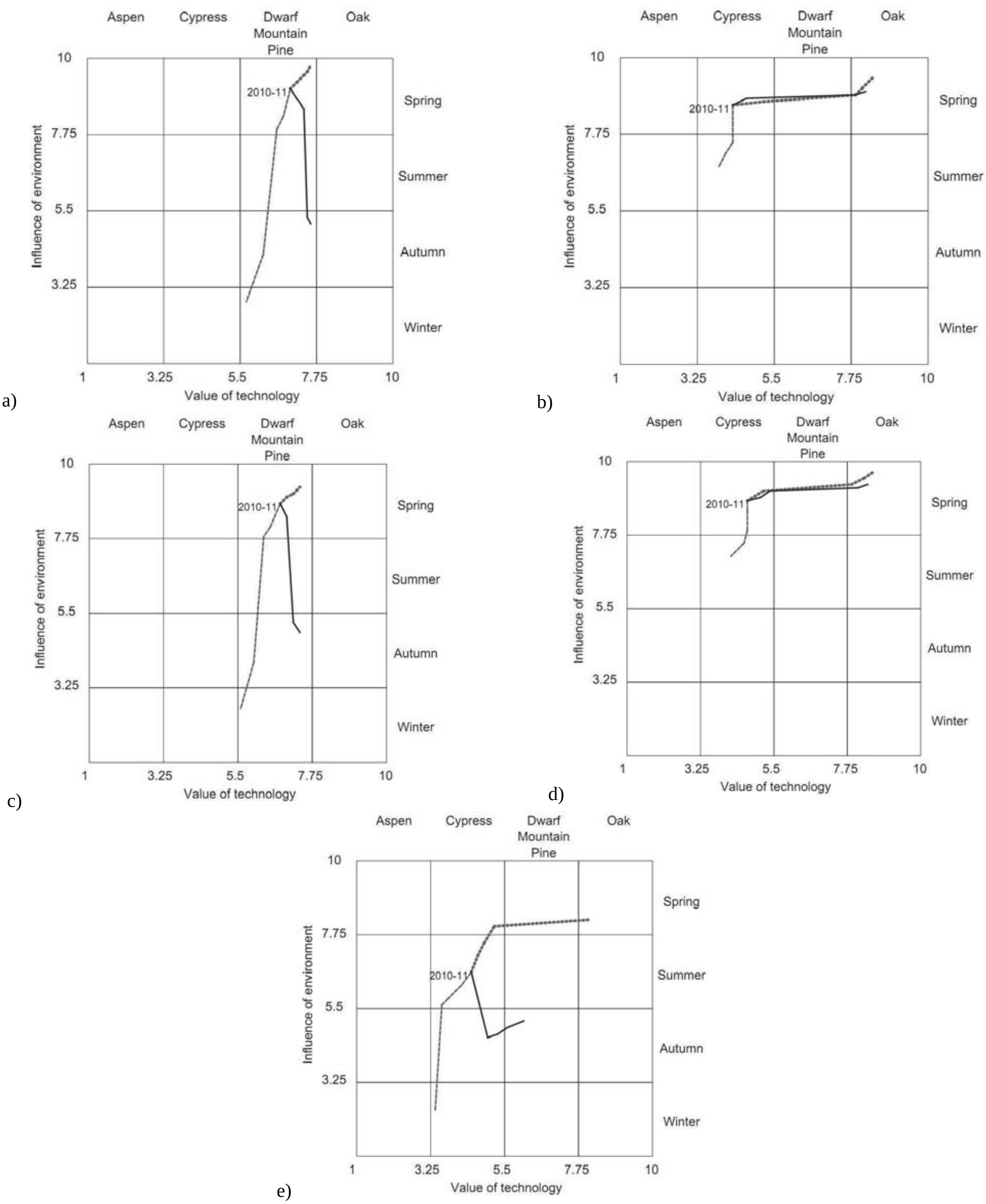


Fig. 19. The matrix of strategies for technologies prepared for, respectively: (A) Corona Treatment, (B) Remote Plasma Treatment, (C) Low Pressure Plasma Treatment, (D) Laser Treatment, (E) Electron-Beam Irradiation



Types of strategic development tracks:
•••••• Optimistic
▬▬ Neutral
▬ ▬ Pessimistic

Fig. 20. Strategic development tracks prepared for, respectively: (A) Corona Treatment, (B) Remote Plasma Treatment, (C) Low Pressure Plasma Treatment, (D) Laser Treatment, (E) Electron-Beam Irradiation

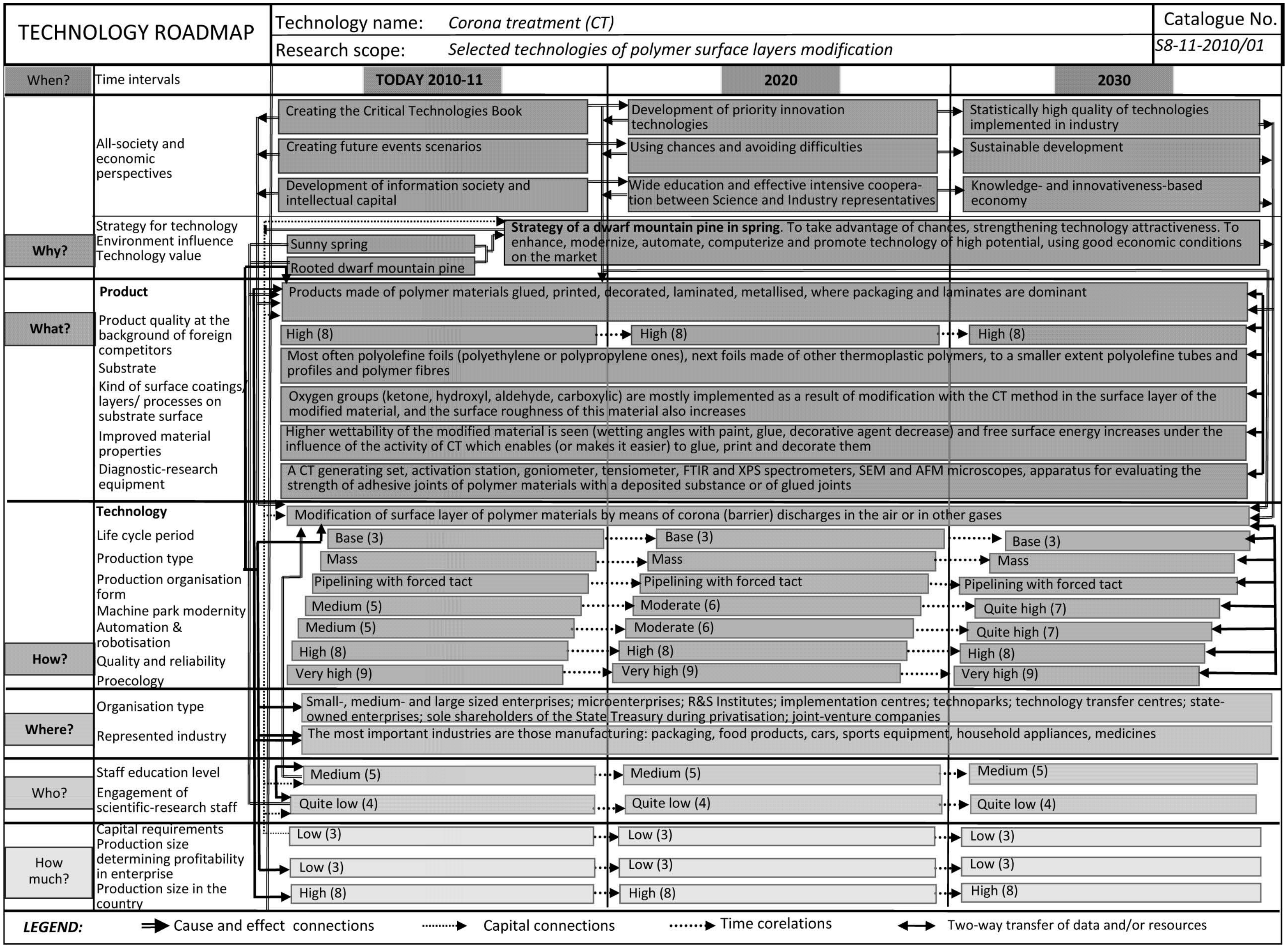


Fig. 21. The technology roadmap prepared for prepared for the (A) technology, i.e. Corona Treatment

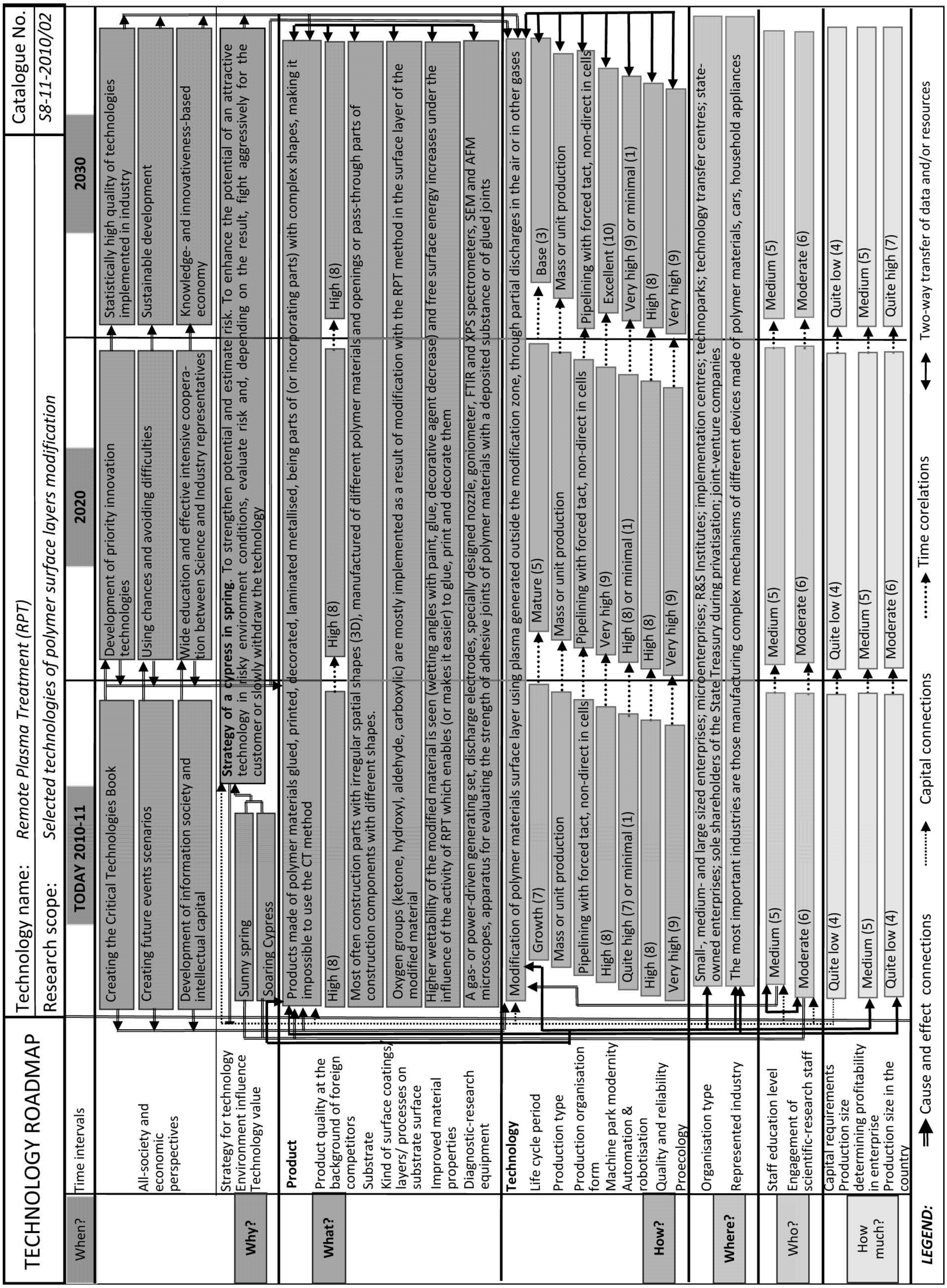


Fig. 22. The technology roadmap prepared for the (B) technology, i.e. Remote Plasma Treatment

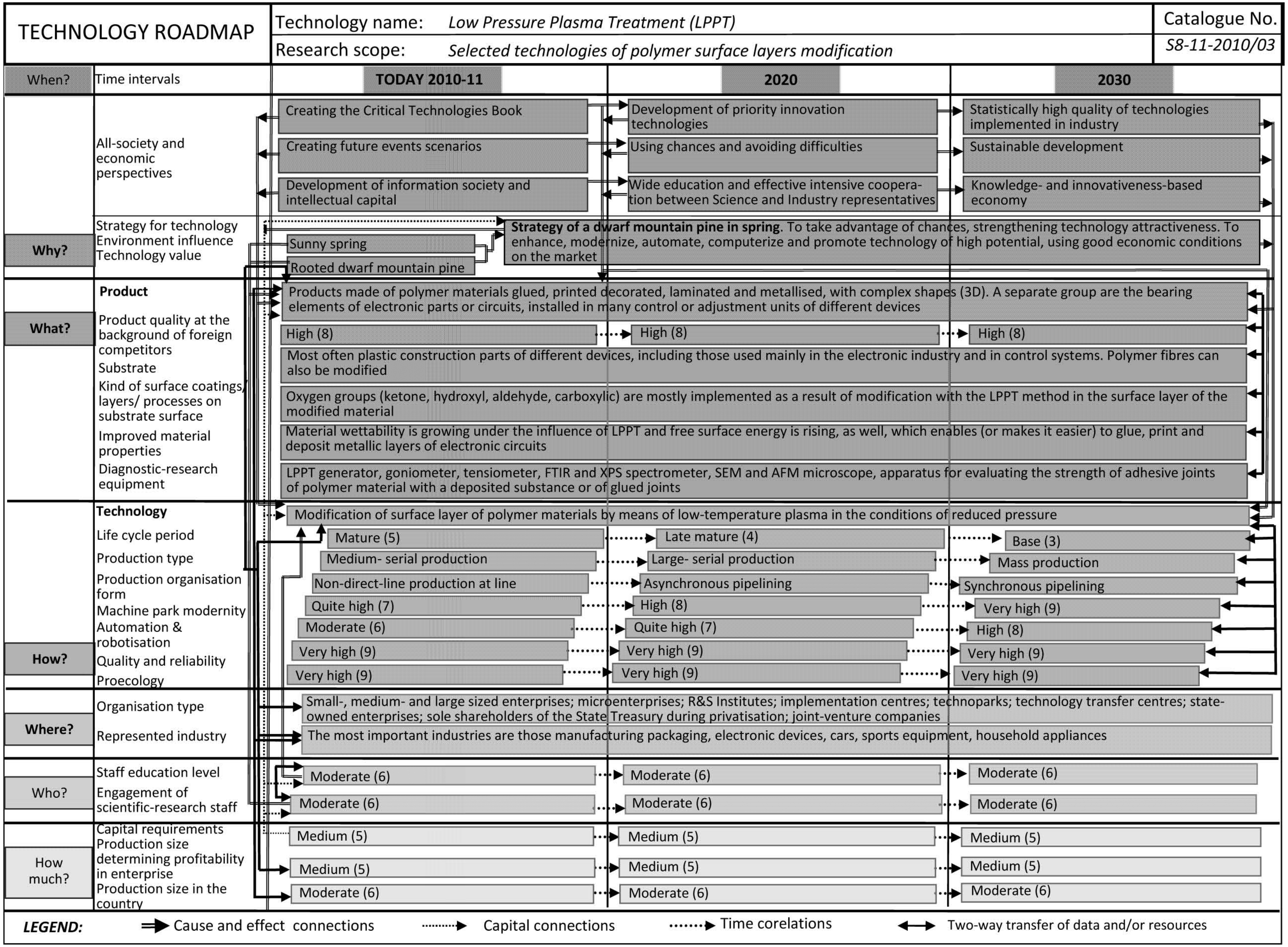


Fig. 23. The technology roadmap prepared for the (C) technology, i.e. Low Pressure Plasma Treatment

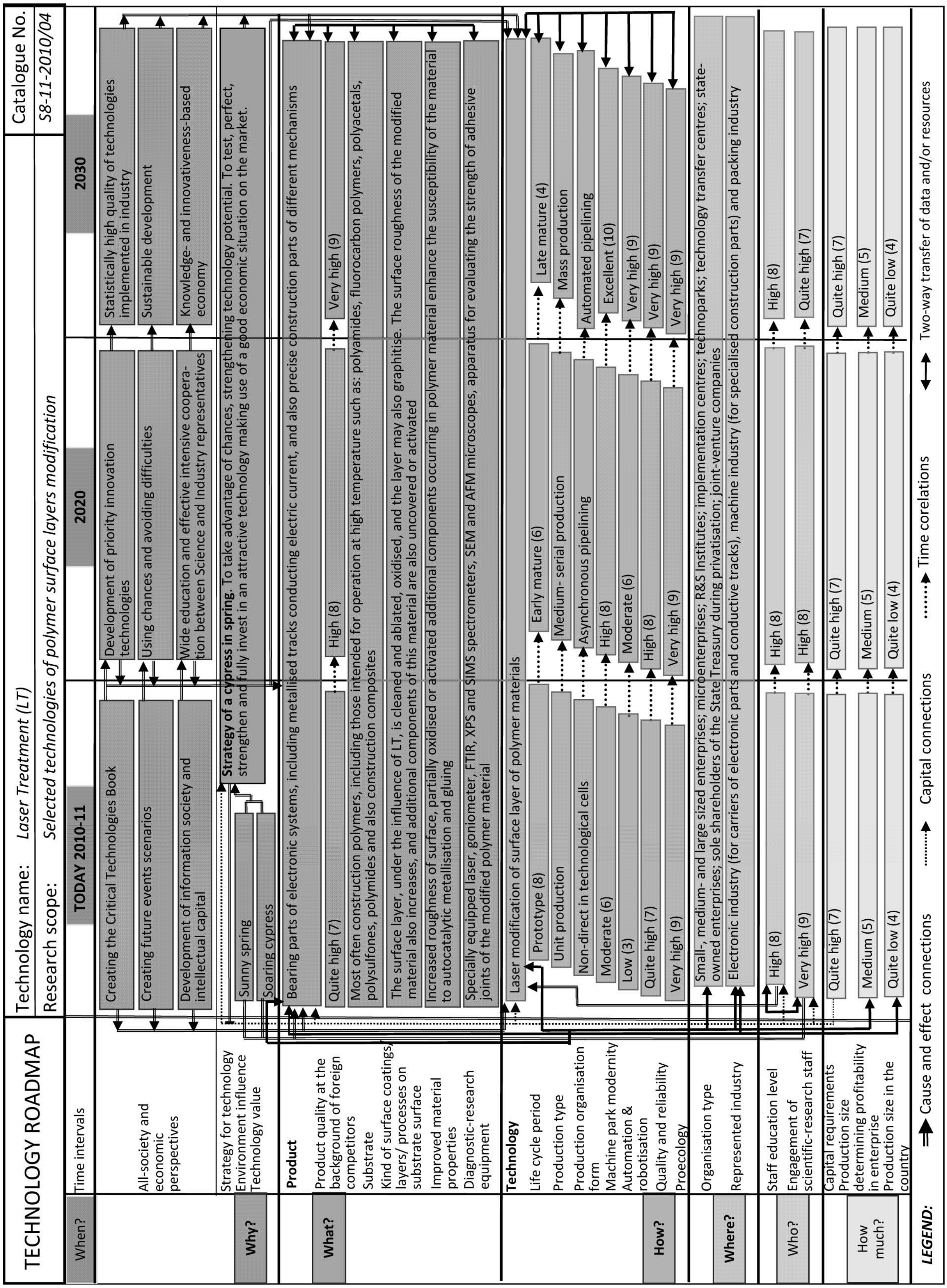


Fig. 24. The technology roadmap prepared for the (D) technology, i.e. Laser Treatment

Fig. 25. The technology roadmap prepared for the (E) technology, i.e. Electron-Beam Irradiation

5. Technology Roadmaps

Technology roadmaps are a useful tool of a comparative analysis for the particular technologies according to the materials science, technological or economic criterion adopted [63-65]. Three time intervals for, respectively, 2010-11, 2020 and 2030, are given on the axis of abscissa of a technology roadmap created with a custom concept [23, 24], and a time horizon for the overall results of the research provided on the map is 20 years. Seven main layers are provided on the axis of coordinates responding, respectively, to the following more and more detailed questions: When? Why? What? How? Where? Who? How much? Each layer of the main maps is split into more detailed sub-layers. An advantage of technology roadmaps is their flexibility and, if needed, additional sub-layers can be added or expanded for the maps according to the industry, size of enterprise, scale of the company's business or an entrepreneur's individual expectations. Technology information sheets, containing technical information very helpful in implementing a specific technology in the industrial practice, especially in SMEs not having the capital allowing to conduct own research in a given field, are detailing and supplementing the technology roadmaps. Technology roadmaps were prepared using reference data such as the results of materials-science and foresight research for all the five analysed technologies and, as the data presented therein is diverse, a decision was made to present them fully in, respectively, Figs. 21-25.

6. Summary

The paper presents a comparative analysis of the five selected technologies of polymer surface layers modification by using physical processes resulting in changes to the structure of surface and properties of polymers as a criterion of classification. The materials science and foresight research pursued represents part of a larger project aimed at selecting and characterising, using a cohesive pool of analytical tools, the priority, innovative materials surface engineering technologies, as discussed by the following series of publications, notably: [66-72].

The analysis made has revealed very high (9 points out of a scale of relative states comprised of ten points) development prospects of the base technology of modification of polymers surface layer by means of corona (barrier) discharges in the air and in other gases (A) that is currently widely used in the industry, especially in the packaging, food, automotive, pharmaceutical, sports equipment and household appliances sector. Oxygen groups are implemented in the polymers surface layer as a result of modification using corona discharges and its roughness increases leading to higher wettability of material and increased surface free energy, enabling to or making it impossible to glue, print and decorate modified polymers. The anticipated progress and unthreatened strategic position of corona discharges in the nearest 20 years stems from the fact that the technology is relatively simple, highly effective, not requiring large expenses at the stage of investment and in further operation, and no highly skilled personnel is required. The disadvantages include a possibility of damaging very thin foils less than 15 μm thick, material shrinkage during the process and the necessity to neutralise or evacuate ozone. The further development of corona discharges will surely relate to better constructions of activators and measuring apparatuses and automatic process control circuits. A new domain of future uses is a sterilisation function for different micro-organisms, and this can be used in the food, pharmaceutical and medical industry.

A strategic position of the technology (C), i.e. polymer materials surface layer modification with low-temperature plasma in the conditions of low pressure (0.05-5 hPa) was also rated 9 points in the ten-point scale, which corresponds to a very high level. This relatively simple technology allows to modify thin polymeric foils and also parts with the similar shape (3D) very uniformly and gently. A separate group of products manufactured this way are the carriers of parts or electronic circuits installed in control or adjustment units for different equipment. The technology of polymers modification with low-temperature plasma in the conditions of lower pressure is used most often for manufacturing packaging, electronic equipment, sports equipment and household appliances and in the automotive industry. The anticipated directions of technology improvement will include shortening the modification time that currently is several dozens of minutes and is causing limited process efficiency; improved construction of discharge chambers with high required tight sealness and the progress of the process itself to eliminate its cyclicity for the sake of ensuring continuous modification.

The development prospects of polymers surface layers modification using different types of lasers, including excimer lasers (D) were also highly valued (9 points). This technology is currently at its prototype stage of life cycle and allows to modify precisely the selected pieces of a given material's surface layer, including narrow conductive layers designed earlier, as well as other areas with their complex shapes. The technology should hence be used in the electronic industry in the future, especially for producing computers and in the machine and packaging industry. The potential of polymer surface layers laser modification will most apparently be reinforced in the nearest future by improving the design of lasers, measuring apparatuses and automatic process control units. A current limitation for the technology is the fact that areas with large surface areas cannot be modified as well as relative high consumption of electricity supplied to the laser per a unit of field of the area modified, and the characteristics will surely be investigated and improved further over the nearest 20 years.

The development prospects of the currently evolving polymer materials surface layer modification technology using plasma generated outside the modification zone through partial discharges in the air or in other gases (B) was rated high (8 points). Regardless the constraints of the technology, i.e. relatively small efficiency of the modification process and the fact that the process at the current stage of development must be carried out manually, it has a crucial advantage as compared with a classical corona discharges method (A), i.e. elements can be modified having complex, irregular spatial shapes (3D) and openings and pass-through parts of construction components. The technology enables to generate plasma with varied properties, in different gases, also using small portable devices or such mounted in the holders of robots, which is currently used mainly for manufacturing complex mechanisms of different devices made of polymer materials and for manufacturing cars and household appliances. The future development trends will surely relate to improved efficiency of the plasma generator and process automation.

The most uncertain development prospects (6 points), for the technologies subjected to foresight and materials science research discussed in this paper, are characteristic for the technology of polymer materials modification using high-energy electron-beam irradiation (E), being in a stormy environment. The environment of the technology brings both, many opportunities such as new applications at attractive markets with a high capital potential (power industry, construction), as well as difficulties associated with high investment and operational costs (energy-intensive process), highly skilled staff needs to be employed, a position of buyers and suppliers in the delivery chain is strong, and the level of specialisation is high and applicability is true for a narrow range of products. If the safeguard system is used improperly or fails, a radiation hazard may occur, which is a disadvantage considering the environmental friendliness of the process. Energy-intensive electron-beam irradiation is used primarily for modifying deeper layers of the material up to 40 mm thick such as usually the insulating sheaths of power cables or polyethylene tubes and plates or structural materials containing different polymers. The purpose of modification causing the netting of the surface layer of the material is to improve mechanical strength, resistance to degradation processes and improved hydrophilicity next allowing to glue, print and/or decorate it. The predicted development of the technology (E) will be aimed at improving the modification devices and optimising the process parameters, and a surprise development scenario for the technology, both an optimistic and pessimistic one, is not out of question [73].

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