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Testing of processing and performance properties of marine degradable material

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Summary

In today's world environmental protection plays an important role. This also includes the rivers, lakes, seas and oceans. The general problem in the seas and oceans, among other things, are the discarded plastic products. Such floating plastic products act as absorbers of heavy metals, pesticides, polychlorinated biphenyls (PCBs) and other toxins that then get accumulated in sea animals, and consequently in humans as well. The most common sources of pollution are the ships (35 to 85%), i.e. people who throw various products into the sea, lost fishermen's nets and waste from rivers or brought by the wind. The need to reduce the quantities of discarded non-degradable plastics in sea, has led to the development of marine degradable materials that after having been discarded into water (sea, lake and river) degrade completely after a certain time. The paper analyzes the possibility of processing the marine degradable material using the injection moulding process, and also the testing of mechanical properties has been performed. Its degradability in the sea has been tested as well as the applicability of the material for manufacturing of products that come into close contact with food.

KEYWORDS:
biodegradation in water
injection moulding
marine biodegradable material
mechanical properties
poly(3-hydroxybutyrate)
poly(hydroxyalkanoate)

KLJUČNE RIJEČI:
biorazgradnja u moru
injekcijsko prešanje
mehanička svojstva
poli(hidroksi-alkanoat)
poli(hidroksi-butirat)
vodorazgradljivi materijal

Ispitivanje preradbenih i uporabnih svojstava vodorazgradljivog materijala

Sažetak

U današnjem svijetu zaštita okoliša vrlo je važna, a u to se ubraja i očuvanje rijeka, jezera, mora i oceana. U morima i oceanima opći su problem, između ostalog, i odbačeni plastični proizvodi. Takvi plutajući plastični proizvodi djeluju kao apsorbansi teških metala, pesticida, polikloriranih bifenila (PCB) i ostalih otrova, koji se akumuliraju u morskim životinjama, a posljedično i u ljudima. Najčešći izvori onečišćenja su brodovi (35 % do 85 %), tj. ljudi koji bacaju razne proizvode u more, zatim izgubljene ribarske mreže, otpad iz rijeka ili donesen vjetrom. Potreba za smanjenjem količine odbačene nerazgradljive plastike u morima dovela je do razvoja vodorazgradljivog materijala, koji se nakon odbacivanja proizvoda u vodu (mora, jezera, rijeke) nakon nekog vremena potpuno razgradi. U radu je ispitana mogućnost prerade vodorazgradljivog materijala injekcijskim prešanjem te su provedena ispitivanja mehaničkih svojstava. Osim toga ispitana je njegova razgradljivost u moru i prikladnost materijala za pravljenje proizvoda koji dolaze u neposredan dodir s hranom.

Introduction

The European project CIP Eco-innovation entitled *MarineClean* (full name of the project is *Marine debris removal and preventing further litter entry*) includes partners from Slovenia, Croatia and Lithuania. The basic aim of the project is the reduction of sea pollution. One of the areas of activities is the design of marine degradable packaging which will contribute to the reduction of sea pollution. For this purpose a biobased, bio-degradable material based on poly(hydroxyalkanoate) (PHA) was selected.

Poly(hydroxyalkanoates) (PHA), a family of biopolyesters with diverse structures, are the only bioplastics completely synthesized by microorganisms. PHA can be synthesized by over 30% of soil-inhabiting bacteria. Many bacteria in activated sludge, in seas, and in extreme environments are also capable of making PHA. PHA can have many properties depending on the structures. Homopolymers, random copolymers, and block copolymers of PHA can be produced depending on the bacterial species and growth conditions. With over 150 different PHA monomers being reported, PHAs with flexible thermal and mechanical properties have been developed. Such diversity has allowed the development of various applications, including environmentally friendly biodegradable plastics for packaging purposes, fibres, biodegradable and biocompatible implants, and controlled drug release carriers.[1]

PHAs degrade in different environments. Unlike some other biodegradable polymers, they do not need high temperatures and humidity for their biodegradation, and are broken down in the soil, in the sea, even in home composting facilities. The most common type of PHA is poly(3-hydroxybutyrate) (PHB), a material of diverse properties, which can be derived from corn, sugar cane and beets, as well as vegetable oil.

Experimental part

A marine degradable material

A marine degradable material under the brand name *EcoOcean* was developed by the *EcoCortec*, company from the USA. Its basis is poly(hydroxybutyrate) (PHB). The material *EcoOcean* is intended for the production of films, foils, and bags using the procedure of tubular film extrusion. The material contains 77% of biobased material and is degraded in seawater (i.e. seas and oceans), anaerobic environment, in soil, water, municipal compost and industrial composting plant under controlled conditions.[2]

Processing parameters and the shape of test specimen

The marine degradable material is intended for the processing by blow film extrusion, but due to the need of development of different packages the test specimens used in the research have been made by injection moulding. Injection moulding machine *Boy tip* was used, and the processing parameters have been presented in Table 1. For the sake of testing mechanical properties, the tensile and bending test specimens were produced (Figure 1).

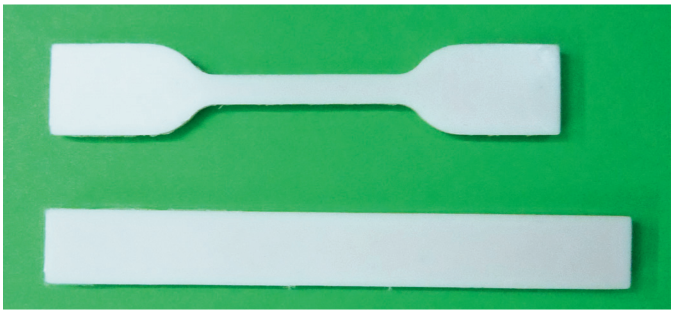


FIGURE 1 – Marine biodegradable material test specimens made by injection moulding

Testing of tensile properties was carried out according to HRN EN ISO 527: 2012 standard (Figure 2), at a velocity of $v = 20$ mm/min.

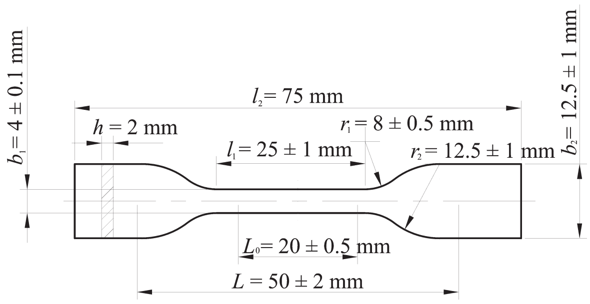


FIGURE 2 – Shape of the tensile test specimen[3]

Calculation of stresses and deformations

Tensile strength is calculated according to equation:[3]

$$R_m = \frac{F_{max}}{A_0} \tag{1}$$

where R_m, MPa – tensile strength, F_{max}, N – force, A_0, mm^2 – area.

Elongation at break is calculated according to equation:[3]

$$\varepsilon_p = \frac{\Delta L_0}{L_0} \tag{2}$$

where ε_p, % – elongation at break, ΔL_0, mm – increase in the specimen length between the gauge marks, L_0, mm – the gauge length of the test specimen

The bending properties were tested according to *HRN EN ISO 178: 2011* standard, with test specimen thickness of 4 mm. The three-point testing has been performed during which the test specimen (Figure 3) is placed on two supports and a load F is applied at the center, until the test specimen breaks or until the deflection reaches the agreed value S_c.[4] The testing velocity is $v = 20$ mm/min.

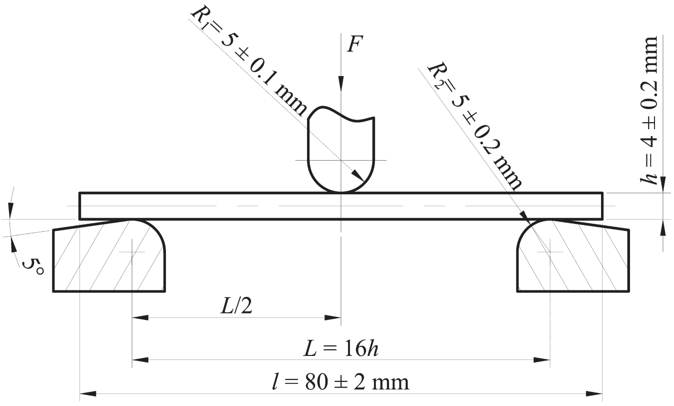


FIGURE 3 – Shape of the flexural test specimen

Flexural stress is calculated according to the equation:[4]

$$\sigma_f = \frac{3F \cdot L}{2b \cdot h^2} \tag{3}$$

where σ_f, MPa – flexural stress, F, N – force, $L = 16$, $h = 16 \cdot 4 = 64$ mm – measuring length, i.e. distance of support, b, mm – width, h, mm – thickness

The toughness is tested using Charpy method according to *ISO 179-1:2000* standard. The gap between the supports on the device is $L = 62^{+0,5}_{-0}$ mm, and the test specimen is made with a notch of type C (Figure 4).

Impact strength of test specimen with notch is calculated according to the equation:[5]

$$a_{CN} = \frac{E_C}{h \cdot b_N} \tag{4}$$

TABLE 1 – Processing parameters

Processing parameters	Tensile test specimen	Flexural test specimen
Displacement of screw, mm	70	70
Injection time, s	7.0	7.0
Injection speed (rate), cm^3/s	9.0 – 14.0	9.0 – 14.0
Injection pressure, bar	400	400
Holding pressure, bar	500	500
Temperature of cylinder, °C	163 – 165 – 155	163 – 165 – 155
Mould temperature, °C	40	40
Shot capacity, cm^3	4.2	5.5
Packing time, s	4	2
Cooling time, s	30	30
Cycle time, s	41.43	41.98

where a_{CN}, J/mm^2 – Charpy impact strength (notched test specimen), E_C, J – energy absorbed by breaking test specimen, h, mm – thickness, b_N, mm – remaining width

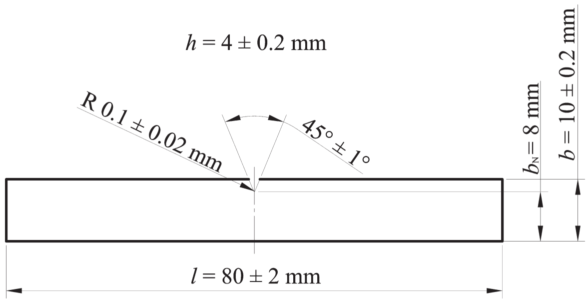


FIGURE 4 – Shape for testing impact strength[5]

Results and discussion

Tensile properties

Table 2 present the values obtained by the extension of the test specimens.

The table shows that the mean value of tensile strength amounts to as little as 15 MPa, and tensile strain at break is about 500%. When this is compared with the conventional materials which are used to produce various packaging, e.g. polypropylene (PP) or high density polyethylene (PE-HD) (R_m = 15 - 40 MPa and ε_p = 150 – 400%[6,7,8]) one may notice that this is the bottom value of tensile strength which is stipulated by many manufacturers, whereas extension is 25% higher.

Flexural properties

Table 3 shows the values obtained during the determination of flexural properties. The test specimen did not break during the bending, so that the agreed bending strength σ_{fc} is determined up to deflection $S_c = 1.5 \cdot h = 6$ mm.

The bending strength of the conventional materials (PP and PE-HD) amounts to about 40 MPa[7,8], whereas in case of marine degradable material which shows high flexibility it is not possible to test either bending strength nor bending strength at break since the test specimen fell into the support of the testing device. At the agreed deflection of 6 mm the bending strength amounts to 9 MPa.

Impact strength

Table 4 shows the values obtained by testing of the toughness.

TABLE 4 – Results of Charpy impact strength

Nr.	Thickness h, mm	Remaining width b_N, mm	Energy absorbed by breaking E_c, J	Charpy impact strength a_{CN}, J/mm^2
1	3.96	7.69	1.4	0.0460
2	3.97	8.06	1.6	0.0500
3	3.98	7.66	1.7	0.0558
4	4.00	8.06	1.8	0.0558
5	3.97	7.24	1.3	0.0452
$\bar{x}$	3.976	7.742	1.56	0.0507
S	0.0152	0.3405	0.2074	0.0051

The mean impact strength value of the marine degradable material is a_{CN} = 0.0507 J/mm^2 which is a 50% lower value when compared with the toughness of polypropylene and polyethylene (0.10 J/mm^2).[8]

Testing of the applicability of the marine degradable material for the production of packaging which is in contact with food

Because of the possible application of the marine degradable material for packaging which comes into direct contact with food, the health safety of *EcoOcean* material was tested to global and specific migration and microbiological purity according to *Regulations NN 125/09, Article 33, Item 1*, which correspond to the *European Regulations EC 1935/2004* and *EU 10/2011*.

TABLE 2 – Tensile properties

Nr.	Thickness h, mm	Width b_1, mm	Area A_0, mm^2	Force F_{max}, N	Tensile strength R_m, MPa	Elongation at break ε_p, %
1	2.98	3.98	11.86	178	15.0	485.7
2	2.98	3.99	11.89	186	15.6	514.3
3	2.97	3.97	11.79	176	14.9	471.4
4	2.97	3.98	11.82	170	14.4	428.6
5	2.97	3.98	11.82	194	16.4	494.3
$\bar{x}$	2.974	3.98	11.84	180.8	15.3	478.9
S	0.0055	0.0071	0.0389	9.3381	0.7777	32.1095

TABLE 3 – Flexural properties

Nr.	Thickness h, mm	Width b, mm	Area A_0, mm^2	Measuring length L=16*h, mm	Force F_c, N	Flexural strength at con. deflection σ_{fc}, MPa
1	3.97	9.85	39.10	63.52	14	8.6
2	3.97	9.84	39.06	63.52	14	8.6
3	3.97	9.89	39.26	63.52	16	9.8
4	3.98	9.94	39.56	63.68	16	9.7
5	3.99	9.93	39.62	63.84	16	9.7
$\bar{x}$	3.976	9.89	39.32	63.62	15.20	9.3
S	0.0089	0.0453	0.2566	0.1431	1.0954	0.6195

The testing was carried out on a foil in the original and unused form of 0.25 mm thickness.

The identification of foil was carried out on the pyrolyzer of brand *Frontier Lab* type *double-shot pyrolyzer PY-2010* from Japan. During 1 minute at a temperature of 550°C there was 0.2 mg of foil tested in the quartz tube in the helium current. The products of the pyrolysis were analyzed on the connected system gas chromatography – mass spectrophotometry GC/MS (*Shimadzu GCMS-QP2010 plus*) using *Frontier Ultra ALLOY⁺-5* metal capillary separating column (6% cyano-propyl-phenyl, 94% dimethyl-polysiloxane). The length of the column amounted to 30 m, internal diameter 0.25 mm. To determine the mass shares of the compounds the calibration was carried out by normalization of the area with the sample quantity of 0.2 mg.

The obtained results of the pyrolysis indicate that it is a polymeric material based on the crotonic acid and polyalcohol which was softened with acetyl 3-n-butyl citrate (ATBC) and adipates (Dioctyl adipate (DOA) and Bis(2-ethylhexyl) adipate (DEHA)).

Microbiological purity has been tested by placing 10 ml of sterile saline solution on the test specimen. The analysis has shown that the test specimen corresponds to the regulations for the direct contact with food, since in the initial diluted swab there were no isolated enterobacteriaceae, staphylococcus aureus, pseudomonas aeruginosa and aerobic maesophylic bacteria.

The test specimen was then used to perform the analysis of global migration according to standards *HRN EN 1186-5* and *HRN EN 1186-14*. The test specimen was left in the migration cell in direct contact with the acid (3% acetic acid), neutral (distilled water) and fatty (iso-octane) solution. For the test specimen to comply with the regulations stipulated by the standard, the maximum allowed quantity which can migrate into the food amounts to 10 mg/dm^2. The test specimen in acid and neutral solutions were left 10 days at a temperature of 40°C, and in fatty solution 2 days at 20°C. The obtained data are presented in Table 5.

TABLE 5 – Global migration

Solution	MDK	Requirements
Acid	181.8 ± 2 mg/dm^2	Does not match with regulations
Neutral	9.7 ± 2 mg/dm^2	Match
Fatty	7.1 ± 3 mg/dm^2	Match

From the obtained extract of 3% of acetic acid after the carried out migration test, the specific migrations of primary aromatic amines (PAA) and metals were determined. The specific migration of primary aromatic amines in the extract with 3% of acetic acid was tested by the procedure *LMBG 2000 L.00.00-6* using the UV-VIS spectrophotometry method and it was PAA < 0.0008 mg/dm^2, and the specific migration of metals and non-metals has been determined by the ICP-OES method (Table 6).

From the Table 6 one can observe that the value of the chemical element strontium is too high Sr = 129.8 mg/L. EcoOcean is a bio-degradable material which contains sugars. The strontium hydroxide ($Sr(OH)_2$) dissolved in water produces strong alkali, and also generates hydrates and is applied in sugar refining, which is probably the reason why it is present in such large quantities. It is also possible that various marine degradable additives (usually starch and glucose) are added to the material, and strontium serves as their stabilizer.

Testing of degradation in the marine water

The testing of the *EcoOcean* material degradation was performed in the coastal area of Slovenia at a depth of ~ 1 m, at the sea temperature of ~ 15°C. The testing was performed on bags and test specimens used to test bending properties of 4 mm thickness (Figure 5).

TABLE 6 – Specific migration

Metal	Specific migration, μg/L
Ag	< 4
Al	25.7
As	< 10
Ba	< 12
Be	< 0.1
Bi	< 10
Cd	< 2
Co	< 2
Cr	2.1
Cu	17
Fe	61.2
Mn	8.7
Ni	< 2
Pb	< 0.1
Sb	< 5
Se	< 6
Sn	< 13
Sr	*129.8*
Ti	< 12
V	< 2
Zn	< 0.1

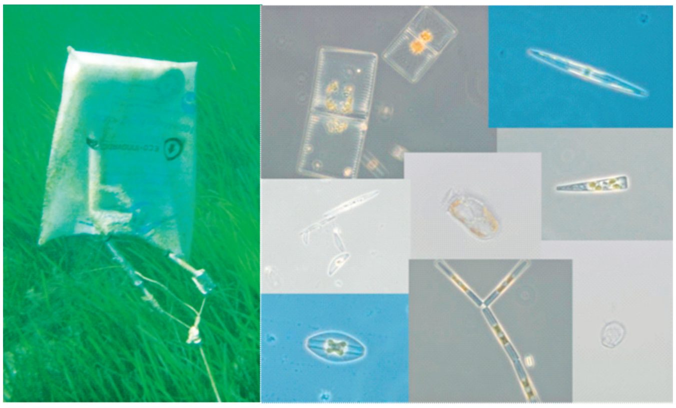
a) b)

FIGURE 5 – Testing of degradation in marine water: a) bag, b) flexural test specimens

After one month a thin layer of sea microorganisms (benthic microalgae of which mostly diatoms, dinoflagellates and nanoflagellates), plants and animals (marine worm - Pomatoceros triqueter) developed on the test specimens (Figure 6).

After 2 months there were some more microorganisms on the test specimens, such as e.g. cyanobacteria, macroalgae and bryozoans (Figure 7).

Parallel to field study, laboratory tests were carried out as well. The bending test specimens were placed into unfiltered sea water, and a piece of cut bag in three different sea waters: one with seawater with almost all organisms removed, one with seawater with phytoplankton and bigger organisms removed, and one with intact seawater (Figure 8).



a) b)

FIGURE 6 – After one month: a) all bags and test specimens were covered by a thin biofilm of different marine microorganisms, plants and animals, b) microalgae under the microscope

a) b)

FIGURE 7 – After two months: a) all bags and test specimens were covered by a thin biofilm of different marine microorganisms, plants and animals, b) macroalgae under the microscope

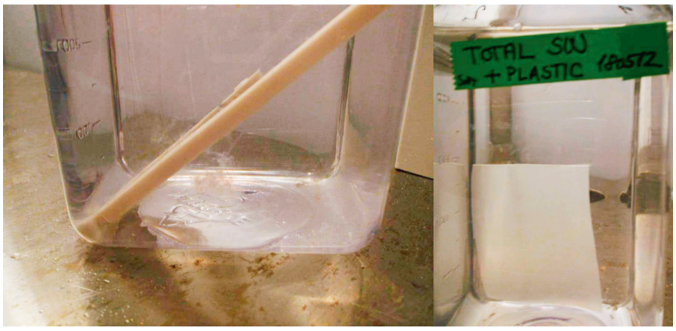
FIGURE 8 – Laboratory testing

After one month at a constant temperature of 14°C the flexural test specimen showed *snow-like* material which indicates the growth of bacteria (Figure 9a), whereas the bag remained the same without any indications of degradation (Figure 9b).

Only after two months at room temperature in unfiltered water the bag started to degrade (Figure 10).

After four months in unfiltered sea water the bag has completely degraded (Figure 11a). At the same time the flexuraltest specimen did not show visible signs of degradation expect that the mould appeared (Figure 11b).

These results were expected since biodegradation is controlled by the part thickness and thicker parts will need more time to degrade.



a) b)

FIGURE 9 – Laboratory degradation after one month: a) bacterial growth on the flexural test specimen, b) plastic bag was unchanged

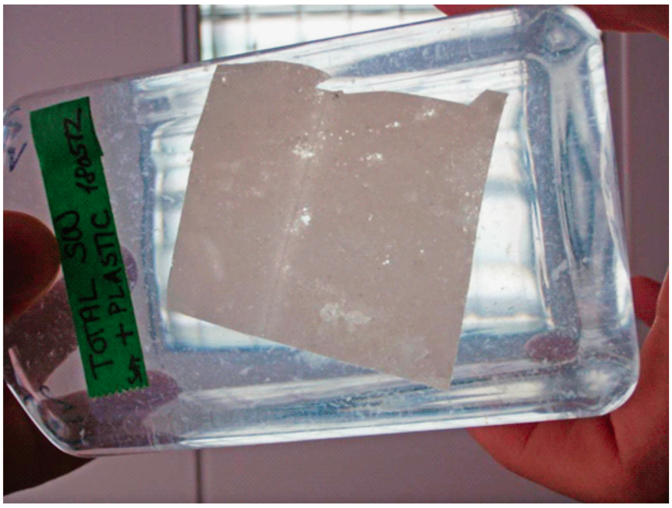
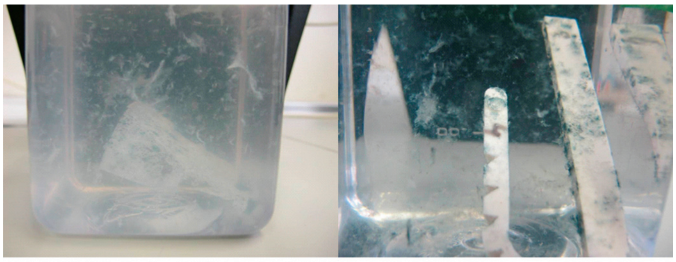


FIGURE 10 – Degradation of plastic bag in non-filtered marine water after two months



a) b)

FIGURE 11 – Laboratory degradation after four months: a) plastic bag, b) mould growth on the flexural test specimens

Conclusion

The material is easy to process with different processes, like extrusion and injection moulding and the test specimens show good mechanical properties. Tensile strength of *EcoOcean* is lower than that of conventional polymers, while the strain at break is over 500%. Given the high strain at break, *EcoOcean* is highly flexible, and because of that, it is not possible to measure the flexural strength at break since the testing is stopped at an agreed deflection of 6 mm.

According to the *Regulation NN 125/09, Regulation EC 1935/2004* on the materials and articles intended to come into contact with food and *Regulation EU 10/2011* on the plastic materials and articles intended to come into contact with food, pyrolysis showed that *EcoOcean* material is a polymer material based on crotonic acid and polyalcohol plasticized with tri-n-butyl acetyl citrate (ATBC) and adipate (DOA and DEHA). The sample complied with microbiological requirements, but did not comply with EU and Croatian legislation for materials and articles intended to come into contact with food because the global migration to 3% acetic acid is above the threshold value.

The testing of degradation in sea water has shown that various micro and macro-organisms appeared on all the test specimens (bentone flora, diatomes, dinoflagellates, nanoflagellates, marine worm, bryozoans, mould), but the visible degradation started after four months and then only on the thin-wall product.

Acknowledgement

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REFERENCES

1. Chen, G.-Q.: *Plastics Completely Synthesized by Bacteria: Polyhydroxyalkanoates,* u Chen, G.-Q. (ed.), Plastics from Bacteria: Natural Functions and Applications, Microbiology Monographs, Vol. 14, Springer-Verlag, Berlin, Heidelberg, 2010.
2. www.ecocortec.hr, 31.01.2013.
3. HRN EN ISO 527: 2012 *Plastika – Određivanje rasteznih svojstava* (ISO 527: 2012, EN ISO 527: 2012) (*Plastic – Determination of tensile properties*).
4. HRN EN ISO 178: 2011 *Plastika – Određivanje savojnih svojstava* (ISO 178: 2010, EN ISO 178: 2010) (Plastic – Determination of flexural properties).
5. ISO 179-1:2000 *Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test*
6. Campo, E. A.: *Industrial Polymers*, Hanser Publishers, Munich, 2008.
7. www.goodfellow.com/E/P.html, 2. 2. 2013.
8. www.matweb.com/, 2. 2. 2013.

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Vijesti is *Assocomaplasta*

Priredila: Gordana BARIĆ

Prema podatcima *Assocomaplasta*, udruženja talijanskih proizvođača strojeva, kalupa i ostale opreme za preradu polimera, 2012. je za tu industriju bila dobra godina.

Podatci o talijanskoj industriji strojeva, kalupa i ostale opreme za preradu polimera (u mil. eura)

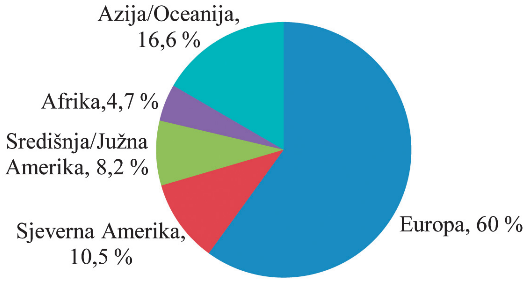
	2011.	2012.	2011./2012., %
Proizvodnja	4 000	4 000	-
Izvoz	2 430	2 575	6,0
Uvoz	605	625	3,3
Domaća potrošnja	2 175	2 050	–5,7
Trgovinska bilanca	1 825	1 950	6,8

Mnogo više nego prijašnjih godina, ali i mnogo više nego u ostaloj talijanskoj strojogradnji, proizvodnja u ovom sektoru bila je okrenuta izvozu, koji je rastom uspio amortizirati smanjenje potražnje domaćega plastičarskog i gumarskog sektora. Narudžbe pred kraj 2012. pokazuju slab interes talijanskih plastičara i gumaraca za nabavu novih strojeva, kalupa i ostale opreme.

Kada se pogleda struktura izvezenih strojeva, 9 % čine ekstruderi, 18 % oprema za puhanje, dok se znatno smanjio udio ubrizgavalica (čak za 20 % u odnosu na 2011.), jer su ih talijanski proizvođači ili prestali proizvoditi ili su imali znatne poslovne teškoće. Glavna tržišta za ekstrudere su Njemačka, Rusija, Francuska i Kina (u koju su zabilježene dvoznamenkaste stope rasta isporuka). Opreme za puhanje izvezeno je najviše u Sjedinjene Američke Države (u vrijednosti od 20 milijuna eura), Rusiju i Poljsku.

Kalupi, na koje je u 2012. otpadala gotovo četvrtina izvoza, zabilježili su rast od oko 19 % u odnosu na 2011. Najviše je porastao izvoz u Srbiju, na čak 21 milijun eura, odnosno 1,5 puta (zbog potreba *FIAT*-ovih pogona u Kragujevcu), zatim u Poljsku i Sjedinjene Američke Države.

Europsko i sjevernoameričko tržište općenito je poraslo za ovaj sektor, dok su južnoameričko i posebice azijsko u padu, a slični su pokazatelji za proizvođače strojeva, kalupa i ostale opreme za preradu polimera iz drugih zemalja. Najviše je izvezeno u Europu (60 %), a kada se pogledaju pojedinačne zemlje, na prvom je mjestu Njemačka (14,8 %), zatim Francuska (6,2 %) te Sjedinjene Američke Države (6,2 %).



Udio izvoza članica udruženja *Assocomaplast* u pojedine svjetske regije

Assocomaplast Press release, 3/2013.