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## THE STRUCTURE AND MECHANICAL PROPERTIES OF PBS, PCL AND PBAT MODIFIED WITH LAPONITE

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An investigation into the effect of a synthetic variety of hectorite, i.e. Laponite (LAP), on changes in the structure and mechanical properties of poly(butylene succinate) (PBS), poly( $\epsilon$ -caprolactone) (PCL) and poly(butylene adipate-*co*-terephthalate) (PBAT) is the aim of the present paper. Polymer composites containing 1, 3, 5, and 7 wt.% LAP were prepared using a co-rotating twin screw extruder. The mechanical properties (under static tension, static three-point bending and impact tests) were investigated. In addition, changes in adhesion at the phase boundary and the surface geometrical structure of the sample fractures were examined. It was found that the studied composites were characterized by a similar structure. Adhesion at the polymer-filler interface was very good for the PBAT and PCL-based composites and slightly worse for the PBS-based composites. The mechanical properties of the investigated polymers generally changed similarly. With the exception of the three-point bending tests, all the polymers exhibited deterioration in the mechanical properties after the addition of LAP. However, considering the results of the significance tests, it is important to note that some results did not differ significantly from one another.

**Keywords:** biodegradable polymers, Laponite, composite, mechanical properties, extrusion

### INTRODUCTION

Smectite minerals constitute a group of the most important and common clay minerals. Some of the most well-known include montmorillonite [1], nontronite [2], vermiculite [3], beidellite [4], saponite [5], stevensite [6] and hectorite [7]. These are minerals with 2:1 type bilayer packages, in which there are two tetrahedral layers and one octahedral layer. They differ in their properties, which are mainly influenced by the type of cation present in the inter-pack space but also by other elements included in their structure. A mineral with interesting properties is hectorite (Htr). In contrast to the most famous in this group – montmorillonite, with its dioctahedral structure – Htr has a trioctahedral structure [8]. As a consequence of isomorphic substitution (replacing some magnesium atoms with lithium atoms), negative charges accumulate on the surface of Htr packets, which are neutralized by sodium cations located in the inter-packet space. In turn, small positive charges accumulate at the edges of these packets. This causes the Htr packets to resemble small dipoles, which can form a spatial network [9]. Packets of Htr, especially its synthetic variety, form flat disks of nanometric size, i.e. with a thickness of ca. 1 nm and a diameter of ca. 25 nm [10].

The use of Htr with strong hydrophilic properties, a large specific surface, and a lamellar structure, whose disks can additionally form physical entanglements or transverse connections between different polymer chains, may prove beneficial when modifying the properties of polymers, which may thus acquire new and valuable functional properties. Modifying the properties of some biodegradable polymers, which themselves are often unable to compare with their non-biodegradable equivalents, can be particularly interesting. This refers to the properties of these polymers, as well as to their processing and price. Furthermore, modifying their properties can be particularly beneficial in the aspect of searching for biodegradable equivalents to the most common non-biodegradable plastics on the market, i.e. polyethylene (PE), especially its low-density varieties for the production of film packaging. Therefore, in this work we used biodegradable polymers that are characterized by high strain (above 100 %) and a relatively low Young modulus (below 1000 MPa), which corresponds to most varieties of PE.

Polymers that meet these criteria are, for example, poly(butylene succinate) (PBS) [11-13], poly(butylene adipate-*co*-terephthalate) (PBAT) [14-16] and

poly( $\epsilon$ -caprolactone) (PCL) [17-19]. Comparing the mechanical properties of these polymers, it can be said that the first one is characterized by the highest tensile strength and the lowest strain; the second one has the highest elasticity as well as the best resistance to dynamic impact, and the last one shows indirect properties except for the strain, which is the highest. This inspired the authors of this article to undertake research works, the main objective of which is to investigate the effect of a synthetic variety of Htr, i.e. Laponite (LAP) [20-22], on changes in the structure and mechanical properties of PBS, PCL and PBAT. The changes in these properties upon the addition of various amounts of LAP were determined.

## EXPERIMENTAL PART

### Materials

The following materials were used in this work:

- Poly(butylene succinate) (PBS), BioPBS<sup>TM</sup> FZ71PM (PTT MCC Biochem CO., Ltd., Thailand). Its melt flow rate (MFR) is 20-22 g/10 min (2.16 kg, 190 °C), density 1.27 g/cm<sup>3</sup> and melting point 115-117 °C.
- Poly( $\epsilon$ -caprolactone) (PCL), CAPA FB100 (Ingevity, USA). Its MFR is 2-4 g/10 min (2.16 kg, 190 °C), density 1.15 g/cm<sup>3</sup> and melting point 58-60 °C.
- Poly(butylene adipate-co-terephthalate) (PBAT), F Blend C1200 (BASF, Germany). Its MFR is 5-8 g/10 min (2.16 kg, 190 °C), density 1.25 g/cm<sup>3</sup> and melting point 110-120 °C.
- To modify the properties of above mentioned polymers, pure and non-intercalated (organically) Laponite (LAP), Laponite-RD (Rockwood Additives Ltd., UK) was used. Its formula is  $\text{Na}_{0.7}^+[(\text{Si}_8\text{Mg}_{5.45}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$ , density 2.53 g/cm<sup>3</sup> and decomposition temperature above 500 °C. This filler was in the form of a white powder with a particle size from ca. 5  $\mu\text{m}$  to ca. 100  $\mu\text{m}$ .

### Sample preparation

Granulated samples of the pure polymers and polymer composites containing 1, 3, 5, and 7 wt.% LAP were prepared using a co-rotating twin screw extruder, BTSK 20/40D (Bühler, Germany), equipped with screws 20 mm in diameter and an L/D ratio of 40. The temperatures of the individual barrel heating zones were 150, 153, 156, and 159 °C. The temperature of the extrusion die-head was 160 °C. The extrusion temperatures were the same for all the types of samples. The screw rotation speed was kept constant at 150 rpm. The plasticizing system was equipped with one non-vacuum degassing zone at L/D 32. Each polymer was dosed directly to the extruder hopper feeder, while LAP was dosed directly to the barrel zone at L/D 12. Prior to processing, PCL, PBS, PBAT and LAP were dried for 24 h at 50, 70, 70 and 120 °C, respectively. The extruded PBS and PBAT, as well as the composites

of these polymers with LAP were intensively cooled in an air stream and then granulated. In the case of PCL and its composites, the extrudate was chilled in a water bath at 10 °C, then dried on a conveyor belt in a dry air stream and then granulated. The extrusion process was carried out with a special shape of screws containing different segments; they consisted of conveying segments, reverse segments and kneading segments, including elements providing intensive dispersive mixing and intensive distributive mixing. The designations and compositions of the extruded granule samples are listed in Table 1. Samples of the granulated pure polymers that were single-processed were used as the reference system.

TABLE 1. Symbols and compositions of studied samples

Sample number	Sample symbol	Polymer matrix	LAP content [wt.%]
1	BS0	PBS	0
2	BS1	PBS	1
3	BS3	PBS	3
4	BS5	PBS	5
5	BS7	PBS	7
6	CL0	PCL	0
7	CL1	PCL	1
8	CL3	PCL	3
9	CL5	PCL	5
10	CL7	PCL	7
11	BAT0	PBAT	0
12	BAT1	PBAT	1
13	BAT3	PBAT	3
14	BAT5	PBAT	5
15	BAT7	PBAT	7

Individual granulates were used to produce standardized specimens for mechanical testing. Standard dumbbell- and bar-shaped specimens were prepared according to a relevant standard (PN-EN ISO 527-2: 2012) by using an injection molding machine (Battenfeld Plus 35/75, Germany). The temperatures of barrel plasticizing zones I and II were 145 °C and 155 °C, respectively, and that of the injection head was 160 °C. The temperature of the injection mold was 20 °C and the injection pressure was in the range of 100 MPa - 140 MPa, depending on the kind of composite.

### Methods

Fractures were made in the bar-shaped specimens after freezing them in liquid nitrogen. The surface geometrical structure of the fractures was determined by scanning electron microscope (SEM), a Hitachi SU8010 (Hitachi, Japan). Imaging studies were performed at an accelerating voltage of 15 kV by means of a BSE detector. A 6-nm thick gold layer was sputtered on all the samples to be analyzed by SEM. For that purpose, a cathode sputtering apparatus was used, which was equipped with a coating thickness gauge based on

a quartz crystal of varying conductivity. The tensile strength ( $\sigma_M$ ) and elongation at break ( $\varepsilon_B$ ) were evaluated according to the PN-EN ISO 527-1:2020 standard, using the extension rate of 50 mm/min. The flexural strength ( $\sigma_{fM}$ ) and flexural modulus ( $E_f$ ) were measured by the three-point bend test, at the bending deflection rate of 5 mm/min. The measurements were carried out in accordance with the PN-EN ISO 178:2011/A1 standard. The mechanical properties tests under static tension and static three-point bending were carried out using a tensile testing machine, TIRAtest 27025 (TIRA Maschinenbau GmbH, Germany). The impact strength ( $a_{cN}$ ) was evaluated according to the PN-EN ISO 179-1:2010 standard and utilizing a pendulum impact tester, IMPats-15 (ATS FAAR, Italy). Five measurements were performed for each sample in the  $\sigma_M$ ,  $\varepsilon_B$ ,  $\sigma_{fM}$  and  $E_f$  tests. In the case of the  $a_{cN}$  test, ten measurements were performed for each sample. The arithmetic mean of five or ten individual results, respectively, was taken as the final result. In addition, due to the essential confidence intervals of the measured values ( $\sigma_M$ ,  $\varepsilon_B$ ,  $\sigma_{fM}$ ,  $E_f$ , and  $a_{cN}$ ) and small differences between the values of these measurements in the case of some samples, a test of significance (Student's t-test or Cochran-Cox test) for the respective two means was performed, assuming the significance level  $\alpha/2 = 0.05$ . The Cochran-Cox test was applied only if the hypothesis as regards the equality of two variances was rejected in favor of an alternative hypothesis based on the Fisher-Snedecor test.

## RESULTS AND DISCUSSION

### Microscopic examinations

The results of the microscopic observations of PBS, PCL, PBAT and their composites with 3 wt.% or 7 wt.% LAP are presented in Figure 1. Micrographs of the composites with 1 wt.% and 5 wt.% LAP are not shown because their structures were similar to those of composites with LAP contents of 0 wt.% - 3 wt.% and 3 wt.% - 7 wt.%, respectively. The results of these observations indicate three main issues. Firstly, it was stated that the morphology of the pure PBAT fractures is slightly different from that observed in the pure PBS and PCL. The surface structure of the latter polymers is more heterogeneous and less smooth compared to PBAT. Despite the fact that the fractures of all the samples may be considered as brittle, the fractures of the PBAT-based samples seem to be the least brittle. This subtle difference may significantly affect the mechanical properties of PBAT and its composites, especially their impact strength, as confirmed in further investigations. The second aspect concerns the dispersion of the LAP particles in the matrix of all the polymers. Regardless of the type of sample, it can be seen that the fairly well-distributed LAP particles in the various matrices are characterized by different sizes. There are particles

with a diameter of ca. 100  $\mu\text{m}$  and also those smaller than 10  $\mu\text{m}$ . Moreover, they did not change their sizes compared to the pure LAP particles. This indicates that they did not undergo significant dispersion during the extrusion process. The most important conclusion from the microscopic observations refers to the adhesion at the polymer-filler interface. The analyzed adhesion is very good in the PBAT and PCL composites. This is particularly evident in the SEM micrographs taken at higher magnification. There are no free spaces there, which indicates the good compatibility of both phases. This may be owing due to the polar nature of these polymers and LAP, caused by the presence of numerous hydroxyl groups in individual components. Nevertheless, the adhesion is slightly worse in the PBS-based composites compared to the PCL or PBAT composites. This is indicated by the small free spaces between the PBS matrix and the filler that can be observed. They are not large and do not always occur, but they can negatively affect the mechanical properties, mainly owing to the worse ability to transfer stress between the two phases.

The changes in individual mechanical properties ( $\sigma_M$ ,  $\varepsilon_B$ ,  $\sigma_{fM}$ ,  $E_f$  and  $a_{cN}$ ) of the studied samples are shown in Figure 2.

The bars correspond to the mean values of the measured quantities, while the confidence intervals from these values are indicated by the relevant line segments. The results in Figure 2 are summarized in three columns and five rows. The left, middle and right columns correspond to the PBS, PCL, and PBAT-based samples, respectively. In turn, each row represents one measured mechanical quantity.

The data presented in Figure 2 points out that in most cases, independent of the type of matrix, the changes in the individual properties are similar. The values of  $\sigma_M$ ,  $\varepsilon_B$  and  $a_{cN}$  usually decrease with the increasing content of LAP. In contrast, with the rising content of LAP in the matrix of individual polymers, the values of  $\sigma_{fM}$  and  $E_f$  increase. The largest deviations from these trends are observed in the PBAT-based samples. In their case, the  $\sigma_M$  values decrease with increasing LAP content, but only up to 3 % by weight LAP. Larger contents of LAP cause a slight rise in the  $\sigma_M$  values compared to the BAT3 sample. Furthermore, in the study of  $\varepsilon_B$  for PBS, it can be seen that this elongation significantly drops with increasing LAP content, but only up to 3 % by weight LAP. Larger amounts of LAP no longer affect further changes in the  $\varepsilon_B$  values of the PCL-based composites. Besides, in the Charpy impact strength test, no specimens with the PBAT matrix underwent breakage, unlike those based on PBS and PCL, which underwent complete breakage or hinge breakage, respectively. The percentage changes in the values of  $\sigma_M$ ,  $\varepsilon_B$ ,  $\sigma_{fM}$ ,  $E_f$  and  $a_{cN}$  of the studied composites with respect to relevant values of unmodified polymers are summarized in Table 2.

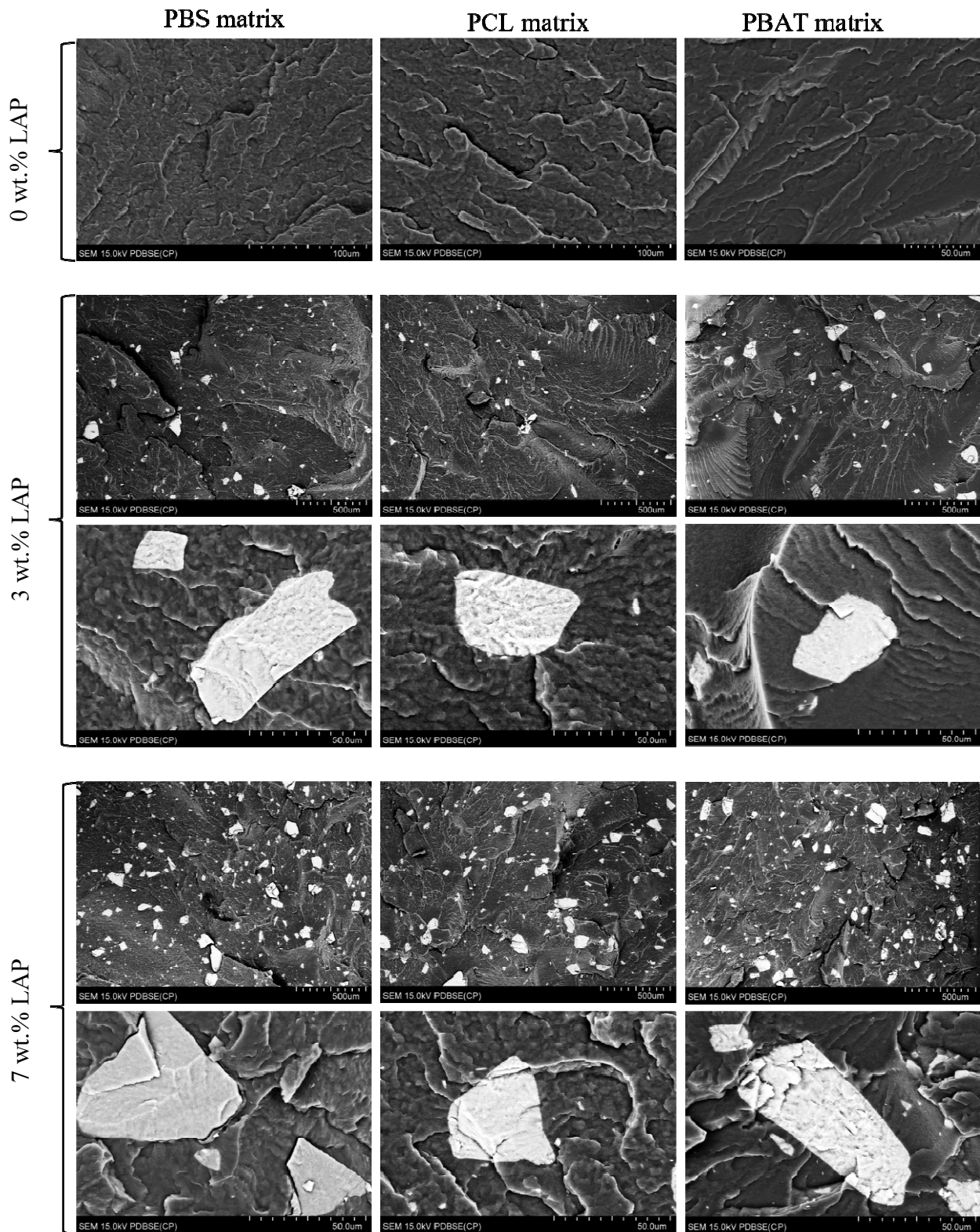


Fig. 1. SEM micrographs of PBS (left column), PCL (middle column) and PBAT (right column) composites; lower and higher magnification images are shown for composites with 3 wt.% and 7 wt.% LAP

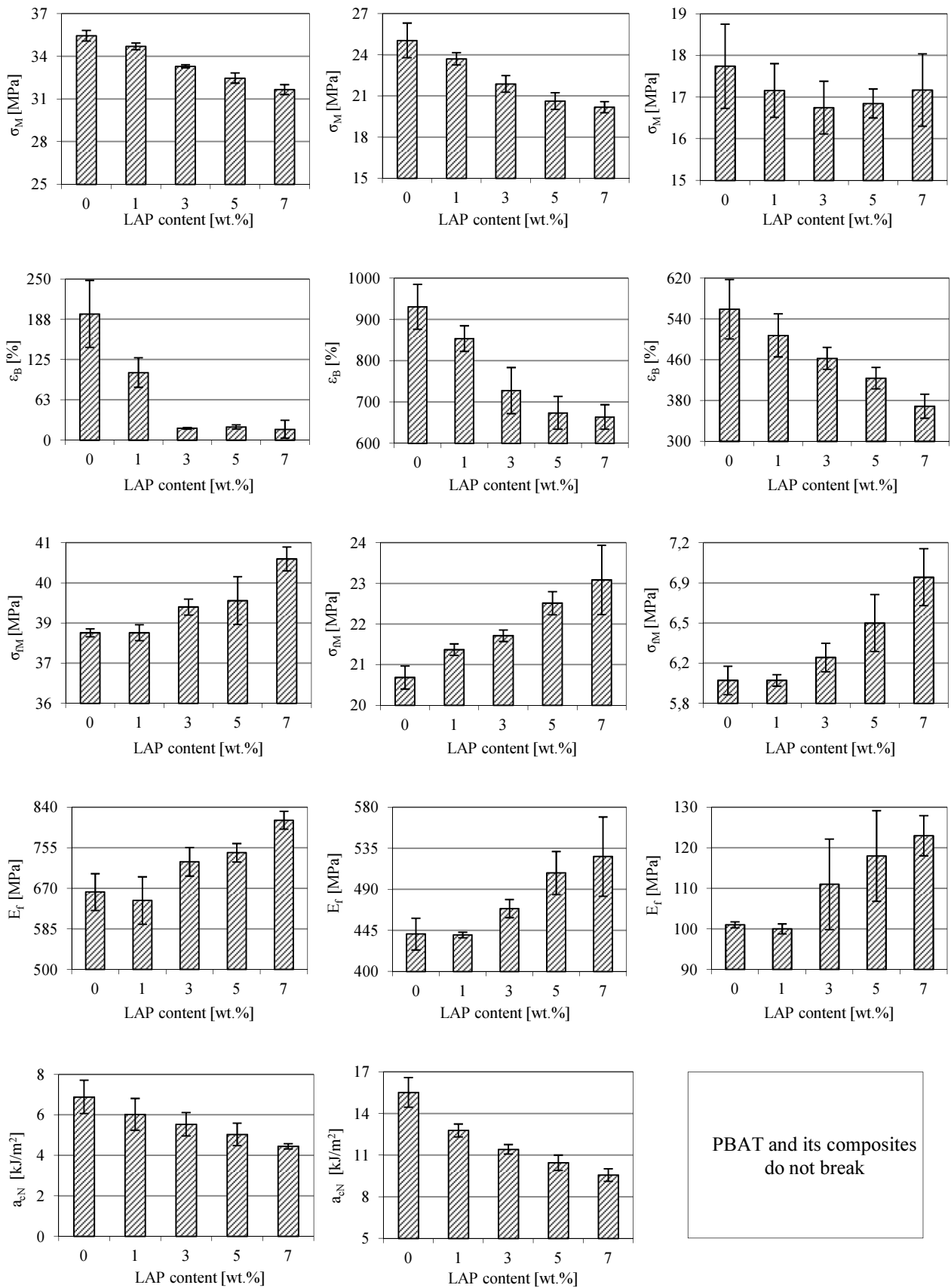


Fig. 2. Mechanical properties of studied samples (PBS-based samples – left column, PCL-based samples – middle column and PBAT-based samples – right column)

TABLE 2. Percentage changes in tensile strength ( $\Delta\sigma_M$ ), elongation at break ( $\Delta\varepsilon_B$ ), flexural strength ( $\Delta\sigma_{fM}$ ), flexural modulus ( $\Delta E_f$ ) and impact strength ( $\Delta a_{cN}$ ) of the studied composites compared to the unmodified polymers

Sample symbol	$\Delta\sigma_M$ [%]	$\Delta\varepsilon_B$ [%]	$\Delta\sigma_{fM}$ [%]	$\Delta E_f$ [%]	$\Delta a_{cN}$ [%]
BS1	-2	-46	0	-3	-12
BS3	-6	-91	+2	+10	-20
BS5	-8	-90	+3	+12	-27
BS7	-11	-91	+6	+23	-35
CL1	-5	-8	+3	0	-18
CL3	-13	-22	+4	+6	-26
CL5	-18	-28	+8	+15	-33
CL7	-19	-29	+10	+19	-38
BAT1	-3	-9	0	-1	-
BAT3	-6	-17	+3	+10	-
BAT5	-5	-24	+8	+17	-
BAT7	-3	-34	+15	+22	-

As follows from Table 2, LAP causes the greatest changes in: (i) the tensile strength of PCL, (ii) elongation at break of PBS, (iii) the flexural strength of PBS and PCL (the observed changes in these polymers are similar), and (iv) the impact strength of PCL. The smallest changes caused by the introduction of LAP into the polymer matrix were observed in: (i) the tensile strength of PBAT, (ii) elongation at break of PCL and PBAT, (iii) the flexural strength of PBS, and (iv) the impact strength of PCL. The changes in the flexural modulus of the tested polymers (PBS, PCL and PBAT) resulting from the addition of LAP to their matrices are similar. Moreover, LAP does not affect the impact strength of PBAT because all the PBAT/LAP composites exhibit the same behavior, i.e. they do not undergo breakage, regardless of the LAP content. Despite the fact that the changes in some of the values shown in Table 2 are large, their full analysis should also include the results of significance tests (Table 3). Performing these tests is important to determine whether the average values of the measurements in individual samples differ significantly from one another or not. Table 3 consists of 15 small tables corresponding to individual properties measured in the PBS, PCL and PBAT-based materials, respectively. The numbers in each of these tables represent a sample with a defined LAP content in the polymer matrix.

The data in Table 3 indicates that most (75 % of cases) of the measured properties are characterized by the fact that the results of individual samples differ significantly from one another. In the remaining 25 % of cases, the results of individual samples are not significantly different from one another. This situation is observed most often when samples differing in a LAP content by 2 wt.% are compared. The PBAT-based samples are also worth noting. In the case of the  $\sigma_M$  and  $E_f$  of these samples, most of the results are not

significantly different from one another. This proves that LAP has a much smaller effect on changes in the mechanical properties of PBAT than on the changes in these properties for PBS or PCL. Moreover, the lack of significance test results for the impact strength of these samples is due to the fact that they did not undergo breakage; nonetheless, this also indicates that their resistance to dynamic impact was similar, and LAP did not significantly affect the impact strength value.

TABLE 3. Results of significance tests (if “+/green field”, value between two samples are significantly different from one another, if “-/red field”, values between two samples are not significantly different from one another)

PBS					PCL					PBAT				
$\sigma_M$	1	3	5	7	$\sigma_M$	1	3	5	7	$\sigma_M$	1	3	5	7
0	+	+	+	+	0	-	+	+	+	0	-	+	-	-
1		+	+	+	1		+	+	+	1		-	-	-
3			+	+	3			+	+	3			-	-
5				+	5				-	5				-
$\varepsilon_B$	1	3	5	7	$\varepsilon_B$	1	3	5	7	$\varepsilon_B$	1	3	5	7
0	+	+	+	+	0	+	+	+	+	0	-	+	+	+
1		+	+	+	1		+	+	+	1		+	+	+
3			-	-	3			-	+	3			+	+
5				-	5				-	5				+
$\sigma_{fM}$	1	3	5	7	$\sigma_{fM}$	1	3	5	7	$\sigma_{fM}$	1	3	5	7
0	-	+	+	+	0	+	+	+	+	0	-	+	+	+
1		+	+	+	1		+	+	+	1		+	+	+
3			-	+	3			+	+	3			+	+
5				+	5				-	5				+
$E_f$	1	3	5	7	$E_f$	1	3	5	7	$E_f$	1	3	5	7
0	-	+	+	+	0	-	+	+	+	0	-	-	+	+
1		+	+	+	1		+	+	+	1		-	+	+
3			-	+	3			+	+	3			-	-
5				+	5				-	5				-
$a_{cN}$	1	3	5	7	$a_{cN}$	1	3	5	7	$a_{cN}$	1	3	5	7
0	-	+	+	+	0	+	+	+	+	0				
1		-	+	+	1		+	+	+	1				
3			-	+	3			+	+	3				
5				-	5				+	5				

### CONCLUSIONS

The studied PBS/LAP, PCL/LAP and PBAT/LAP composites are characterized by similar structures. Some changes, however, can be observed in the adhesion at the polymer-filler interface, which is slightly worse for the PBS-based composites. In addition, the fracture nature of PBAT and its composites appears slightly less brittle compared to other samples. Furthermore, in none the composites did LAP change its structure or disperse. As a consequence of the observed changes in the structure of the examined samples, there are changes in their mechanical properties.



These properties generally change similarly, regardless of the type of matrix into which LAP was introduced. Except for the three-point bending tests, the mechanical properties of all the investigated polymers generally deteriorate when LAP is added. Some changes in the measurements are large, especially if they are compared with the unmodified polymers. Nevertheless, taking into account the results of the significance tests, it is important to note that some results are not significantly different from one another, even if a trend in their changes is observed.

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