

Biodegradable Poly(Butylene Sebacate) Modified By Dimerized Fatty Acid And Poly(Ethylene Glycol)

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Abstract: The accumulation of non-degradable, synthetic polymers in the environment is a major problem, gaining increasing attention. One way to address this growing issue in waste management is to replace bioresistant synthetic polymers in use today with biodegradable polymers. Aliphatic polyesters are one of the most promising biodegradable materials, because they are readily susceptible to hydrolytic and enzymatic degradation. The present work includes the synthesis and properties of such biodegradable polymers based on aliphatic esters of sebacic acid, dimerized fatty acid, and polyglycol. These materials belong to the group of multiblock thermoplastic elastomers and the aim of this study was to examine changes in selected properties depending on the relative content of the components. Polycondensation in the melt was successfully carried out to obtain a series of copolyesters containing butylene esters of dimerized fatty acid (DLA), sebacic acid (PBSe) and a hydrophilic sequence – poly(ethylene glycol) (PEG 1000). All of the obtained copolymers had the same PBSe hard segment content of 50% wt., while the amount of DLA and PEG in the soft segments was varied. The thermal and mechanical properties, water uptake and contact angle, as well as biodegradability under composting conditions were studied. The results of the tests confirmed that the obtained copolymers belong to the group of thermoplastic elastomers and are biodegradable under composting conditions. With an increase in PEG content, there was an increase of hydrophilicity, but the elasticity of copolymers decreased.

Keywords: biodegradable aliphatic polyesters, dimerized fatty acid, multiblock thermoplastic elastomers, oligoether, PEG.

1 Introduction

Aliphatic polyesters are a group of materials attracting growing interest, because of their diverse applications and potential susceptibility to degradation in the environment [1-3]. Additionally, many polyesters are also biocompatible and this, combined with their biodegradability and easy processing, makes them attractive for applications in medicine, as a surgical materials, systems for controlled release of drugs or in tissue engineering [4,5]. The properties of these polyesters can be tuned by varying their chemical composition or by chemical and physical modification. For example, the introduction of a hydrophilic aliphatic polyester ether block can significantly change the properties of copolymers of this type, while preserving the biodegradability [6,7].

Many thermoplastic elastomers are linear multiblock copolymers having characteristic microphase-separated structure, due to the incompatibility between the hard and soft segments. Polymers with low glass transition temperatures, such as aliphatic polyesters and polyethers, are used as soft segments, endowing the elastomers with the necessary flexibility and extensibility. Meanwhile, the glassy or semicrystalline hard segment phase acts as a thermally reversible physical crosslinking site, as well as reinforcing filler for the soft phase. Additionally, the extent of mixing between the two phases is a very important factor determining the physical properties of the resulting elastomers. The mixing depends on the chemical structure, molecular weight, crystallinity, and composition of the hard and soft segments [8-10].

This work investigates polyesters belonging to the family of multiblock thermoplastic elastomers (TPE), with hard segments consisting of poly(butylene sebacate) (PBSe) and soft ester blocks of dimerized fatty acid (DLA) and sequences of poly(ethylene glycol) (PEG).

2 Experimental Methods

The following materials were used for the synthesis of multiblock copolymers: sebacic acid (Sigma-Aldrich, Germany), dimerized fatty acid (DFA) Pripol 1009, molecular weight ~575 g•mol⁻¹, (C36) (Croda, The Netherlands), 1,4-butanediol (Fluka, Germany), poly(ethylene glycol) (PEG, 1000 g/mol) (Sigma-Aldrich, Germany).

The synthesis was carried out in two stages. The first stage involved the esterification reaction of sebacic acid and DLA with 1,4-butanediol, carried out in the presence of MgTi catalyst. Next, poly(ethylene glycol) and vitamin E (to act as a stabilizer) were introduced into reactor and the second stage, the polycondensation reaction, was carried out. We were able to obtain copolymers with the same PBSe hard segment content of 50% wt., but with variable composition of the soft segment (Fig. 1) [6,7,10].

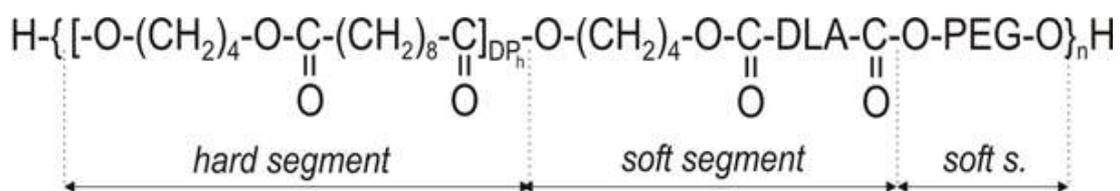


Figure. 1. Scheme of copolymers structure.

The obtained PBSe/DLA/PEG copolymers were subjected to a series of thermal, mechanical, and physical testing.

To prepare samples, the synthesized materials were first compression-moulded at a temperature approximately 10°C higher than the melting temperature of the individual copolyesters and under an applied pressure of 15 to 20 MPa. The samples were pressed into films 1 mm in thickness for tensile testing and ca. 0,5 mm for composting test. Finally, microdumbbells were cut out from the material with a cutting tool according to DIN 53504.

Measurements by differential scanning calorimetry (DSC) was performed using a Q100 calorimeter (TA Instruments), at a heating rate and cooling rate of 10 °C/min, over a temperature range of -100 to 100 °C.

Instron TMM testing machine was used to examine the tensile properties of the materials. Measurements of the tensile stress and elongation were carried out at a crosshead speed of 20 cm/min. The limiting viscosity number (LVN) was determined in chloroform at 25 °C, using an Ubbelohde viscometer.

The Melt Flow Index (MFI) was determined using a plastometer CEAST II-c-type CA-MAN-001, using a standard load of 2.16 kg at 70 ° C, with nozzle diameter $d = 2.095$ mm, nozzle length $L = 8$ mm.

The Hardness (H) was measured using a Zwick/Material Testing 3100 Shore D hardness tester.

Notched impact strength measurements were performed using Zwick 5102 "Hammer" impact tester over a range of 0.5 to 4 kJ.

Measurements of Charpy impact strength were performed at room temperature (23 °C) and at 40 °C according to PN-81/C-89029, with type 2 samples and type A notch.

Density measurements were carried out on with RADWAG model PS digital balance with built-in density determination function.

To test the water uptake of the materials, approx. 2 g polymer was placed in 50 ml of distilled water for 12, 24 and 72 hours at room temperature.

Contact angle tests were performed on polymer surfaces prepared by spin coating, using DataPhysisc, Contact Angle System OCA using ultra-pure water (5 μ L droplet).

Biodegradation tests were carried out on thin polymer films (60x60x0,5 mm) in a mixture of sand and compost (1:1), at 50 °C for 3 month [5].

3 Results and Discussion

The composition of the obtained copolymers and the results of selected physicochemical properties are presented in Table 1. The values of most of the parameters are similar, because the content of hard segments in the copolymers determines the majority of the properties. Thus, the chemical composition of the soft segments of these copolymers does not have a significant effect on the indicated properties. Only in case of density can a slight increase be observed, with increasing PEG content in the macromolecule.

Table 1. Composition and selected properties of the copolymers

No	Composition [% wt.]			LVN [dl/g]	Hardness [ShD]	Impact strength		MFI [g/10 min.]	Density [g/cm ³]
	PBSe	DLA	PEG			-40°C	23°C		
1.	50	50	0	1,316	50	w.b.	w.b.	59,1	1,045
2.	50	37,5	12,5	1,294	52	w.b.	w.b.	62,3	1,082
3.	50	25	25	1,387	54	w.b.	w.b.	63,6	1,120
4.	50	12,5	37,5	1,271	57	w.b.	w.b.	63,0	1,156
5.	50	0	50	1,298	59	w.b.	w.b.	61,7	1,184

w.b. – without break under conditions of measurement

The obtained copolymers are characterized by having substantial molecular weights (LVN) and exhibiting ease of melt flow during processing (MFI) and low hardness. The results in Table 1

indicate that the obtained materials can be considered high impact copolymers, especially in cold temperatures, due to the low glass transition temperature of soft segments, which for these polymers is much lower than $-40\text{ }^{\circ}\text{C}$.

The DSC cooling and 2nd heating scans for copolymers are shown in Figure 2. The results of the DSC measurements indicate that the obtained polymers exhibit a single low-temperature glass transition (T_g) in the range -60 to $-65\text{ }^{\circ}\text{C}$, corresponding to the glass transition temperature of a homogeneous amorphous phase. However, as the content of ether units increases, an increase of T_g is observed.

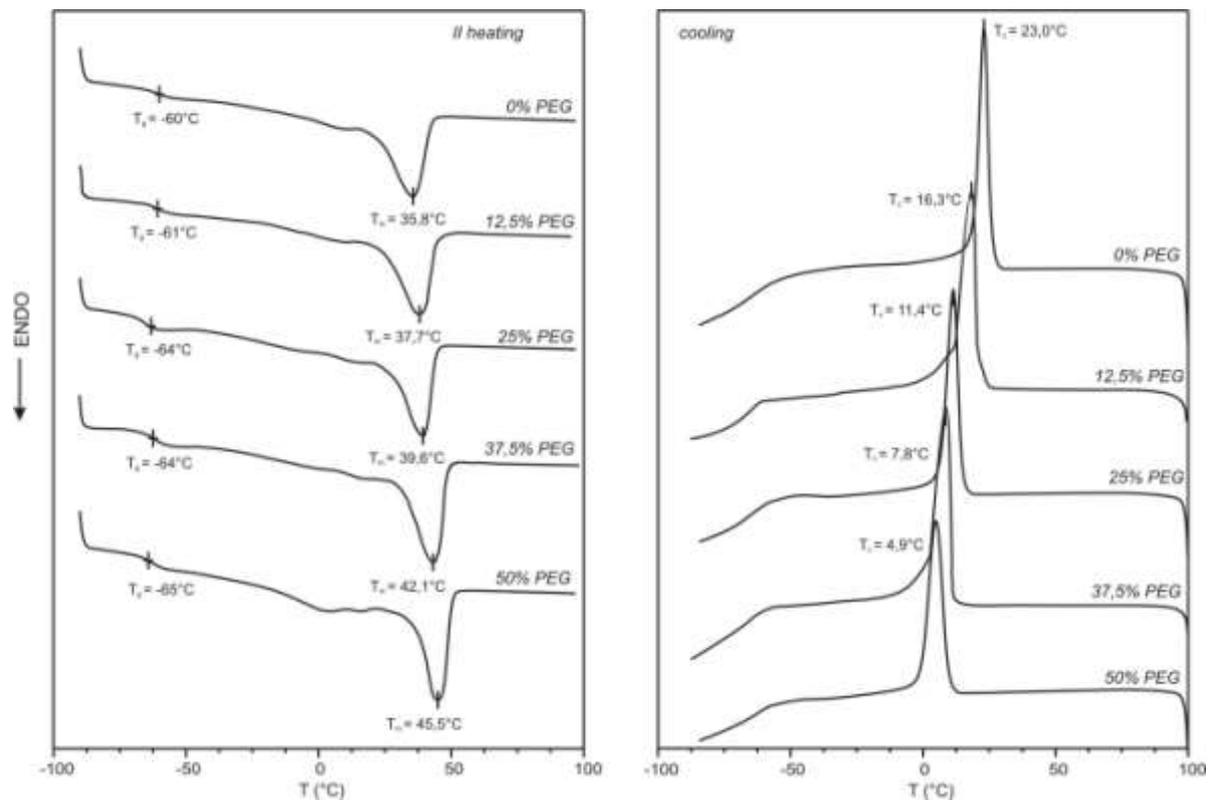


Figure. 2. DSC 2nd heating and cooling thermograms of the PBSe/DLA/PEG copolymers.

The slight shift of the glass transition temperature attributed to the soft phase is a result of its composition. This phase consists of soft segments and the amorphous part of hard segments, which depends on the hard to soft segment ratio in the copolymer, and their ability to create a homogeneous mixture.

Endotherms associated with the melting point of the hard segments PBSe (T_m) can also be observed on the DSC thermograms. The shape and number of peaks observed in the melting range depends on the molecular weight of the polymer and the dispersion of the hard segments, as well as the temperature and time of crystallization. Meanwhile, a shift in the position of the main melting peak of polymers with similar thermal history depends on the molecular weight of hard segments and their content in the copolymer. Here, in the case of equal content of poly(butylene sebacate) hard segments, we observe that the melting point T_m shifts toward higher values with increasing PEG content. This increase in the melting point combined with a decrease of in glass transition temperature

is an indication of increasing microphase separation. At the same time, well-defined crystallization temperatures of hard PBSe segments (T_c) can be observed. The increasing difference between the melting points and increasing tendency towards crystallization is associated with the crystallization of PEG.

The PBSe/DLA/PEG polymers have very good elastic properties, as confirmed by the results of mechanical tensile tests presented in Fig. 3 and 4. The obtained copolymers are characterized by a high elasticity and the shape of the stress-strain curve is typical of multiblock thermoplastic elastomers. On the curves, the yield point is clearly evident, along with considerable elongation at break (Fig. 3).

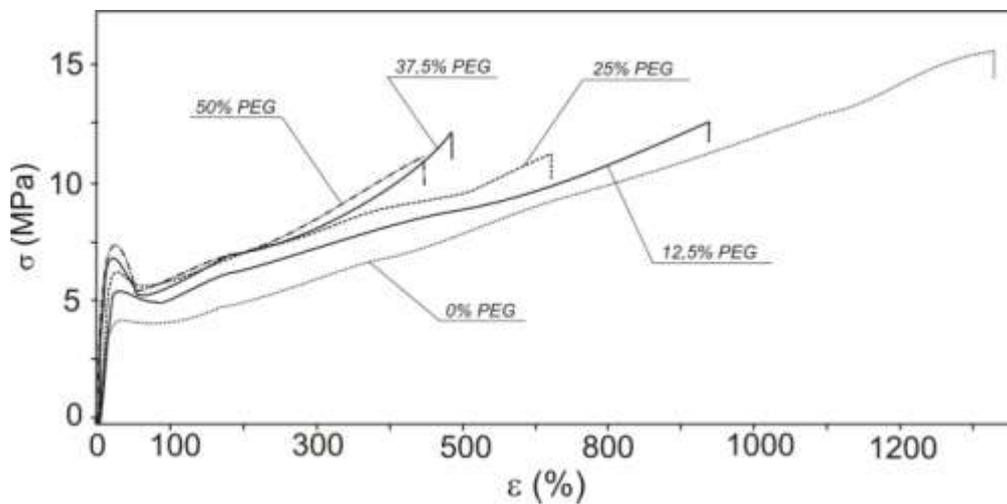


Figure. 3. Stress-strain curves for investigated copolymers.

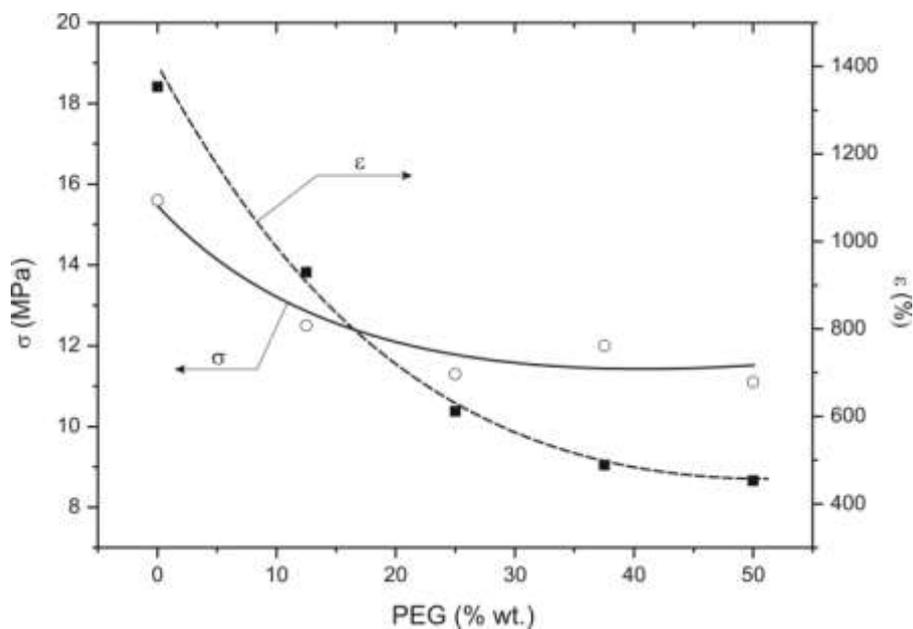


Figure. 4. Tensile strength and elongation at break vs. PEG content.

With increasing ether blocks, a decrease in the tensile strength and elongation at break can be observed. This decrease in elasticity can be explained by the greater tendency of PEG to crystallize, yielding harder soft segments, as compared to the greater ability to mobility of elastic polymer chain fragments containing more sequences of dimerized fatty acid (Fig. 4).

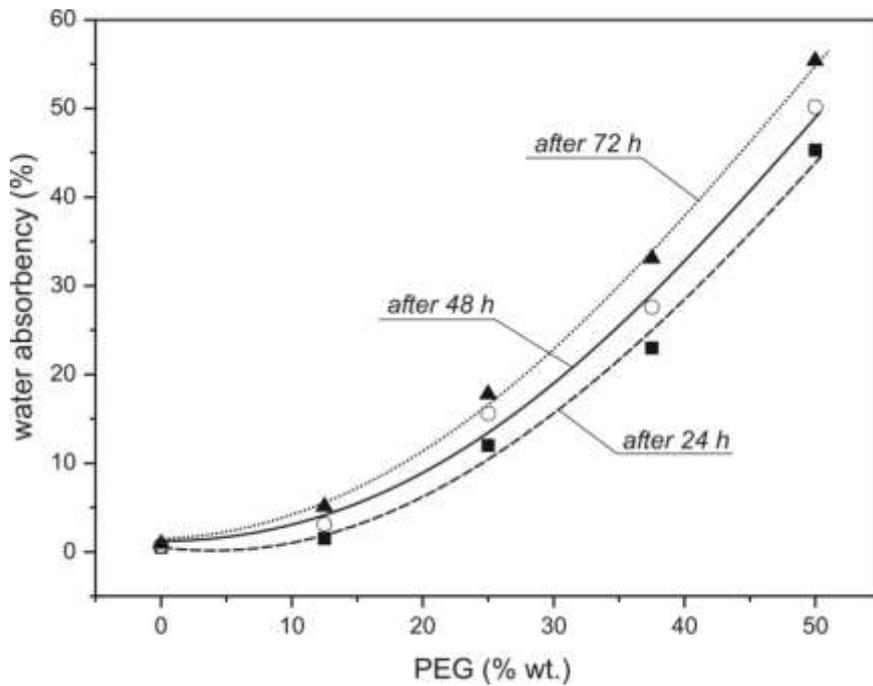


Figure. 5. Water uptake after 24, 48 and 72 hours of PBSe/DLA/PEG copolymers.

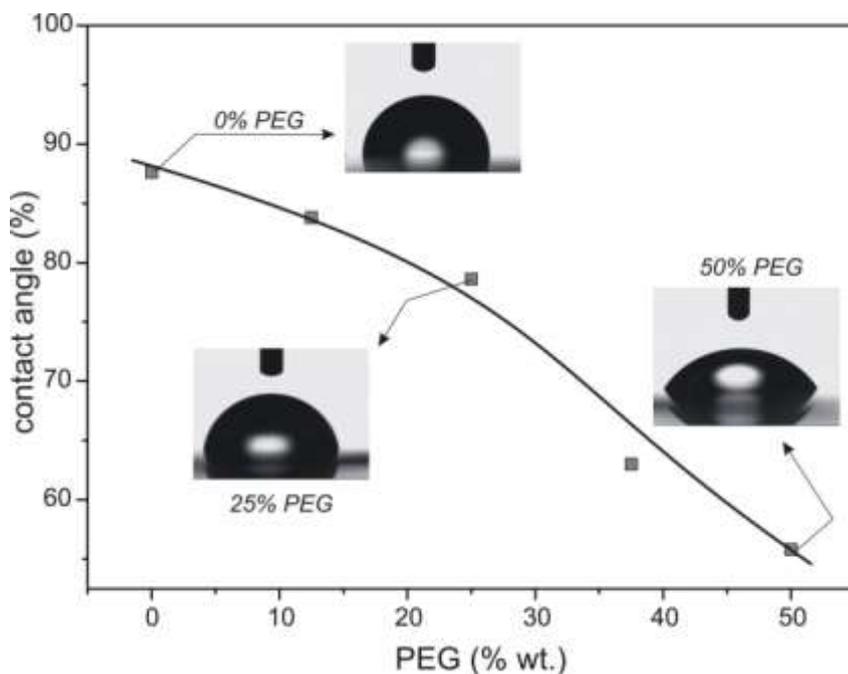


Figure. 6. Contact angle vs. PEG content in the copolymers.

The results of water uptake after 24, 48 and 72 hours are shown on Fig. 5. An increase in water uptake was observed with increasing content of poly(ethylene glycol), due to the hydrophilicity of PEG. Fig. 6 presents the results of water contact angle measurements for all investigated polymers, as well as selected representative images of drops on copolymers with differing PEG content. As expected, the highest contact angle is observed for the polymer not containing any ether moieties and with increasing content of poly(ethylene glycol), the contact angle decreases, indicating that the hydrophilicity of the polymers significantly increases.

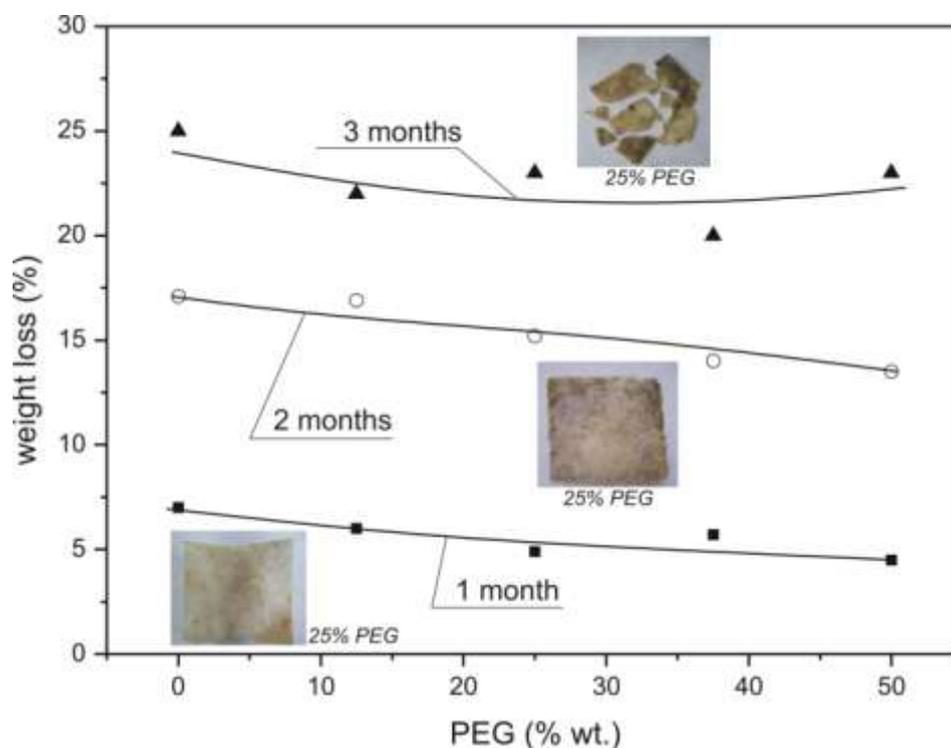


Figure. 7. Weight losses of the PBS/DLA/PEG copolymers vs. biodegradation periods.

Finally, a preliminary study of the susceptibility to environmental biodegradation of the obtained copolymers was carried out in a mixture of sand and compost (1:1), at 50 °C for 3 months. Fig. 7 presents the mass loss of the samples at different incubation times, as a function of PEG content. Mass loss of up to 25% can be observed following 3 months of incubation, with higher mass loss observed for samples with lower content of oligoether sequences.

4 Conclusion

Biodegradable multiblock thermoplastic elastomers were successfully synthesized based on aliphatic oligoesters with poly(butylene sebacate) as hard segments and soft phase derived from dimerized fatty acid and poly(ethylene glycol).

The DSC results show that the obtained PBSe/DLA/PEG copolymers exhibit two main transition temperatures: low-temperature glass transition attributed to the soft segments and high-temperature melting transition attributed to the hard segments. These results are indicative of microphase separation of, at least, two phases.

Overall, the copolymers are characterized by moderate melting temperatures. The incorporation of the ether sequence into structure of the copolymers causes an increase in the melting temperature, as well as an increase in hydrophilicity. Finally, tensile testing and resultant stress-strain curves confirmed the typical thermoplastic elastomer behaviour for all of the synthesised copolymers.

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