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Study of welding of poly(ether-ester) elastomers

Part I. INFLUENCE OF CONTENTS OF FLEXIBLE SEGMENTS ON MORPHOLOGY AND MECHANICAL PROPERTIES

Summary — Weldability of poly(ether-ester) (PEE) multiblock elastomers, which belong to the group of the thermoplastic elastomers (TPE), was investigated. Investigated PEE consisted of soft polyoxytetramethylene (*FS*) blocks and hard poly(butylene terephthalate) (*RS*) blocks; with the *FS:RS* ratio variable. Welds were prepared using the wire (rod) welding technique and extrusion welding. Optical and scanning electron microscopy were used to characterize weld morphology and their mechanical properties (elongation, bending, impact strength). Materials for the seams were not dried prior to welding, so hydrolytic degradation took place during welding (250—300 °C), visible particularly in PEEs with higher *RS* content, as shown by results of flow rate measurements (*MFR*). The investigations demonstrate that the PEE elastomers containing predominantly the PTMO rich soft phase are well weldable using the applied techniques, even when non-dried material is used for the welds.

Key words: multiblock thermoplastic elastomers, wire welding, extrusion welding, welding of polymers, soft blocks to hard blocks ratio, weld morphology, weld mechanical properties.

Welding method gaining importance for partial cost reduction because of the increasing use of thermoplastics and thermoplastic composites in load-bearing applications. Selection of appropriate technique and parameters depends primarily on the material of the parts to be joined and on the nature of the product.

Hot-tool welding is most often applied for joining plastic pipes and sheets *e.g.* PE, PP. Polymers contain moisture which, depending on polymer, deteriorates the weld strength to greater or smaller extent. Stokes [1] compared the hot-tool welding of dried and non-dried polycarbonate specimens. These examinations indicated that dried specimens exhibited greater weld strength, but when suitable welding parameters were provided it was possible to obtain similar weld strength of the dried and non-dried specimens.

Diffusion of macromolecules occurs during welding between the plasticized joined material and the seam, and a durable cohesive joint is formed after cooling. Diffusion in the formed joints is restrained when plastics are contain mineral fillers, which deteriorate its properties [2, 3]. Sufficient mobility and similar chemical structure of the diffusing chains are the prerequisites of forming a good seam, therefore most often welding techniques are used for joining parts made of the same material. It is also possible to produce joints of different polymers *e.g.* seams of poly(methyl methacrylate) (PMMA) parts made from rod-wire plasticized suspension PVC have higher strength than if made with a PMMA rod. Good results have been obtained *e.g.* in welding of polycarbonate (PC) and polyetherimide (PEI) to each other [4] and also in welding of certain blends [5].

If the polymer is polar and exhibits appropriate dielectric losses, *e.g.* PVC, an advantage can be taken of the high frequency welding technique. Laser and microwave welding techniques are continuously gaining importance in industrial applications [6]. Plastics exhibiting high elasticity modulus can be joined by ultrasonic welding [7]. Wire and extrusion welding are inexpensive and efficient joining methods suitable for most thermoplastics. The weldability and welding conditions of

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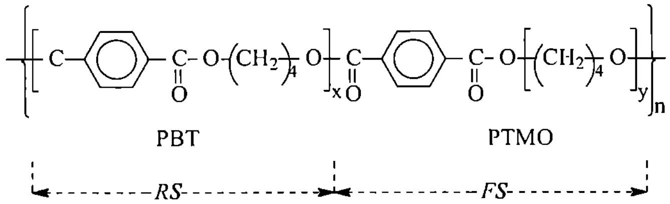
common thermoplastics have been the subject of many publications, as well as of monographs published by welding associations [8, 9].

Thermoplastic elastomers (TPE) show high rubber-like elasticity similar to the properties of vulcanized rubber and processability typical for thermoplastic materials [10]. TPE are a relatively new and constantly evolving group of construction materials. Their thermoplastic properties point to the existence of an efficient method of jointing them using welding techniques. So far there are only few publications in this topic. Tuchert *et al.* [11] examined the weldability of the ethylene—propylene—diene terpolymer (EPDM)/polypropylene blend, a typical TPE, and obtained remarkable strength of weld seams, but strain lower than for the initial material. Hollande *et al.* [12] investigated high-frequency welding of thermoplastic polyurethane elastomer (TPUR) coated fabric. Their experiment indicated that high-frequency welding of TPUR was possible.

Poly(ether-esters) (PEE) are block copolymers in which polyether segments form a soft phase with a low glass transition temperature providing the rubber elastic properties, and polyester segments form a crystalline hard phase responsible for strength and mechanical properties of the material. In the melt, this polymer is homogenous, but separates into a micro heterophase structure during cooling [13].

The objective of this work was to examine morphology and mechanical strength of PEE welded joints. Furthermore, we investigated properties of the seams made from elastomers of the same type, but with hardness different from that of the joined material.

As the PEE elastomers are susceptible to the hydrolytic degradation [14], the melt flow rate (*MFR*) of dried and non-dried materials as a function temperature was investigated in order to determine the susceptibility ratio. Poly(tetramethylene oxide)/poly(butylene terephtalate) multiblock elastomers with different content of the flexible segments (*FS*) and of the rigid segments (*RS*) were used [Formula (I)].



$$\left[\left[\overset{\displaystyle O}{\underset{}{C}}-C_6H_4-\overset{}{\underset{\displaystyle O}{\overset{\|}{C}}}-O-(CH_2)_4-O\right]_x\left[\underset{\displaystyle O}{\overset{\|}{C}}-C_6H_4-\underset{\displaystyle O}{\overset{\|}{C}}-O-\left[(CH_2)_4-O\right]_y\right]\right]_n$$

(I)

EXPERIMENTAL

Materials

Elitel®, Elana SA, Toruń (Poland) with PTMO ($M_n \approx$ 1000 g/mol) elastomers, *FS*, were used in the study. Molecular weight, RS, are variable and depend on their content in the copolymer. The materials in the form of pellets with Shore D hardness: 68, 58, 47, 42, contained 20, 40, 50 and 55 wt. % of flexible segments, respectively. Physical properties of Elitels are given in [15].

The following specimen numbering structure has been applied to facilitate analysis of the results: first number denotes the percent content of the *FS* in the joined material, the letter denotes the welding technique (*E* — extrusion, *W* — wire), the second number denotes the percent content of the *FS* in the binder material. A specimen denoted by a number, only, refers to the original, not welded material and shows the percent content of *FS*. For example 40W50 denotes specimens containing 40 % *FS* welded with wire containing 50 % *FS*.

Welding method

Welding was performed during the wire and extrusion methods. In both techniques the materials were welded in a stream of hot atmospheric air. Wire welding was performed by creating a bevel joint, with the being joined material first plasticized in hot air, and wire being laid to form the seam by using a welding nozzle equipped with a special foot (Fig. 1). Extrusion welding was performed by extruding the plasticized binder material from an extruder equipped with a special head (welding shoe), which shapes the weld seam between the bevelled welded material plasticized with hot gas (Fig. 2).

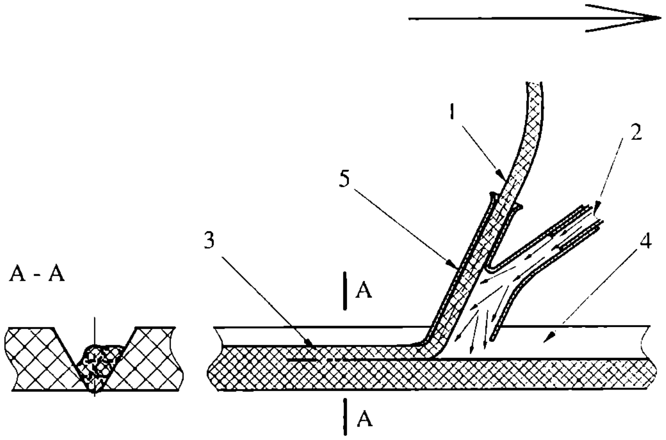


Fig. 1. Wire welding in a stream of hot air; 1 — welding wire, 2 — hot air, 3 — weld, 4 — bevelled welded material, 5 — welder nozzle; the arrow shows direction of weld nozzle movement

Leister-Triac welder from Leister, Kagiswil (Switzerland) was used for wire welding, and the extrusion welder from Baumbach (Germany) was applied for extrusion welding. Temperature of hot air for welding was chosen experimentally individually for each of the sam-

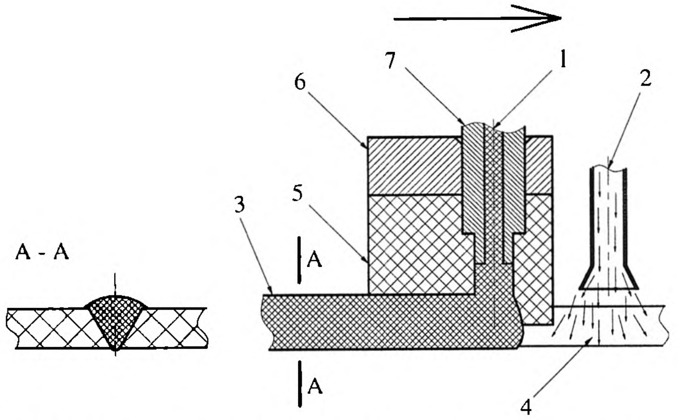


Fig. 2. Extrusion welding in the stream of hot air; 1 — molten material from extruder, 2 — hot air, 3 — weld, 4 — bevelled welded material, 5 — welding shoe made of PTFE, 6 — mount of the shoe; the arrow shows direction of welding shoe movement

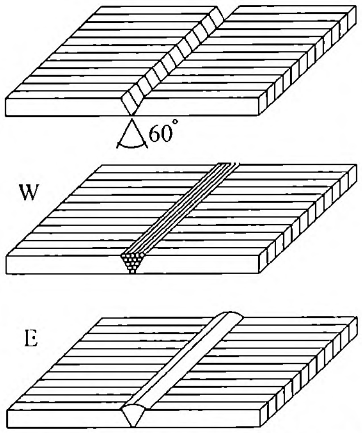


Fig. 3. The arrangement and method of joining the specimens: W — wire welding, E — extrusion welding

ples by visual assessment of the course of the welding process and the formed weld; temperature was in the 250—300 °C range. The lowest air temperatures at which equal plastification of both the welded material and the wire occurred were chosen, and the welder nozzle advance was kept constant at approx. 30 cm/min.

Preparation of samples

Extrusion of wires for wire welding

Welding wires were produced from granulates under the specified below conditions using the referred to above extrusion welder and the specially designed cooling-receiving system:

— Drying of granulate — 6 h at 110 °C in air,

— Melt temperature — 20 °C above T_m by Boetius,

— Extrusion pressure — 5 MPa,

— Nozzle diameter (ϕ) — 4 mm.

Preparation of the specimens for joining by welding

Specimens in the form of square bars 10×10 mm were molded on an injection molding machine under the following conditions:

— Drying of granulate — 6 h at 110 °C in air,

— Injection pressure — 60 MPa,

— Melt temperature — 20 °C above the melting point (T_m) by Boetius,

— Mold temperature — 40 °C.

Drying of the wires, granulate and the joined samples immediately before welding was omitted to fulfill industrial requirements, where costs play an important role. The material was conditioned for 72 hours at room temp. of 23 °C and relative humidity of 50 %, with welding performed under the same conditions.

A bevel was made in the bars by milling. Water cooling and appropriately low machining feed rates were applied to avoid changes in material structure. The bars were set into series (welded packs) and, next, V-groove butt welded (Fig. 3).

Methods

Morphology

Photographs of the weld cross sections were taken using a CCD (*charged-coupled device*) camera. A red penetrant was coated onto the weld of the material containing 20 % of the soft phase in order to outline the defects.

Morphology of the weld fracture surfaces was evaluated on the basis of micrographs taken with a field emission scanning electron microscope (SEM) (Leo 1530 Gemini from LEO Electron Microscopy Ltd., Germany) at 10 kV accelerating voltage. Fracture surfaces were produced after cooling of specimens by immersing in liquid nitrogen for 2 min. Fracture surfaces were sputtered with 10 nm of gold.

Mechanical properties

Standard bars were produced from the welded packs of specimens by cutting and milling for the purpose of tensile strength and bending strength testing, with additional bars produced for the needs of tensile, bending and impact strength tests.

Static tensile test (at 100 mm/min) and bending test were performed on Instron TMM 1161 (USA) testing machine. Impact strength was determined in compliance with the standard. Bending test and impact test were performed from the side of back of the weld. The obtained results were referred to the non-welded material in order to determine relative properties of the welds.

Melt flow rate

The measurements of the melt flow rates (*MFR*) were performed on dried and non-dried PEE (according to ASTM D1238) on Extrusion Plastometer (Melt Flow T.Q. Ceast, Italy). Preheating 4 min, load 2.16 kg. The material was dried in a vacuum drier for 4 h at 120 °C and tested immediately after removing from the drier. The non-dried material was conditioned for 72 hours at room temp. of 23 °C and 50 % relative humidity. In order to plot the dependence of *MFR* as a function of temperature, the materials were tested in six different temperatures from +5 °C to +30 °C above T_m by Boetius.

RESULTS AND DISCUSSION

Morphology

No defects are visible on photographs of the extrusion seams cross sections with *FS* content above 50 % (Fig. 4a), but those of specimens with 40 % *FS* content exhibit bubbles visible for the unaided eye, and those with 20 % *FS* content exhibit bubble migration and aggregation, leading to a hole developing in the middle of the seam. Absence of bubbles in proximity of the hole proves that the cavity has been formed out of them. More bubbles are visible only at some distance from the cavity. The cavity was removed by milling of the 20E20 material specimen for mechanical testing.

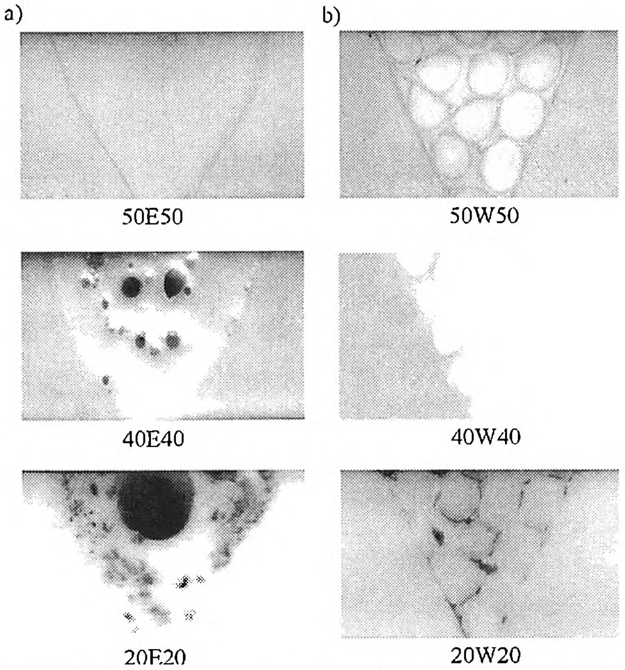


Fig. 4. Macroscopic photographs of the weld cross-sections: a) extrusion welds, b) wire welds

No bubbles are visible on photographs of the wire weld seams cross sections (Fig. 4b) in the material with 40 % *FS* content, even though they were visible the extrusion weld seams of the same material. Bubbles have been disclosed only on the photographs of wire weld seams cross sections for the material containing 20 % *FS*.

Hydrolytic degradation is expected during melting non-dried polymers containing ester bonds. Ester bonds in the PBT segment and ester bonds between the *FS* and terephthalate units were present in the hydrolytically degrading PEE. The phenomena of degradation can cause, among other effects, the evolution of byproducts in the form of bubbles. The higher rigid ester segment content in the material the larger is the extent of degradation. Deterioration of weld seam properties with decrease of the *FS* content and increase of the *RS* content is a consequence of the described above phenomena.

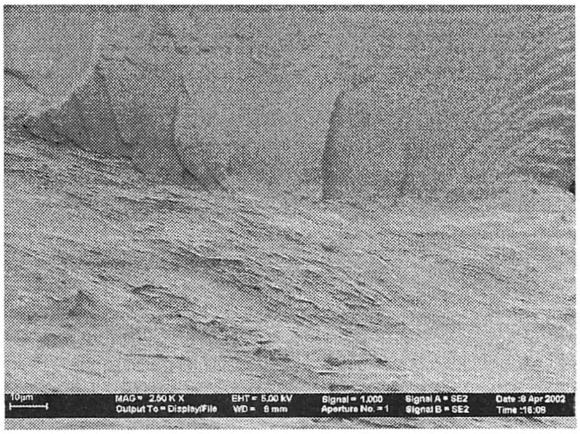


Fig. 5. SEM micrograph of a fracture surface of 55E55 weld. Boundary material weld runs horizontally. Welded material on top, weld underneath

Photograph of the 55E55 weld seam (Fig. 5) reveals that diffusion proceeded properly and a defects-free cohesive bond was produced. SEM micrograph of the 50E50 weld seam (Fig. 6) already shows presence of defects in the form of bubbles, even though these were not visible on the macroscopic photograph of that seam (Fig. 4a). SEM micrograph of the 50W50 wire seam (Fig. 7) shows that diffusion does not occur to the same high degree as in the case of extrusion welding, and the break surface clearly displays existence of material-wire boundaries.

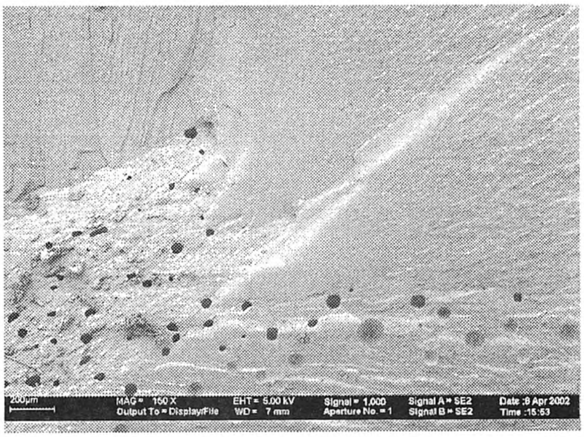


Fig. 6. SEM micrograph of a fracture surface of 50E50 weld. Boundary material weld runs horizontally. Welded material on top, weld underneath

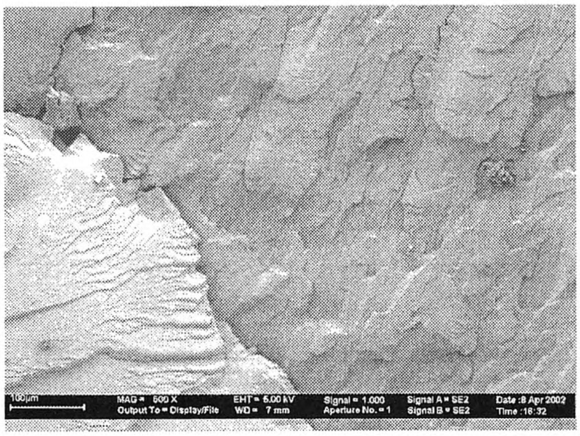


Fig. 7. SEM micrograph of a fracture surface of 50W50 weld. Welding wire is in the left lower part in the micrograph

Multiple beads were laid during wire welding, so the material experienced multiple heating cycles; nevertheless the wire was not cross-melted. Multiple heating cycles in course of wire welding leads to higher progress of degradation as compared with extrusion welding degradation, thus accounting for the inferior properties of wire-weld seams. Bubbles can be released only in a melt having sufficiently low viscosity, so less bubble are visible in the wire-weld seams as compared with extrusion-weld seams, despite higher degradation of the wire-welds. Extrusion welding involves just one heating cycle, so the seam is stronger, but cross-melting leads to uniform release of bubbles throughout the entire seam, with onset of aggregation also being possible.

Mechanical properties

Table 1. Mechanical properties of the welded points

Samples	Tension		Bending		Impact strength
	maximum tensile stress MPa	elongation at break %	maximum bending stress MPa	fractured /all	fractured /all
55	19.2	410	11.3	0/5	0/5
55E	13.0	180	10.0	0/5	0/5
55W	11.0	40	9.1	0/5	0/5
50	20.0	330	11.4	0/5	0/5
50E	10.0	24	10.5	0/5	0/5
50W	9.8	25	10.1	0/5	0/5
50E40	9.5	21	10.7	0/5	0/5
50W40	11.2	30	10.3	1/5	1/5
40	21.0	188	22.4	0/5	0/5
40E	16.3	23	19.0	0/5	5/5
40W	15.5	15	17.0	0/5	4/5
40E50	13.0	25	16.7	0/5	5/5
40W50	10.0	10	11.0	5/5	4/5
20	27.0	143	40.7	0/5	0/5
20E	18.0	4	27.0	5/5	5/5
20W	8.6	1.7	15.0	5/5	5/5

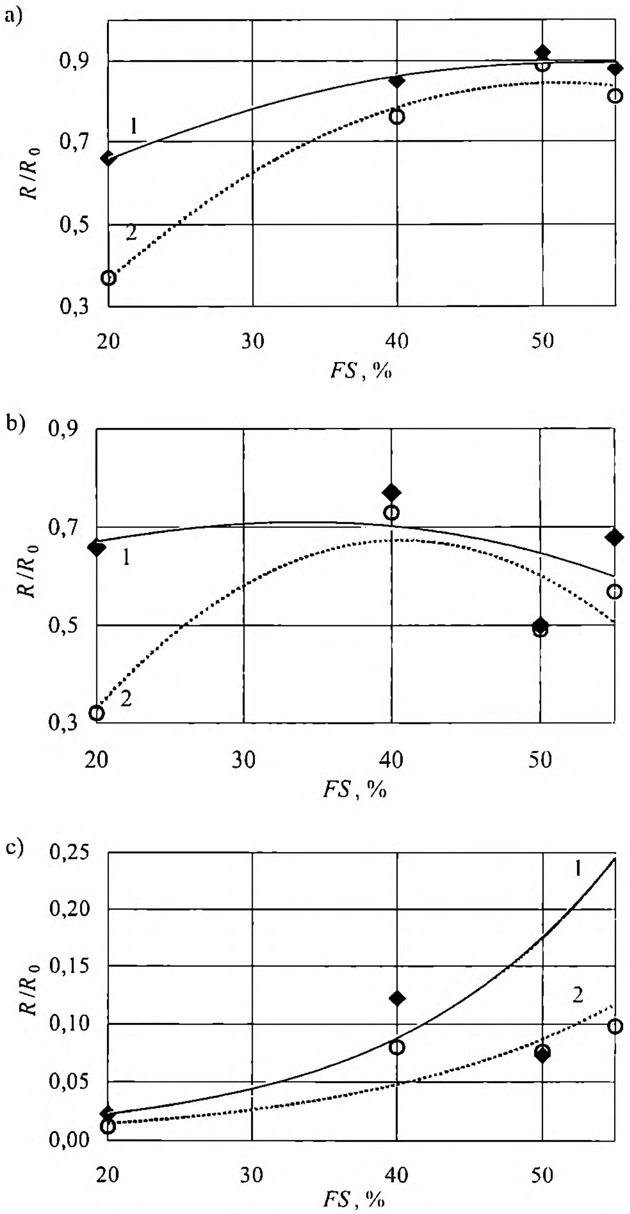


Fig. 8. Dependence of bending strength (a), tensile strength (b), elongation at break under tension (c) of welded PEE elastomers on the FS content; R/R_0 — relative value of mechanical property referring to primary non-welded polymer; 1 and solid marks — extrusion welding, 2 and empty marks — wire welding

Results of the mechanical tests are given in the Table 1 and presented graphically in Fig. 8 and Fig. 9. Elongation at break is the most negatively affected of the investigated mechanical properties of the seams. Its value is approximately 0.5 for the 55 % *FS* polymer, only. Weld seams lose their elastomeric properties at lower *FS* contents, what is manifested by fracture in impact tests and even by fracture during bending tests. Figure 9 graphically presents results of mechanical tests of mixed seams (materials 40/50 and 50/40), *i.e.* the seam is made of a material having different hardness than the being joined material *i.e.* having different *FS* content. Seams made of

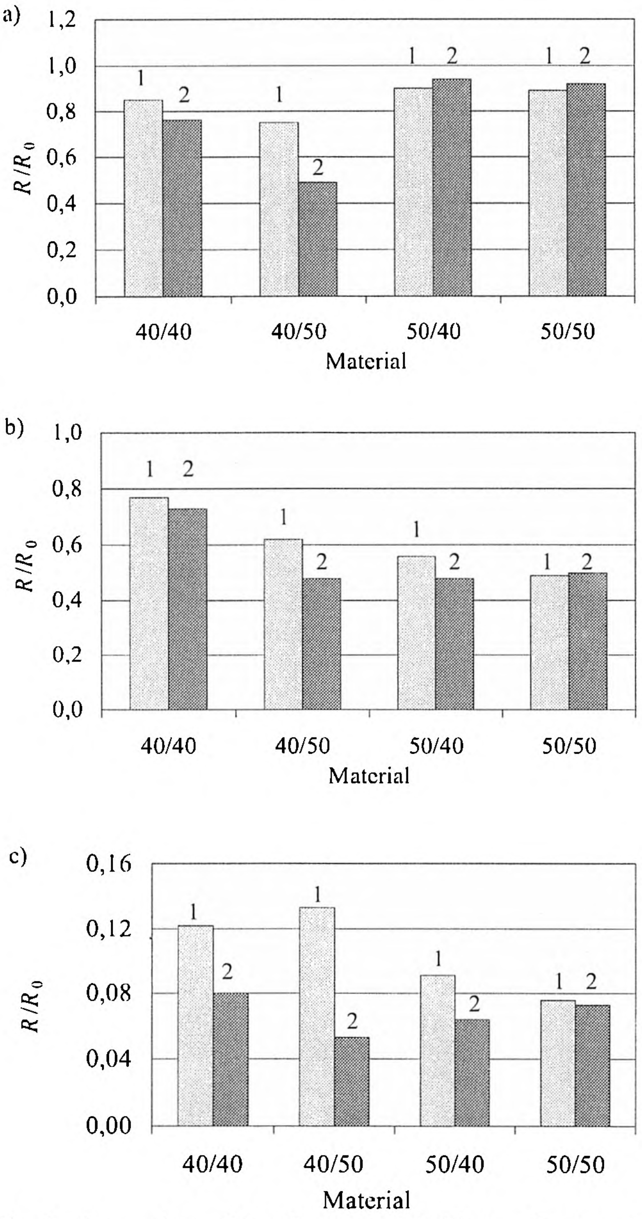


Fig. 9. Comparison of bending strength (a), tensile strength (b), elongation at break under tension (c) of welded PEE elastomers with weld seams made of the original material (40/40 or 50/50) and of material with different content of the FS; (R/R_0) — relative value of mechanical property referring to primary non-welded polymer, (material) — content of the FS in the welded/binder material

lower hardness material show much improved relative elongation at break, but the maximum stress in bending and tension tests deteriorate compared to the seams made using materials of the same hardness (40/40 or 50/50). This can be explained by the fact that besides larger elongation under tension, the softer material exhibits higher resistance to tension and bending. Generation of seam using a material harder than the being joined materials was expected to impart higher resistance to tension and bending as compared with welding using a material of the same hardness. Experiments do confirm this hypothesis, but the results were not significant, and reported in extrusion welding, only. The seam of such type contained defects in the form of bubbles visible on the SEM micrograph.

Melt flow rate

The viscosity of a polymer is positively correlated with its molecular weight and approximately inversely correlated with *MFR*. If *MFR* measurements performed on two identical materials under the same conditions, except for different thermal history and drying conditions, give differing results, this means that the material with a higher MRF value (*i.e.* lower molecular weight) has underwent more pronounced deterioration. *MFR* tests results expressed as a function of the temperature of poly(ether-ester) elastomers used for welding indirectly show how degradation is severely affected by omission of the drying step (Fig. 10). *MFR* lines as functions of temperature for dried materials show increase of *MFR* related to the normal viscosity drop resulting from thermal vibrations of macromolecular segments. In contrast, the omission of drying causes unnatural increase of *MFR* with temperature, related to hydrolytic degradation; the lower *FS* the content the steeper the increase.

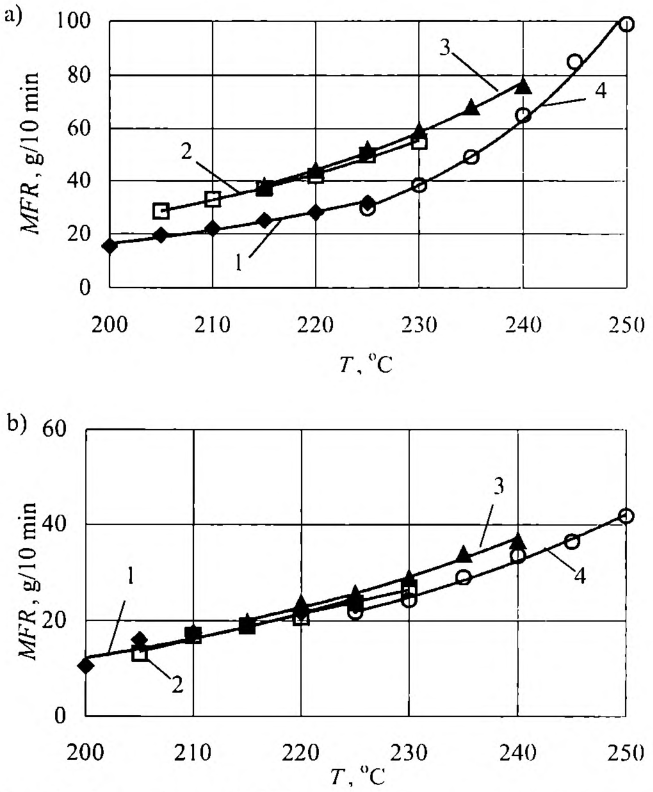


Fig. 10. Dependence of MFR on the measurement temperature (T); a) non-dried materials, b) dried materials. Content of FS in % wt.: 1 — 55, 2 — 50, 3 — 40, 4 — 20

CONCLUSIONS

Poly(ether-ester) elastomers containing predominantly the PTMO soft phase are well weldable. SEM micrograph of the weld fracture surface of these specimens shows a correct joint existing between the weld and the being joined material. Mechanical properties of this weld are similar to those of the original material, except for the elongation. Elongation at break of the welds in welded PEE decreases considerably compared to the original material. Mechanical properties deteriorate with increasing of *RS* content. Ester bonds in rigid segments are susceptible to hydrolytic degradation, which occurs in seams produced using non-dried material. SEM micrographs of weld cross sections show defects in the form of bubbles. Mechanical properties of extruded welds are generally a slightly better than those of the wire welds. In our case, when a polymer is thermally sensitive, wire welding gives better results, as the weld is not melted through. Attempts to produce seams using materials with hardness different than that of the being joined materials were promising, and allowed to influence seam properties. This is important, because almost always the same material has to be used both for the seam and the welded parts. It is useful to investigate welding of PEE elastomers with materials dried immediately before processing. Stabilizing agents for this polymer should be developed in parallel in order to protect it from hydrolytic degradation, what could lead to improved weldability of elastomers with higher content of ester *RS*. It is also recommended to perform weldability tests on PEE elastomers originating from different producers.

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