EFFECT OF TEMPERATURE ON THE MECHANICAL PROPERTIES OF THE HIGHLY FILLED COMPOSITES BASED ON POLYPROPYLENE AND GROUND RUBBER SCRAP

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Abstract

The mechanical properties of the dispersion-filled composites based on polypropylene (PP) and ground rubber scrap are studied in the temperature range from 40 to 120 °C. The content of the rubber particles is varied from 40 to 80 wt %. The peculiarities of the realization of a brittle-to-ductile or ductile-to-ductile transition in the composites are determined. The change in the deformation behavior occurs through the intermediate tension of the composite with the formation of several delocalized necks in the range of the filler concentrations. The negative effect of large particles during macrouniform tension of rubber plastics is shown for the first time. Their presence in the composite composition facilitates its fracture while the matrix polymer is underloaded (the effect of a single defect).

Key words: composite, elastic filler, brittle-to-ductile transition, ductile-to-ductile transition.

Introduction

The development of methods for recycling the wastes of rubber goods and determining the directions for their further rational use is one of the most important environmental issues [1]. One of the possible solutions to this problem is the application of ground rubber scrap as the fillers for thermoplastic polymers [2, 3]. Polyethylene (PE), PP, poly(vinyl chloride) (PVC), thermoplastic elastomers, and polyolefin wastes can be used as matrix polymers [2–8]. In Russian literature, these dispersion-filled composites are called rubber plastics [9, 10]. The composites that found practical application as waterproofing materials, rolled roofing materials, soft slate, and rubber tile contain at least 40 vol % of an elastic filler [2, 3, 10, 11].

The mechanical properties of rubber plastics as well as the properties of conventional dispersion-filled systems depend on the characteristics of the matrix polymer, the content of the elastic filler, the sizes of the rubber particles, and the level of adhesion between the matrix and the filler. Each of these factors can be considered as a separate direction for optimizing the properties of these materials. For example, the mechanical characteristics of the composites based on LDPE (or waste LDPE) are better than the characteristics of rubber plastics based on other matrix polymers (PVC, PP, and poly(ethylene terephthalate) (PET)) [2, 3]. The introduction of various compatibilizers, pre-treatment of the rubber surface in order to increase the level of adhesion are also aimed at improving the deformation properties of rubber plastics [7, 10–13]. However, in most cases, the investigations are limited to achieving the effect without a comprehensive analysis of its reasons. The
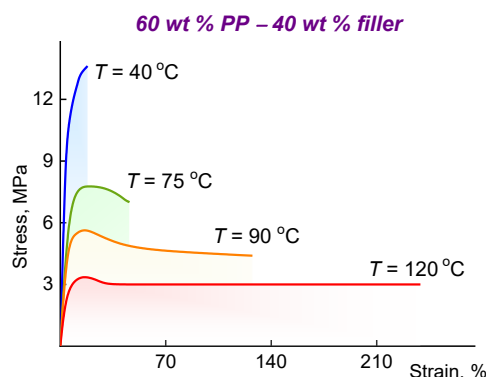
search for optimal solutions is predominantly empirical and, as a result, refers to specific thermoplastic–ground rubber scrap compositions.

To predict the mechanical properties of dispersion-filled composites, Bazhenov *et al.* [14, 15] suggested an approach which is based on the analysis of the concentration dependences of engineering (*i.e.*, related to the initial cross section of the sample) values of tensile strength, yield stress, and neck draw stress of the material. It considers three independent competing mechanisms of deformation of filled polymers, namely, neck propagation, brittle fracture, and uniform plastic flow. Each of these deformation mechanisms has its own formal parameter which depends on the particle content. The neck propagation is characterized by the neck draw stress; the brittle behavior—by the composite tensile strength; the uniform plastic deformation—by the yield stress. The deformation behavior of the composite is determined by the minimum value of one of the three mentioned parameters: if the neck draw stress is lower than the tensile strength and yield stress, then a neck is formed and propagates over the sample; if the strength of the composite is lower than the neck draw stress and yield stress, the fracture is brittle; if the yield stress of the filled polymer is lower than the strength and neck draw stress, deformation of the material is macrouniform plastic.

The basis of this phenomenological concept of the minimum parameter that determines the type of deformation and fracture of a dispersion-filled composite is the Ludwig–Davidenkov–Orowan hypothesis [16], according to which the brittle fracture or plastic flow of a polymer are independent processes. Under certain test conditions, the process that corresponds to a lower value of the critical stress is realized; this can be either brittle

fracture, or formation of a neck, or uniform plastic deformation. The results of investigations on filled thermoplastic polymers experimentally confirmed the credibility of the above-mentioned approach to predicting the type of deformation behavior of composites [17].

The reasons for the deviation from the predicted type of composite fracture, in particular, in the case of rubber plastics are associated mainly with the particle sizes. In rubber plastics, the particle sizes can reach several hundred microns. Large particles of an elastic filler initiate the formation of dangerous defects (rhomboid pores, microcracks), the growth of which across the tension axis of the rubber samples leads to their break at low strain values [17, 18].

It is known that the rubber plastics based on PP feature lower break strain than the rubber plastics of the same composition based on LDPE or HDPE [6, 17]. The introduction of an extremely small amount of PP particles (one or two was enough) led to brittle fracture of the polymer due to the formation of crazes which quickly developed into a main crack. However, at elevated temperatures (90 °C, 120 °C), the PP-based composites retained their plastic properties and fractured at the strain values above 300% at the content of the rubber particles up to 26 vol % (30 wt %) [19]. The plastic properties of these composites were caused by a change in the type of defect formed near the filler particles, namely, from dangerous (microcrack) to innocuous (slit-like pore), which in turn is associated with an increase in the polymer strain in the neck region. A similar result was obtained while studying the rubber plastics based on HDPE [18]. Therefore, the tests at elevated temperatures allowed for unraveling the "self-protective potential" of the matrix polymer: an increase in the crack resistance due to a decrease in the neck draw stress and an increase in the neck draw ratio. This conclusion can be used as a basis for the development of methods for directed rational modification of rubber plastics.

While the composites containing no more than 30–40 vol % of an elastic filler are well explored (the role of particle sizes and their ability to deform along with the matrix polymer during pore formation and fracture are determined; the main requirements to the matrix polymer for maintaining the plastic properties of the composite are established, *etc.*), the highly filled systems have been studied to a lesser extent.

The goal of this work was to study the effect of elevated temperatures on the stress–strain properties of the highly filled rubber plastics based on PP.

Results and discussion

PP is deformed with the formation of a neck and fractures during uniform tension when the neck has been propagated over the entire working part of the sample (Fig. S1 in the Electronic supplementary information (ESI)). Table 1 presents the mechanical characteristics of the polymer at different temperatures. The character of PP tension does not change with its increase. Its tensile strength at both 40 °C and 120 °C exceeds the yield stress. As the temperature rises, the tensile strength, yield stress, and neck draw stress of PP decrease, while the neck strain and relative elongation at break, in contrast, increase.

Changes in the deformation behavior of the rubber plastics based on PP with an increase in the content of the rubber particles from a few ones to 77 wt % at 22 ± 30 °C were described earlier [19]. It was shown that, at the elastic filler content of up to 36 vol %, these materials fracture in a brittle mode, while at $V_f \geq 56$ vol %, the composites undergo macrouniform plastic deformation. At the filler concentration within the range of 36 vol % < V_f < 56 vol % of the particles, a transition from brittle fracture to macrouniform deformation of the materials takes place.

A detailed analysis of the deformation behavior and fracture of the highly filled composites at elevated temperatures will be carried out using the example of the systems containing 36, 46, and 56 vol % (40, 50, and 60 wt %, respectively) of the rubber particles.

Figure 1 depicts the stress–strain curves of the composites containing 36 vol % of the filler. Figure 2 shows the samples fractured at elevated temperatures. At $T = 40$ °C, the rubber plastics of this composition fracture in a brittle mode, which is evidenced by the shape of the stress–strain curve (Fig. 1, curve *1*) and the appearance of the decomposed sample (Fig. 2a) which surface contains many microcracks (crazes) (Fig. 2b). The relative elongation at break does not exceed $15 \pm 3\%$. At 75 °C, the stress–strain curve of the rubber sample shows a diffuse maximum (Fig. 1, curve *2*). At this temperature, the deformation of the samples is accompanied by the formation of shear bands, which broaden as the draw ratio increases; thinning of the material is observed in these zones, while the transverse contraction is weakly expressed (Fig. 2c). The break of the materials is initiated by the fracture of one of the zones of plastic flow of the matrix polymer.

At 90 °C and 120 °C, a yield peak is observed on the stress–strain curves of the samples; their break occurs at the neck growth step (Fig. 1, curves *3*, *4*). At similar types of the stress–strain curves, the samples fracture at different values of relative elongation: at 90 °C it is equal to $120 \pm 10\%$, while at 120 °C it is $230 \pm 20\%$. In the first case, the tension of the samples is accompanied by the formation of several necks, and the break occurs in one of them (Fig. 2d); in the second case, the resulting neck is able to propagate over the entire working part of the sample (Fig. 2e). Both at 90 °C and at 120 °C, the break is

Table 1. Mechanical properties of PP at elevated temperatures

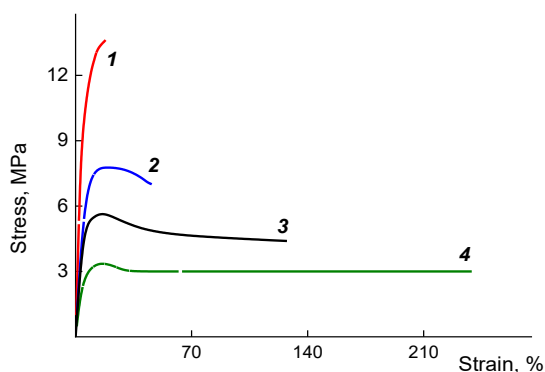| Properties	Temperature, °C				
	40	60	75	90	120
Tensile strength, MPa	34 ± 3	28 ± 2	23 ± 3	17 ± 1	11 ± 2
Yield stress, MPa	27 ± 2	20 ± 2	16 ± 1	11 ± 1	7 ± 2
Neck draw stress, MPa	20 ± 1	14 ± 1	12 ± 2	8 ± 1	4 ± 1
Break strain, %	820 ± 50	900 ± 70	880 ± 60	870 ± 50	1100 ± 100
Neck strain, %	310 ± 30	330 ± 20	370 ± 30	380 ± 40	400 ± 20

Figure 1. Stress–strain curves of the composites PP–36 vol % of ethylene–propylene rubber (EPR) at 40 °C (*1*), 75 °C (*2*), 90 °C (*3*), and 120 °C (*4*).
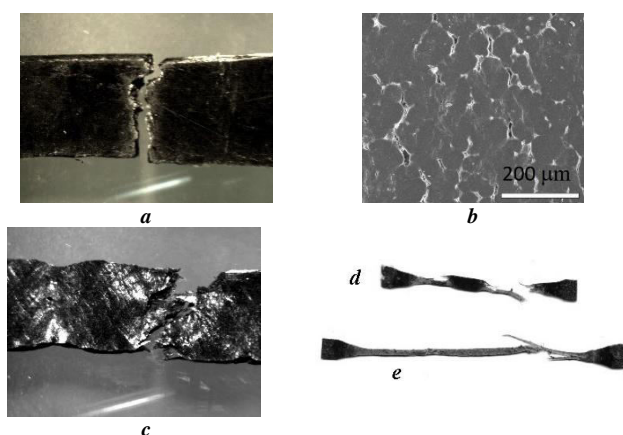

Figure 2. Samples of the composite PP–36 vol % of EPR fractured at 40 °C (*a*, *b*), 75 °C (*c*), 90 °C (*d*), and 120 °C (*e*).

caused by the appearance and growth of a rhomboid pore (a dangerous defect) in the neck region.

Therefore, as the temperature rises from 40 to 120 °C, the PP-based rubber plastics containing 36 vol % of the rubber particles undergo a transition from brittle to plastic tension with the formation and growth of a neck. The change in the deformation behavior proceeds through an intermediate stage, namely, the tension with the formation and broadening of shear bands. The change in the deformation behavior of the composites PP–36 vol % of the rubber particles is caused by the change in the mechanism of their deformation from microcracking to the formation of shear bands which, as the strain grows, pass into zones of plastic flow and then into a neck.

Figure 3 shows the stress–strain curves of the PP-based composites containing 46 vol % of the rubber particles at different temperatures. Figure 4 demonstrates the fractured samples. At 40 °C, the stress–strain curve of the composite (Fig. 3, curve *1*) and the view of the fractured sample (Fig. 4a) testify to the break in a brittle mode. At 75 °C, the tension of the rubber plastics is accompanied by the formation of shear bands, the appearance of which is reflected in the stress–strain curve in the form of a plateau (Fig. 3, curve *2*); the break occurs along one of the shear bands (Fig. 4b). The subsequent temperature rises to 90 °C and 120 °C do not change the shape of the curves (Fig. 3, curves *3*, *4*); however, the composites deform with the formation

of several delocalized necks in which the deformation of the matrix polymer clearly exceeds the macrodeformation of the sample (Fig. 4c,d). Their formation is possible if, after the appearance of the first zone of plastic flow, the material in it does not decompose, and the tensile force is sufficient for the appearance of the next neck in another region of the sample.
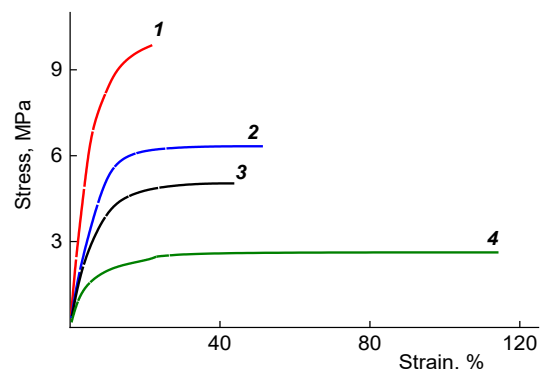

Figure 3. Stress–strain curves of the composites PP–46 vol % of EPR at 40 °C (*1*), 75 °C (*2*), 90 °C (*3*), and 120 °C (*4*).
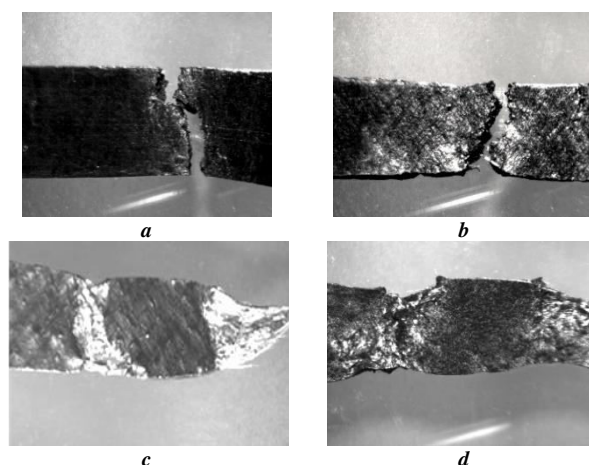

Figure 4. Samples of the composite PP–46 vol % of EPR fractured at 40 °C (*a*, *b*), 75 °C (*c*), 90 °C (*d*), and 120 °C (*e*).

The composites with the EPR concentration of 56 vol % are deformed macrouniformly in the whole temperature range. The stress in them increases monotonically with an increase in the neck draw ratio (Fig. 5). Independent from the test temperature, the tension of the material is accompanied by the formation of shear bands (Fig. 6a). Figure 6b shows a photograph of the surface of the sample fractured at 120 °C. In the region of the shear band, the oriented structure of the matrix polymer can be seen. Furthermore, elongated oval pores are also formed in this zone. The plastic deformation of the composite is further evidenced by strands of the matrix polymer observed in the fracture plane of the sample (Fig. 6c). Consequently, the macrouniform tension of the composite has a plastic character.

A further increase in the filler concentration does not change the tension character of the rubber plastics at elevated temperatures. Both at 20 °C and 120 °C, their deformation is macrouniform plastic (Fig. S2 in the ESI).

The results obtained can be conveniently summarized using the scheme of variation of the deformation behavior of rubber plastics in the temperature range from 75 to 120 °C (Fig. 7).
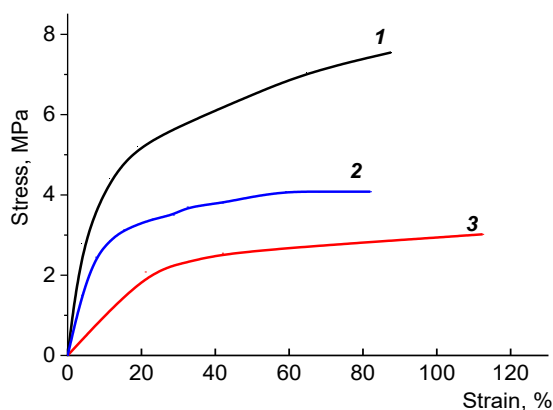
Figure 5. Stress–strain curves of the composites PP–56 vol % of EPR at 40 °C (*1*), 90 °C (*2*), and 120 °C (*3*).
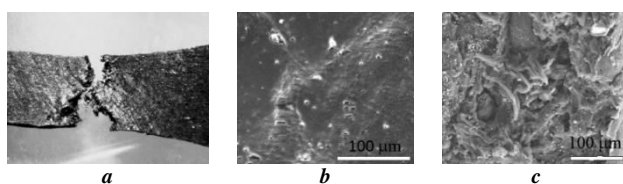

Figure 6. Photographs of the fractured samples of the composite PP–56 vol % of EPR: a general view of the sample fractured at 75 °C (*a*); a shear band zone on the surface of the sample deformed at 120 °C (*b*); a break zone of the sample at 120 °C (*c*).

75 °C corresponds to the temperature at which shear bands, rather than microcracks, are formed in the composites during tension. At $V_f = 36$ vol %, as the temperature rises, the material undergoes transitions from deformation with the formation of shear bands to tension with the formation of delocalized necks and then to tension with a localized neck (Fig. 7a). At $T = $ const, as the filler content increases ($V_f \geq 36$ vol %), the tension character of the composites changes in the opposite direction. The "starting point" of the reverse change of the achieved type of sample tension depends on the test temperature (Fig. 7b). The lower its value, the fewer stages of the deformation behavior are realized in a rubber plastic with an increase in the filler concentration.
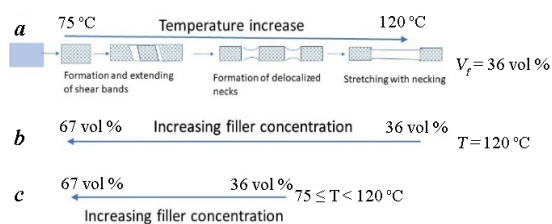

Figure 7. Scheme of variation of the deformation behavior of rubber plastics depending on one of the parameters (*T* or *V*): increase of the test temperature at $V_f = 36$ vol % (*a*), increase of the filler content at $T = 120$ °C (*b*); increase of the filler content at $75 \leq T < 120$ °C (*c*).

The tension of highly filled rubber plastics with the formation of delocalized necks at elevated temperatures was also observed in the case of the systems based on PE and rubber particles [20]. Taking into account the previously obtained results and the findings of this work, it can be concluded that deformation with the formation of several delocalized necks is a prerequisite for macrouniform tension of the composite, *i.e.*, an

intermediate stage during the transition from brittle fracture to macrouniform plastic tension. Therefore, the transition from brittle to ductile tension (brittle-to-ductile transition in the case of the PP-based rubbers) or the transition from tension with the formation and growth of a neck to macrouniform plastic tension (ductile-to-ductile transition in the case of the PE-based rubbers [20] and the PP-based rubbers at 90 or 120 °C) is "evolutionary". This means that it is realized as V_f grows in a certain range of filler concentrations and not when a specific value of V_f^* is reached. The condition for its realization is the tension of the matrix polymer with the formation of shear bands, *i.e.*, the absence of microcracks (in the case of PP) or dangerous rhomboid pores in the zones of plastic deformation of the matrix (in the case of PE).

Figure 8a shows the dependences of the relative elongation at break of the rubber plastics (ε_c) on the concentration of the elastic filler at different temperatures. At 40, 60, and 75 °C, the values of ε_c increase with an increase in the content of the particles and a temperature rise. The dependences of ε_c on V_f at higher temperatures contain a minimum at $V_f = 46$ vol %, which is caused by a change in the deformation behavior of the composites from tension with the formation and growth of a neck to tension accompanied by the formation of several delocalized necks. At $V_f > 46$ vol %, the values of ε_c of the composites increase.
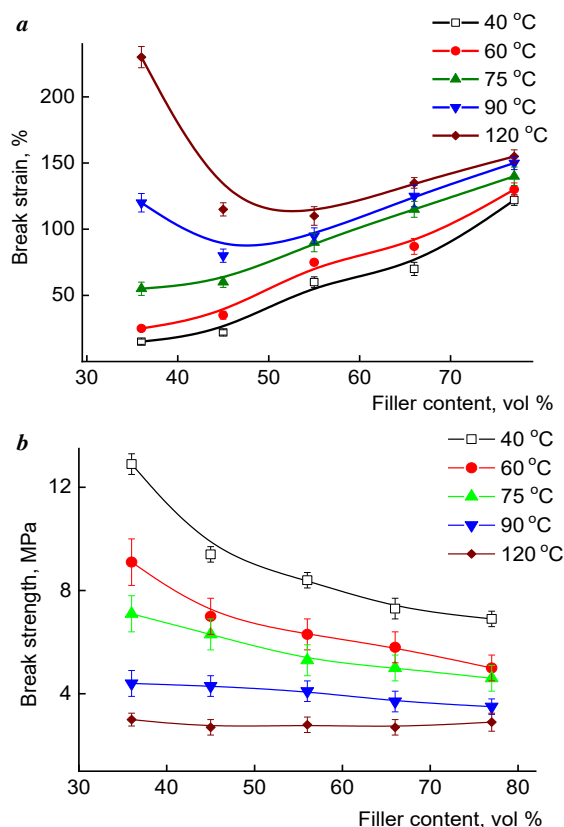

Figure 8. Dependences of the relative elongation (*a*) and tensile strength (*b*) of the PP-based rubber plastics on the content of the rubber particles at different temperatures.

The dependences of the tensile strength of rubber plastics (σ_c) on V_f are depicted in Fig. 8b. An increase in the content of the rubber particles or an increase in the test temperature leads to a monotonic decrease of σ_c. The strength of rubber plastics

under macrouniform tension is described by the following equation [17].

$$\sigma_c = \sigma_{dm}(1-V_f^{2/3}) + \sigma_f V_f^{2/3} \qquad (1)$$

Here σ_{dm} is the neck draw ratio of the matrix polymer, σ_f is the tensile strength of the particles (or the adhesion strength of a particle–matrix contact). Presenting the experimental values of σ_c in the coordinates of equation (1), let us estimate the stress in the matrix at the composite break (σ_{extr}) by extrapolating the linear dependence to $V_f \to 0$. Figure 9 shows the correlation between the draw stress of the PP neck and the values of σ_{extr} at different temperatures. It can be seen that $\sigma_{extr} < \sigma_{dm}$. Consequently, when the composite breaks, the matrix remains underloaded. In other words, its fracture occurs at the stress value less than it is able to "withstand". The result obtained allows for concluding that, during tension with the formation of delocalized necks and macrouniform plastic deformation, the composite break is initiated by a dangerous defect. Its appearance and transverse growth lead to the material fracture. Obviously, the cause of this type of fracture (the effect of a single defect) is the presence of large rubber particles (up to 800 μm) in the composite composition.
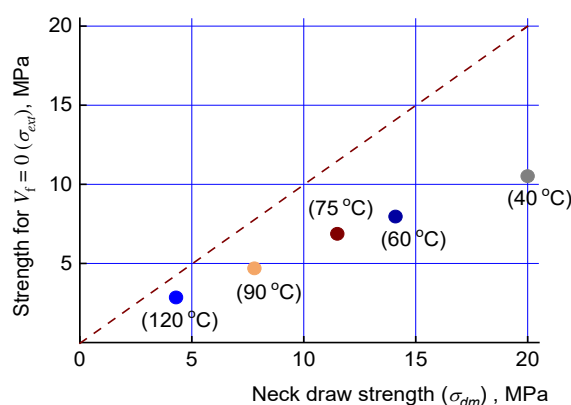

Figure 9. Correlation between the draw ratio of the PP neck (σ_{dm}) and the strength values of rubber plastics at $V_f \to 0$ (σ_{extr}) at different test temperatures.

Experimental section

The target composites were prepared using polypropylene of 21060 grade with the MFI of 2 g/10 min. The rubber particles based on EPR obtained by elastic-deformation grinding of automobile seals were used as the filler. The sizes of the rubber particles ranged from 10 to 800 μm. The polymer and filler were mixed in a single-screw extruder; the temperature in its zones was 180 and 190 °C. The concentration of the crumb rubber V_f was varied from 36 to 77 vol % (40–80 wt %). The resulting blends were processed by hot pressing at 190 °C and 10 MPa for 10 min, followed by cooling to 25 °C under the same pressure. The time of cooling from 190 to 25 °C did not exceed 15 min. The thickness of the resulting plates was ~ 2 mm.

The samples in the form of double-sided blades with the dimensions of the working part of 5×35 mm were cut from the resulting plates. The mechanical tests of the composites were carried out on a 203R-005 force-measuring device equipped with a heating chamber. The test temperature (T) was varied

from 20 to 120 °C. The temperature measurement accuracy was ±1 °C. Before tension, the samples were preliminarily kept at the given temperature for ~5 min. The tension speed was 20 mm/min.

The microscopic studies were performed using a Motic DM-143-FBGG-B optical microscope equipped with a video camera and a Hitachi S-520 scanning electron microscope.

The stress values calculated for the initial cross section of the samples were used.

Conclusions

The investigations on the highly filled rubber plastics ($V_f \geq$ 36 vol %) at elevated temperatures allowed for determining the peculiarities of the realization of a brittle-to-ductile or ductile-to-ductile transition in the composites with the elastic filler particles. It was established that, at a certain content of the particles, they occur through the intermediate composite tension with the formation of delocalized necks in the range of filler concentrations, rather than in discrete steps. The negative effect of large particles during macrouniform tension of the rubber plastics was shown for the first time. Their presence in the composite composition facilitates the fracture while the matrix polymer is underloaded.

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Electronic supplementary information

Stress–strain curves of the initial PP and the composites PP–67 vol % of the rubber particles at different temperatures. For ESI, see DOI: 10.32931/io2220a.

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