LONG-TERM DURABILITY OF WOOD-FLOUR-POLYPROPYLENE-ELASTOMER COMPOSITES

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ABSTRACT

Investigations on the long-term durability of wood flour-polypropylene-elastomer composites at static loading and high stresses are reported. This is an extremely important characteristic that makes possible the fairly accurate prediction of the service life of polymeric articles. The long-term strength is investigated under conditions of uniaxial tension of polypropylene, elastified with 10% polyisoprene, and polypropylene, filled with 5% and 10% wood flour. It was established that the elastomer and the filler change the fracture mechanism of the polymer in opposite directions. This result oriented the work towards investigations on the durability of polypropylene, elastified with polyisoprene and filled with wood flour simultaneously. The presence of polyisoprene in the wood flour-filled polypropylene increases the elasticity of the composition, and at the same time retards the processes of ageing.

INTRODUCTION

Wood-filled polyolefin composites are the subject of increasing interest /1-5/. These polymer composites are processed by conventional methods for thermoplastic materials. Articles made of them have a pleasant wood-like appearance and possess good sound and thermal insulation properties.

The main shortcomings of this type of composites is their low impact strength and the low atmospheric and cold resistance, typical of the polyolefin polymer matrix. One of the most efficient methods for improvement of these characteristics is by mixing with elastomers /6,7/. For these reasons, one of the major objects of our investigations in recent years has been tri-component compositions based on polypropylene (PP), modified simultaneously with wood flour and elastomers.

In our previous investigations it was found that composites on the basis of PP, containing 5- 15% polyisoprene (PI) and 10 - 20% wood flour (WF), possess an optimum complex of rheological and physico-mechanical properties /8/. As is well known, an especially important operation parameter is the long-term strength that makes possible the fairly accurate prediction of the real performance of the articles under the action of mechanical stresses. This is why the subject of our scientific research is the

durability of wood flour-polypropylene-elastomer composites (WFPPE) under the action of static loading and high stresses.

OBJECTS AND METHODS OF INVESTIGATION

The investigations were carried out on PP, type "Buplen-6631", produced by Nephtochim, Bourgas, Bulgaria. The investigated polypropylene has the following parameters: MFI = 2.67 g/10 min; yield point = 30 MPa and Izod impact strength – 30 J/m.

The elastifying modifier was stereo-regular 1,4-cis polyisoprene rubber "Ski-3", a Russian product. In our previous investigations this elastomer exhibited good elastifying action on PP /9/. The elastomer was plasticized in advance on a two-roll mill with friction coefficient = 1.1, still Mooney plasticity = 15.5.

The filler is coniferous wood flour, produced by the Maritsa company, Bulgaria with a grain size in the range of 140 - 160 μm .

Mixing of WF and PI is carried out on a two-roll mill. The mixture is drawn in sheets and is granulated by cold cutting, after which it is mixed with PP in a special mixing extruder /10/, providing dispersing homogenization of the components in the polymer matrix.

The samples are blanked from pressing plates, prepared under the following conditions: $T = 180^{\circ}\text{C}$, pre-pressing time = 8 min, pressing time = 8 min and cooling rate = $20^{\circ}\text{C}/\text{min}$. Their shape and size conform to the requirements of ISO-527.

The determination of the long-term strength at static loading is carried out in chambers at a constant temperature, $T = 10 \pm 2^{\circ}\text{C}$. The samples are suspended on a metal frame, and loading is accomplished with metal weights, ensuring uniform distribution of the load.

Testing of the samples under super-high stresses is carried out with specially designed equipment /11/, in which the force is created electrodynamically, and the time to fracture is measured with an electronic timer with an accuracy of 10^{-8} s. The equipment is placed in a chamber, maintaining constant temperature.

The microscopic investigations are conducted with a scanning electron microscope, Olympus-BH2-BHSP. The X-ray structural analyses are made with Philips equipment with iron radiation. The thermal and mechanical analysis performed on UIP-70M.

RESULTS AND DISCUSSION

It is known that the long-term durability of polymers is determined by measuring the time interval between the onset of loading and the fracture of the specimen. Under real operating conditions, the articles are most frequently subjected to constant loads for a certain period of time. For this reason the present work reports on investigations of the long-term durability of WFPPE composites, containing PP, PI and WF, at static loading under conditions of uniaxial tension.

The first closely examined problem was the influence of PI on the long-term strength of PP (Fig. 2) on the basis of the preliminary rheological and physico-mechanical examinations /8/. The PI concentration was chosen to be 10% because it enhances the fluidity and the strength parameters of the polymer matrix. The times to fracture of the specimens (τ) under the action of stresses (σ) with different values are measured.

Our previous investigations showed that the time dependence of the strength can be represented by a complex curve with a general view presented in Fig. 1 /11,12/. As seen from the figure, in a wide range of mechanical stresses there are four areas on the graphical relationship $\ln \tau - \sigma$ that feature specific fracture mechanisms:

1. durability depends on the limited growth rate of the crack in the material;
2. brittle or quasi-brittle fracture;
3. plastic deformation, characterized by neck formation in a narrow range of stresses;
4. mechanico-chemical fracture at very low stresses, taking place for years.

Fig. 1: General view of the time dependence of the strength: 1 – limiting durability; 2 – brittle fracture; 3 – plastic deformation, and 4 – mechanochemical fracture.

The complex shape of the time-stress relationship is typical of each polymer /13/. Besides, it changes with the molecular mass /14/ or with the temperature /15/, but the general appearance is similar to the one in Fig. 1. These non-linear dependences of the time-strength curves are described analytically by the equation:

$$\tau = \tau_0 \cdot \exp \frac{U_0 - \gamma\sigma}{RT + \alpha\sigma^n} \quad (1)$$

where τ_0 is the limiting time at high mechanical loads;
 U_0 is the activation energy of the fracture process;
 R is the universal gas constant;
 T is the absolute temperature; and
 α, γ, n are coefficients, depending on the type of material and testing conditions.

The semi-logarithmic form of Eq. (1) allows a clearer graphical presentation of the functional dependence of $\ln \tau$ on σ :

$$\ln \tau = \ln \tau_0 + \frac{U_0 - \gamma\sigma}{RT + \alpha\sigma^n} \quad (2)$$

Fig. 2 illustrates the relationships $\ln \tau - \sigma$ for PP and PP containing 10% PI. As is evident, the break of polypropylene under the action of static loading is characterized by clearly pronounced zones of brittle (2) and plastic (3) fracture. Brittle or quasi-brittle fracture is observed at loads of 25 to 40 MPa in the linear part in which fracture takes place as a result of the propagation of the most dangerous Griffith's crack. At stresses below 25 MPa, a zone of neck formation, typical of semi-

Fig. 2: Semi-logarithmic form of the time dependence of the strength for PP (▲) and PP containing 10% PI (●).

crystalline thermoplastics, is observed /16/, in which the deformation to break increases considerably in a narrow stress range. As far as the elastified PP is concerned, the neck formation starts at quite low mechanical stresses (of the order of 10-12 MPa) and is observed in a considerably wider stress range. It should be noted that the boundary between quasi-brittle fracture in the second zone and zone 3, featuring neck formation, is rather smooth. It is known that during crack formation and microcrack propagation, only local plastic deformation is observed. Obviously, the presence of elastomer in the polypropylene matrix stimulates considerably the composite's tendency for plastic deformation in the zone of neck formation. The elongation of the neck was observed for 25 days. These processes could be explained by taking into consideration two factors: the higher conformation mobility of the mechanical segments in the rubber macromolecules, ensuring their higher susceptibility to deformation under loading, and the partial dissolution of the elastomer in the harder chain matrix, along with uniformly distributed spherical rubber domains in the whole volume of the composite (Fig. 3) that prevent the growth of the dangerous microcracks. Nevertheless, the investigations at superhigh stresses – zones 1 of the curves in Fig. 2 – show that the addition of PI to the polypropylene matrix reduces its durability, similarly to the elastomer action in other semicrystalline polymers /17/. This is due to the fact that at high loads the fracture process proceeds at a higher rate than the relaxation redistribution of stresses, leading first to the destruction of the weakest links, in this case the rubber domains. On the other hand, the elastomer, partially dissolved in the polypropylene matrix, acts like a high molecular plasticizer that reduces the durability of PP.

The filler in the composite has an opposite effect to that of the elastifying additive, so we investigated separately the long-term durability of PP, containing different quantities of wood flour

Fig. 3: Scanning electron micrograph of the fracture surface of PP containing 10% PI specimen.

(WF). Fig. 4 illustrates the relations $\ln \tau - \sigma$ for PP, containing 5% WF (curve 1) and 10% WF (curve 2). It is important to note that the addition of wood flour changes the fracture mechanism of PP – the phenomenon of plastic susceptibility that is the cause of neck formation disappears completely. In this case, brittle fracture is observed in the whole investigated range and the linear zone has a less steep slope for the composite with higher WF content. It must be pointed out that the increase in the filler content substantially increases the limiting strength at the highest stresses relative to that of PP, or PP containing 10% PI (Table 1). The limited durability is lower than that of PP but is higher than that of the elastified PP (Table 1). Therefore, as expected, filling the polypropylene with wood flour results in “hardening” of the polymer matrix. This enhances the possibilities of using the material for construction purposes.

Fig. 4: Semi-logarithmic form of the time dependence of the strength for PP containing 5% WF ($\diamond$), PP containing 10% WF ($\square$) and PP ($\blacktriangle$).

We assumed that this effect is mainly due to the structure-nucleating action of the particles. Indeed, both the X-ray structural (Fig. 5) and microscopic (Fig. 6) analyses revealed an increased degree of crystallinity of the wood-flour filled composites in comparison with the polymer crystallinity.

The melt temperature of composites, measured by thermogravimetric analysis, is higher for the PP composite, containing 10% WF (Fig. 7).

It was also found that the addition of wood fillers reduces the strength and deformation characteristics of PP [1,8,18]. This makes additional elastification, aimed at improving the properties

Table 1
Limiting durability (τ) and limiting strength (σ) of the WFPPE composites

Composites	Limiting durability (τ), s	Limiting strength (σ), MPa
PP	5.25×10^{-3}	40
PP & 5% WF	2.47×10^{-3}	43
PP & 10% WF	2.73×10^{-3}	54
PP & 10% PI & 5% WF	1.93×10^{-3}	48
PP & 10% PI & 10% WF	2.02×10^{-3}	48
PP & 10% PI	1.50×10^{-3}	40

of wood flour-filled polypropylene composites, attractive. For this reason, an extensive investigation was conducted on the durability of PP, containing simultaneously PI and WF. Fig. 8 shows the relationships $\ln \tau - \sigma$ for PP containing 10% PI and 5% WF (curve 1), for PP containing 10% PI and 10% WF (curve 2), and for the PP (curve 3). It is clear that the addition of elastomer to PP filled with wood particles restores the polymer's ability of neck formation, and also retains the higher limiting durability, due to the addition of WF to PP. It was found that the increase in the WF concentration in the elastified PP does not change the fracture mechanism. The curves illustrating the time dependence of the strength of elastified PP containing 5% and 10% WF almost overlap.

The articles made of the developed composite material have a pleasant woodlike appearance and may substitute wooden profiles, plates and ornaments with complex shapes for the furniture and construction industry. Their production is easily accomplished using conventional methods of thermoplastics processing: extrusion, injection moulding, compression moulding, vacuum forming. The durability of WFPPE composites complies completely with the requirements.

Fig. 5: Diagram of the degree of crystallinity for the WFPPE composites.

Fig. 6: Optical micrographs (magnification – x20) of microtome sections of: a) PP; b) PP containing 10% PI; c) PP containing 10% PI and 10% WF, and d) PP containing 10% WF.

Fig. 7: Diagram of melt temperature of the WFPPE composites.

Fig. 8: Semi-logarithmic form of the time dependence of the strength for PP containing 10% PI and 5% WF (◆); PP containing 10% PI and 10% WF (□), and PP (▲).

CONCLUSIONS

The durability of PP, elastified with 10% PI, and PP, filled with 5% and 10% WF, was investigated at static loading and high stresses. It was established that the elastomer and the filler change the fracture mechanism of the polymer in opposite directions. This result oriented the work towards investigations on the durability of polypropylene, elastified with polyisoprene elastomer and filled with wood flour simultaneously. The presence of polyisoprene in the composites restores the neck-forming ability of the polymer, and at the same time does not diminish the limiting durability, due to the addition of wood flour to the polypropylene.

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REFERENCES

1. Kotka, B.V., Raj, R.G. & Daneault, C., *Polym.-Plast. Technol. Eng.*, **28** (1989), 247-59.
2. Myores, G.E., Chahyadi, I.S., Gonzales, C., Coberty, C.A. & Ermer, D.S., *Int. J. Polym. Mat.*, **15** (1991), 171-86.
3. Wright, J.R. & Mathias, J., *J. Appl. Polym. Sci.*, **48** (1993), 2225-39.
4. Maiti, S.N. & Subbarao, R., *Int. J. Polym. Mater.*, **15** (1991), 1-16.
5. Klason, C., Kubat, J. & Gatenholm, P., *ACS Symp. Ser.*, **489** (1992), 82-98.
6. Nonura, T., Takeyoshi, N., Niroki, S. & Hironari, S., *Kobunshi ronbunshu*, **50** (1993), 19-25.
7. Gupta, A.K. & Ratnam, B.K., *J. Appl. Polym. Sci.*, **42** (1991), 297-315.
8. Natov, M., Vassileva, St. & Kowatschewa-Welewa, S., *Die Angew.-Makromol. Chem.*, **225** (1995), 73-81.
9. Natov, M., Vassileva, St. & Delev, B., [*_____*], **38** (1991), 85-9.
10. Natov, M., *Plaste und Kautschuk*, **19** (1972), 765-8.
11. Natov, M., Vassileva, St., & Haralampiev, *Mehanika polimerov*, **4** (1977), 737-40.
12. Natov, M., *Prerabotvane na plastmasite*, Tehnika, Sofia, 1976.
13. Natov, M. & Vassileva, St., *Plaste und Kautschuk*, **23** (1976), 213-5.
14. Natov, M., Vassileva, St. & Evtimova, S., *J. Appl. Polym. Sci.*, **35** (1988), 1161-7.
15. Vassileva, S. & Natov, M., *Die Angew. Makromol. Chem.*, **137** (1985), 2233-91.
16. Natov, M., Vassileva, S. & Hristova, H., *Mehanika polimerov*, **5** (1977), 936-8.
17. Trifonova, D. & Vassileva, S., *J. Mat. Sci. Lett.*, **12** (1993), 695-6.
18. Maiti, S.N. & Chawla, C.P., *J. Polym. Mater.*, **4** (1987), 155-63.