Novel Polyurethane Elastomer Continuous Carbon Fiber Composites: Preparation and Characterization

Jenő Borda,[1] Sándor Kéki,[1] Istvánné Ráthy,[2] Ildikó Bodnár,[2] Miklós Zsuga[1]

[1]*Department of Applied Chemistry, University of Debrecen, H-4010 Debrecen, Hungary*
[2]*Technical College Faculty, University of Debrecen, H-4028 Debrecen, Hungary*

Received 18 April 2006; accepted 24 July 2006
DOI 10.1002/app.25283

ABSTRACT: Preparation and characterization of novel polyurethane (PUR)–carbon fiber (CF) composites are reported. The reinforcement of PUR elastomers was achieved using unidirectional continuous CFs with different coatings (uncoated and epoxy and polyester resin coatings) by applying molding for the preparation of PUR-CF composites. Considerable reinforcement of PUR was attained even at relatively low CF content, e.g., maximum stress and Young's modulus of PUR-CF composite at CF content 3% (m/m) were found to be 3–5 and 4–10 times higher than those of the PUR-matrix, respectively. In addition, a linear relationship between the Young's modulus and the CF content was found as well as linear variation of maximum stress with the CF content was also observed. The adhesion of CF to the PUR-matrix was strong in each case as concluded from the strain–stress and the scanning electron microscopy (SEM) investigations. However, the extent of reinforcement of PUR at a given CF content was found to depend greatly on the coatings of CF, and increased in the following order: epoxy resin < polyester resin < uncoated. The effect of the coating of CF on the reinforcement of PUR is also discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 287–292, 2007

Key words: polyurethane; reinforcement; composite coatings

INTRODUCTION

Recently, considerable efforts have been devoted to the production and processing of plastics with good mechanical and chemical properties which not only meet the requirements of special applications but are also compatible with the increasing environmental aspects (e.g., biodegradable polymers) and energy-effective (construction materials and processing) demands. To achieve these specific issues the advantageous properties of two or more materials (matrix and other components) are combined to result in a specific mixture called composite whose properties exceed those of the matrix. One of the reasons of using composites is to improve the mechanical properties with respect to the matrix. Nowadays, several types of composites, including various matrices and reinforcement materials such as carbon and glass fibers are used in different areas. In addition, numerous reports on the reinforcement of different polymers such as polyamide, polyether-etherketone (PEEK), polycarbonates with continuous or discontinuous (short) carbon fibers (CF) have appeared.[1–4]

Of the polymer-based composites, polyurethanes (PUR) reinforced with CF have received considerable attention because of the unique combination of the elasticity of PUR with the rigidity of CF.[5–7] Therefore, the PUR-CF composites span a wide range of applications, including vehicle interiors, sporting goods, electronics, and constructing materials.[8,9] The short CFs can be embedded into the matrix in a relatively fast process using, e.g., injection molding or molding,[10,11] but the random orientation and the undesirable fracture of fibers under processing conditions may result in the loss of reinforcement or only weak reinforcement can be attained. On the other hand, the adhesion of CFs to the matrix plays a crucial role in determining the extent of reinforcement.[12] For example, it has been pointed out for the thermoplastic polyurethane (TPU)-short CF composites[12] that the extent of reinforcement is determined by the surface polarity of the CF, i.e., by the strength of the matrix–CF bond and the diameter and the length of CF have also been shown to affect the mechanical properties of the resulting TPU-CF composites.

Although, the incorporation of continuous (long) CFs into a matrix is a relatively slow process compared with that of the short fibers (the highly uniform fiber orientation is preserved during processing) it benefits from the high level of reinforcement

---

Correspondence to: M. Zsuga (zsugam@tigris.unideb.hu).

Contract grant sponsor: Hungarian Research Foundation; contract grant numbers: OTKA T 042740, M 28369, M 36872, and RET 006/2004.

Journal of Applied Polymer Science, Vol. 103, 287–292 (2007)

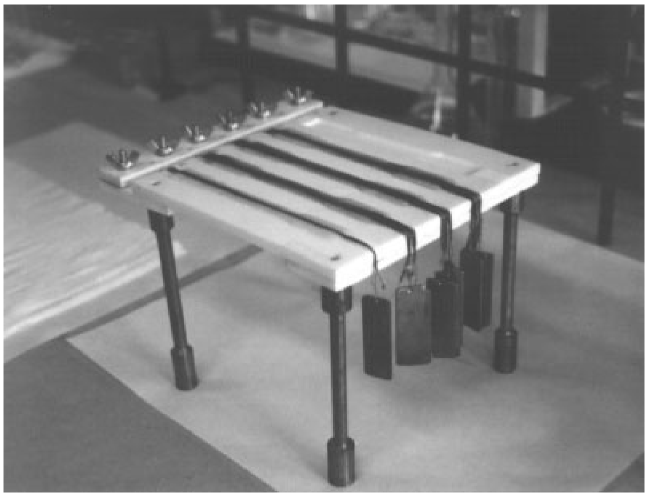


Figure 1 Experimental setup for the preparation of PUR-CF composites.

which are considerably higher than those that can be attained with short fibers.

This inspired us to prepare novel PUR composites with continuous CFs. In this work, we also report the investigation of the mechanical properties of the composites prepared from various PURs and continuous CF with and without coatings.

EXPERIMENTAL

Materials

D,L-Lactic acid (LA) from Reanal (Budapest, Hungary) was used as-received. Tin octoate, poly(ethylene glycol)s (PEG), poly(propylene glycol) (PPG), 2,6-toluene diisocyanate (TDI), and prepolymer MDI were received from BorsodChem Co. (Kazincbarcika, Hungary) and used without purification.

Three types of continuous CFs: uncoated (CF 48K), coated with 1.5% (m/m) epoxy resin (PX33TW-ϕ48-121), and 0.5% (m/m) polyester (PX33TW-ϕ48X10) were received in staples from Zoltek Co. (Nyergesújfalu, Hungary). One staple of CFs contained ∼ 48,000 yarns with an average diameter of 7.4 μm and density of 1.78 g/cm^3. The measured tensile strength and Young's modulus of yarns were 412 MPa and 39 GPa, respectively.

Preparation

Preparation of PUR elastomer from PPG and prepolymer PPG-MDI. PPG (M_n = 2000 g/mol) and prepolymer PPG-MDI (M_n = 2500 g/mol) were mixed together in a 4 : 1 weight ratio, and to facilitate the urethane formation tin octoate in 0.1% (m/m) was added to the mixture.

Preparation of poly(lactic acid)-TDI-PEG (PLA-TDI-PEG) and of PLA-TDI-PPG partially biodegradable PUR. The synthesis of PLA-TDI-PEG and PLA-TDI-PPG is described in Ref. 13.

Preparation of PUR-CF composites. The carbon yarns were evenly and parallely distributed and pre-stretched gravitationally using weights of 20 g. Into the mold made of Teflon, five mold patterns corresponding in size and shape to the Hungarian standards[14,15] for mechanical testing were engraved. The lengths of the probes were 172 mm and CFs with a length of 350 mm were cut off from the continuous carbon yarns. The mixtures of the components for a given PUR were then poured into the mold containing the prestretched CFs. After completion of the reaction (24 h) the mold was removed and the resulting PUR-CF composites were analyzed. The home-made experimental setup for the preparation of PUR-CF composites is shown in Figure 1.

Instruments

Mechanical testing

An Instron 4032 mechanical testing instrument was used to determine the Young's modulus and the stress at maximum values of the matrices and the composites.

Scanning electron microscopy

An Amray 1830 I scanning electron microscope was applied to study the surface failure of the composite after break.

RESULTS AND DISCUSSION

The PUR-CF composite even at low CF content showed an improved mechanical property as compared with the PUR matrix and this was concluded from the stress–strain curves (Fig. 2).

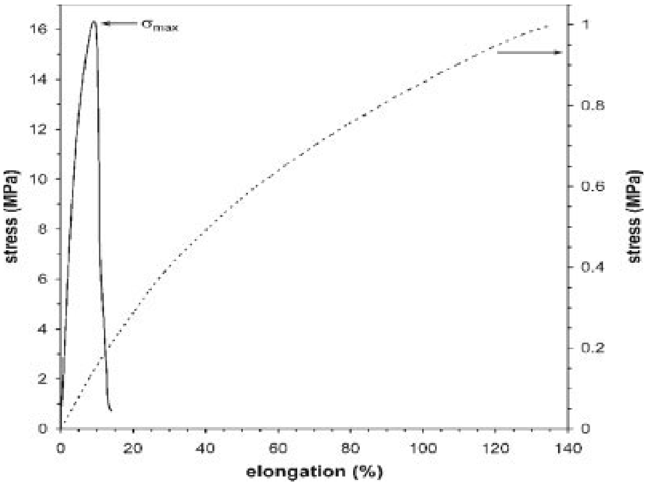


Figure 2 Stress–strain curve for the PUR-CF composite (—) and the matrix (- - -). Polyester-coated CF content: 3% (m/m).

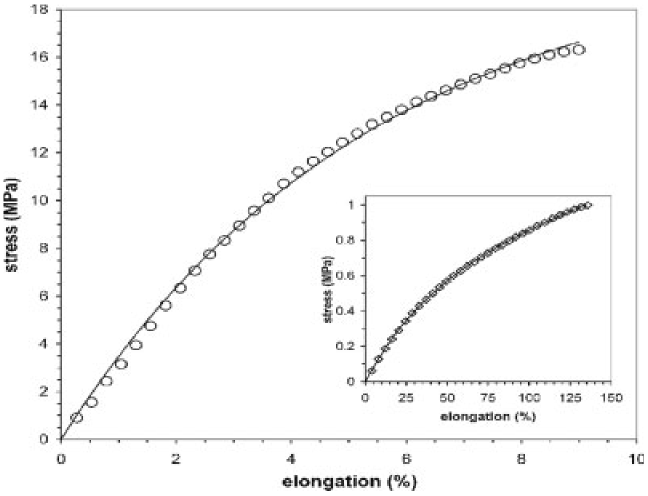


Figure 3 Stress–strain curves for PUR-CF composite and the matrix (inset). The solid lines represent the fitted curves. The fitted parameters for the composite are $b_1 = 20.48$ MPa, $b_2 = 18.59$ and for the matrix: $a_1 = 0.34$ MPa, $a_2 = 1.65$, and $a_3 = 2.48$.

As shown in Figure 2 the initial slope of the stress–strain curves, i.e., the Young's modulus for the PUR-CF composites is significantly higher than those for the PUR matrix. On the other hand, the maximum stress ($\sigma_{\max}$) value for the PUR-CF composite is also higher as compared with that of the PUR-matrix as a result of reinforcement. It should be noted, however, that the PUR-CF composite exhibits rather unusual stress–strain curves. As can be seen in Figure 2, the PUR-CF composite produces a relatively sharp maximum on the stress–strain curves, and similar stress–strain curves were observed for the other PUR-CF composites. Considering the elongation at break of the PUR (140%) and that of the CF with a value of 2%, and also that the stress at maximum for the composite PUR-CF occurs at $\sim$ 10% strain the following can be rationalized: (i) because considerable reinforcement occurs, the adhesion of CF to the matrix is appropriate, (ii) the sharp maximum on the stress–strain curves can be explained by breaking of the CFs and/or their partial slipping within the matrix.

The dependence of the stress on the strain can be evaluated using the Poynting–Thomson [eq. (1)] and/or the Maxwell model [eq. (2)] to describe the viscoelastic properties of polymeric solids.[16]

$$\sigma = a_1[\varepsilon + a_2(1 - e^{-a_3\varepsilon})] \tag{1}$$

$$\sigma = b_1(1 - e^{-b_2\varepsilon})] \tag{2}$$

where σ is the stress, a_1, a_2, a_3, b_1, and b_2 are parameters including the Young's modulus of the Hookien springs and the viscosity coefficient of the viscous liquid in the model; and ε is the strain.

Equations (1) and (2) were fitted to the experimental stress–strain curves handling a_1, a_2, a_3, b_1, and b_2 as adjustable parameters. It was found that the matrix obeys the Poynting–Thomson model, while the stress–strain curves of the PUR-CF can be better evaluated by the Maxwell model, and examples of such fits are shown in Figure 3.

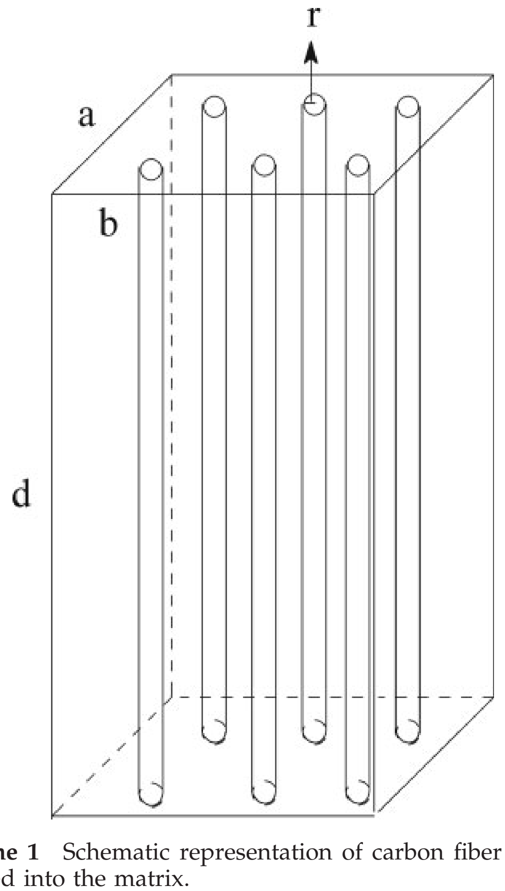
The mechanical properties such as the Young's modulus (E_{comp}) and the value of $\sigma_{\max}$ of the PUR-CF composites as a function of CF content were thoroughly investigated. To describe the variation of E and $\sigma_{\max}$ with the CF content a simple model depicted in Scheme 1 was proposed.

According to Scheme 1, pieces of n CF with a radius of r and density of ρ_{CF} are embedded into the matrix of density ρ_m and with dimensions of a, b, and d. The weight fraction of CF (w_{CF}) is expressed using eq. (3).

$$w_{\text{CF}} = nr^2\pi\rho_{\text{CF}}/[nr^2\pi\rho_{\text{CF}} + (ab - nr^2\pi)\rho_m] \tag{3}$$

Providing that the matrix is completely stick to CF the stress (σ) at low strain (ε) can be calculated using eq. (4):

$$\sigma = [nr^2\pi(E_{\text{CF}} - E_m)/(ab) + E_m]\varepsilon \tag{4}$$



Scheme 1 Schematic representation of carbon fiber incorporated into the matrix.

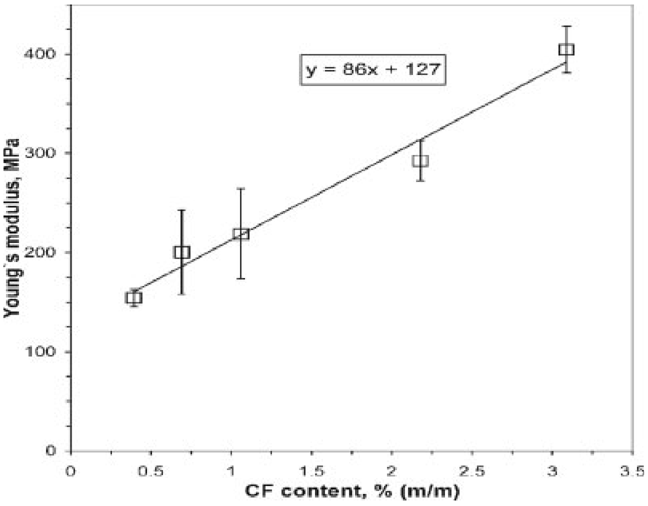


Figure 4 Variation of the Young's modulus of the PUR-CF composite with the polyester-coated CF content. The solid line represents the fitted curve.

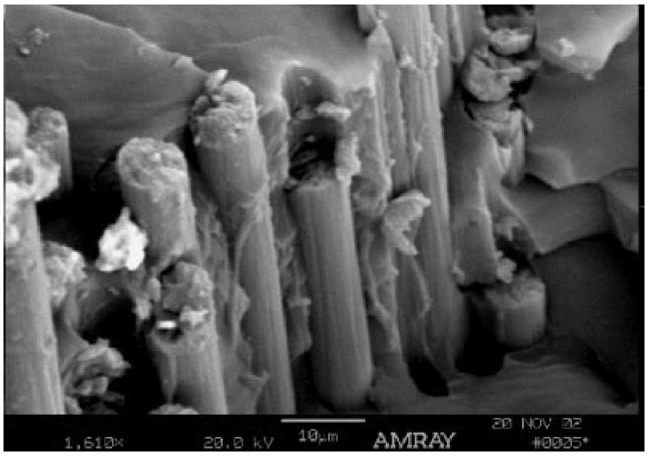


Figure 5 SEM image of PUR-CF (polyester coated) composite on the surface failure (after break). CF content: 3% (m/m).

where E_{CF} and E_m stand for the Young's modulus of CF and the matrix, respectively.

Substituting eq. (3) into eq. (4), eq. (5) is derived:

$$E_{\mathrm{comp}} = w_{\mathrm{CF}}\rho_m(E_{\mathrm{CF}} - E_m)/[\rho_{\mathrm{CF}} - w_{\mathrm{CF}}(\rho_{\mathrm{CF}} - \rho_m)] + E_m \tag{5}$$

If $\rho_{\mathrm{CF}} \gg w_{\mathrm{CF}}(\rho_{\mathrm{CF}} - \rho_m)$ is fulfilled, i.e., at low CF content, then eq. (5) simplifies to eq. (6).

$$E_{\mathrm{comp}} = w_{\mathrm{CF}}(E_{\mathrm{CF}} - E_m)\rho_m/\rho_{\mathrm{CF}} + E_m \tag{6}$$

According to eq. (6), the Young's modulus of the composite can be expected to depend linearly on the CF content. Figure 4 shows the variation of the Young's modulus as a function of the CF content.

Indeed, it can be seen from Figure 4 that the Young's modulus varies linearly with the CF content. However, the slope of the fitted line is lower than that expected on the basis of eq. (6), i.e., considering the value of $E_{\mathrm{CF}} = 39$ GPa, $E_m = 1.5$ MPa, $\rho_m = 1.12$ g/cm^3, and $\rho_{\mathrm{CF}} = 1.78$ g/cm^3 one would expect a value for the slope of ~ 25 GPa with respect to the value of 8.6 GPa (determined from the slope in Fig. 4). On the other hand, the intercept should reflect E_m, but the extrapolated value is significantly higher than that predicted by eq. (6). Nevertheless, it should be kept in mind that eq. (6) is strictly valid only in the cases when no slipping and breaking of the CFs occur. These results indicate albeit considerable reinforcement can be reached most probably due to the appropriate bind of the matrix to the surface of the CF, partial slipping of the CFs within the matrix and/or more presumably breaking of CFs may also take place causing deviances from the theoretically predicted values. To support that the matrix binds to the surface of the CFs scanning electron microscopy (SEM) investigations on the surface failure after breaking were performed (Fig. 5).

As shown in Figure 5 the surface of the CFs is completely covered by the matrix, and no significant fiber pull-out can be recognized, indicating strong adhesion of the matrix to the fiber.

Similar to eq. (6) an equation for the variation of $\sigma_{\max}$ with the CF content [eq. (7)] can also be rationalized:

$$\sigma_{\max,\mathrm{comp}} = w_{\mathrm{CF}}(\sigma_{\max,\mathrm{CF}} - \sigma_{\max,m})\rho_m/\rho_{\mathrm{CF}} + \sigma_{\max,m} \tag{7}$$

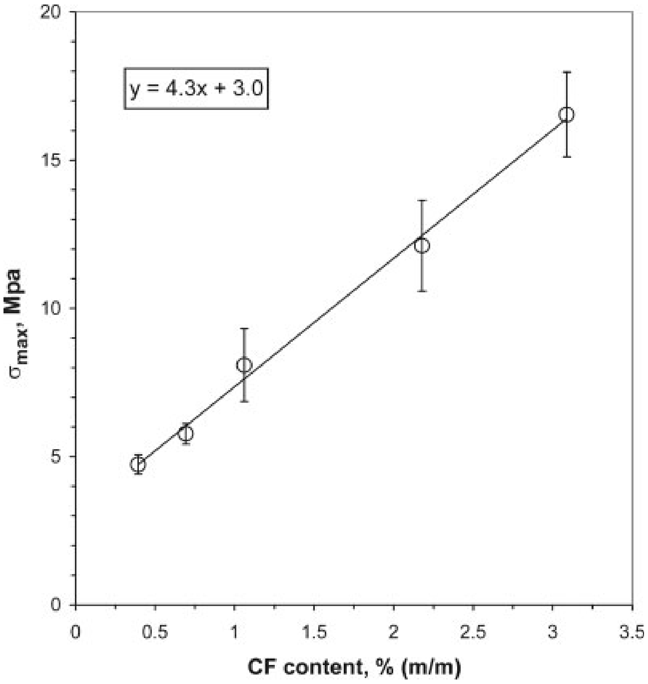


Figure 6 Variation of $\sigma_{\max}$ as a function of the polyester-coated CF content for the PUR-CF composite. The solid line represents the fitted curve.

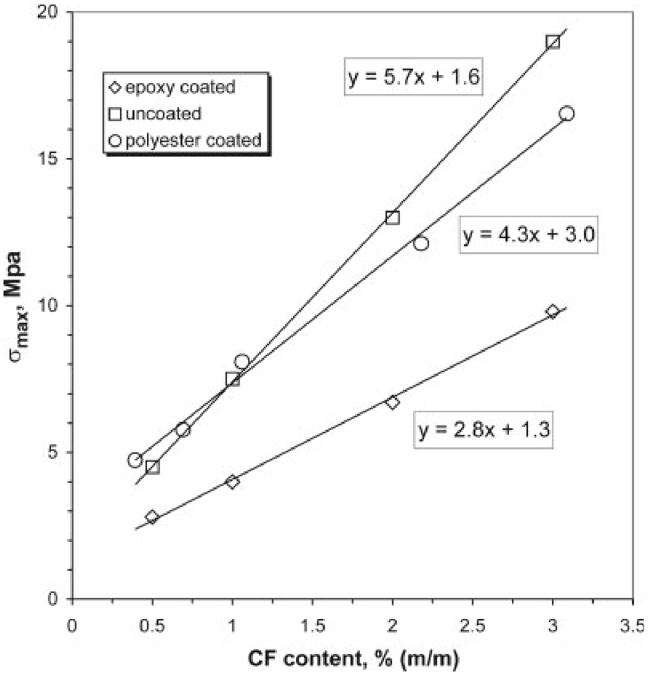


Figure 7 Change of σ_{max} with the CF content for the PUR-CF composite for two differently coated and uncoated carbon fibers.

TABLE I
Values of σ_{max} and Young's Modulus for the Partially Biodegradable PLA-TDI-PEG and PLA-TDI-PPG Carbon Fiber Composites

Sample	%CF content (m/m)	σ_{max} (MPa)	Young's modulus (MPa)
PLA-TDI-PEG	–	15	197
PLA-TDI-PEG	1.6	28	1758
with CF	3.5	39	2070
PLA-TDI-PPG	–	16	227
PLA-TDI-PPG	1.6	36	1847
with CF	3.5	41	1948

where $\sigma_{max,comp}$, $\sigma_{max,CF}$, and $\sigma_{max,m}$ are the maximum stress for the composite, for the CF, and the matrix, respectively.

In Figure 6 the values of $\sigma_{max,comp}$ are plotted as a function of the CF content.

As expected, the values of $\sigma_{max,comp}$ change linearly with the CF content. The theoretical $\sigma_{max,comp}$–CF content curve predicted by eq. (7) ($\sigma_{max,CF} = 412$ MPa and $\sigma_{max,m} = 0.9$ MPa) is close to the experimental one.

In the next series of experiments, the effect of CF's coatings on the mechanical properties of the resulting PUR-CF composites was investigated. Figure 7 shows the variation of σ_{max} with the CF content in the cases of uncoated and coated (polyester and epoxy resin) CFs.

As can be seen from Figure 7 the value of σ_{max} changes linearly with the CF content in each case and the extent of reinforcement (based on the slope of line) decreases in the order: uncoated > polyester coated > epoxy resin coated CF. To explain the observed effect of coatings on the extent of reinforcement two major issues should be considered. The reinforcement is determined by the strength of the matrix–CF bonds on one hand, and the roughness of the surface of the CF on the other hand. Similar polarity of the matrix to that of the CF's surface may result in strong matrix–CF bonds. The CF coated with polyester resin seemed to have similar polarity to that of the PUR matrix resulting in stronger adhesion of the matrix to the CF's surface as compared with the epoxy-coated CF. Moreover, the difference in polarity between the matrix and the CF's surface is expected to be the highest in the case of uncoated CF, i.e., the poorest matrix–CF bonds may exist in that case, the results showed the highest reinforcement. This apparent contradiction can be resolved if one takes into account the roughness of the surface of the uncoated CF (the coated CF has relatively smooth surface). On the other hand, domains on the uncoated surface that are out-of-plane may significantly increase the transfer of the stress from the matrix to the CFs.

The reinforcement in the case of partially biodegradable copolymers with CFs was also demonstrated. The results of these investigations are summarized in Table I.

Stemming from the data of Table I one can realize that significant improvement in the values of both σ_{max} and Young's modulus can be attained in PURs which contain biodegradable polylactic acid (PLA) and/or more polar PEG segments. CF in a relatively low content (1.6% (m/m)) doubled the value of σ_{max}, while the Young's modulus is approximately higher by one order of magnitude with respect to the matrix in the case of both PLA-TDI-PPG and PLA-TDI-PEG.

CONCLUSIONS

Significant improvement in the value of the Young's modulus and maximum stress of PUR matrices was achieved using continuous CFs. Linear dependence of maximum stress and Young's modulus of PUR-CF composites were observed which allow a simple control to prepare PUR-CF composites with desired mechanical properties. The coatings of the CF's surface were also shown to influence the mechanical properties of the resulting composite. Although the molding method developed is relatively slow (as compared with other methods e.g., injection molding) the accessible extent of reinforcement of PURs is much higher than those using short CFs.

S.K. acknowledges the Bolyai János fellowship.

References

1. Gong, X. Y. Polym Adv Technol 1996, 7, 141.
2. Correa, R. A.; Nunes, R. C. R.; Franco, W. Z. Polym Compos 1998, 19, 152.
3. Karger-Kocsis, J.; Czigány, T.; Mayer, J. Plastics Rubber Compos 1996, 25, 109.
4. Czigány, T.; Karger-Kocsis J. Polym Polym Compos 2001, 9, 491.
5. Correa, R. A.; Nunes, R. C. R.; Lourenco, V. L. Polym Degrad Stab 1996, 52, 245.
6. Borda, J.; Tesléry, B.; Zsuga, M. Műanyag és Gumi 1999, 1, 28.
7. Buzási, L. Műanyag és Gumi 2005, 1, 12.
8. Xin, L.; Xu, G.; Hofstra, P.; Bajcar, R. C. J Polym Sci Part B: Polym Phys 1998, 36, 2259.
9. Chou, P.; Ding, D. J Thermoplast Compos Mat 2000, 13, 207.
10. Correa, R. A.; Nunes, R. C. R.; Filho, W. Z. F. Polym Test 1996, 15, 467.
11. Chen, C. H.; Ma, C. C. M. J Appl Polym Sci 1992, 46, 937.
12. Sánchez-Adsuar, M. S.; Linares-Solano, A.; Cazorla-Amorós, D.; Ibarra-Rudea, L. J Appl Polym Sci 2003, 90, 2676.
13. Borda, J.; Bodnár, I.; Ráthy, I.; Zsuga, M. Polym Adv Technol 2003, 14, 1.
14. ISO. Plastics—Determination of Tensile Characteristics; MSZ ISO 527-1, 527-2 Standard; 1999.
15. ISO. Plastics—Determination of Tensile Characteristics, MSZ ISO 527-3, Standard; 1996.
16. Ward, I. M. Mechanical Properties of Solid Polymers; Wiley Interscience: London, 1971; Chapter 5, p 92.