

# Preparation and Characterization of Poly(vinyl chloride)–Continuous Carbon Fiber Composites

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**ABSTRACT:** In this article, we report on the preparation and characterization of novel poly(vinyl chloride) (PVC)–carbon fiber (CF) composites. We achieved the reinforcement of PVC matrices with different plasticizer contents using unidirectional continuous CFs by applying a warm press and a cylinder press for the preparation of the PVC–CF composites. We achieved considerable reinforcement of PVC even at a relatively low CF content; for example, the maximum stress ( $\sigma_{\max}$ ) of the PVC–CF composite at a 3% CF content was found to be 1.5–2 times higher than that of the PVC matrix. There were great differences among the Young's modulus values of the pure PVC and PVC–CF composites matrices. The absolute Young's modulus values were in the range 1100–1300 MPa at a 3% CF content; these values were almost independent of the plasticizer content. In addition, we found a linear relationship between  $\sigma_{\max}$  and the CF

content and also recognized a linear variation of the Young's modulus with the CF content. The adhesion of CF to the PVC matrix was strong in each case, as concluded from the strain–stress curves and the light microscopy and scanning electron microscopy investigations. The mechanical properties of the PVC–CF composites with randomly oriented short (10 mm) fibers were also investigated. At low deformations, the stiffness of the composites improved with increasing CF content. Dynamic mechanical analysis (DMA) was used to determine the glass-transition temperature ( $T_g$ ) of the PVC–CF composites. The high increase in the Young's modulus entailed only a mild  $T_g$  increase. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 190–194, 2012

**Key words:** composites; fibers; poly(vinyl chloride) (PVC); reinforcement

## INTRODUCTION

In recent years, considerable efforts have been devoted to improving the mechanical properties of polymers used as structural materials by the development of composites whose properties exceed those of the matrix. The mechanical properties of fiber-reinforced plastics can be tailored for a desired application, that is, for the aerospace, automotive, marine, sport, and construction industries.

Formerly, the reinforcement of poly(vinyl chloride) (PVC) matrices with short glass fibers has been investigated.<sup>1–5</sup> In recent years, great efforts have been directed at the study of the use of natural fibers as reinforcements in PVC. Natural fibers, such as green coconut fiber, sisal fiber, wood fiber, rice straw, and bagasse fiber, have shown considerable

benefits, such as low cost, low density, high toughness, enhanced strength properties, and last but not least, biodegradability.<sup>6–9</sup>

Nowadays, numerous reports on the reinforcement with continuous or short carbon fibers (CFs) of other polymers, such as polyamide, poly(ether ether ketone), polycarbonates, and polyurethanes (PURs),<sup>10–13</sup> but only a few of PVC, have been published.<sup>14</sup> Because the price of CFs has decreased in recent times, the use of CF can be considered for the improvement of the mechanical properties of mass-produced plastics such as PVC.

The long, continuous fibers should be embedded in the polymer matrix with a slower process than the short ones, but this can result in a higher improvement of the mechanical properties. This inspired us to construct novel PVC composites with continuous CFs.

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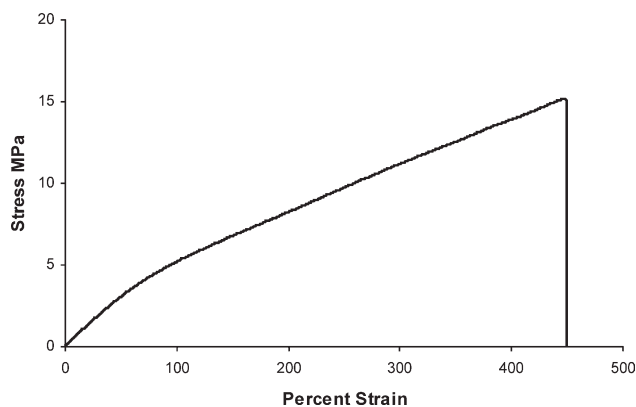
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## EXPERIMENTAL

### Materials

Plasticized PVC granules (LE 411/009) and PVC powders with different plasticizer contents (1720/1, 1720/2, and 1720/3) were obtained from Borsod-Chem (Kazincbarcika, Hungary).



**Figure 1** Stress–strain curve of the plasticized PVC matrix with 62% plasticizer content.

Continuous CF (CF 48K) was received from Zoltek Co. (Nyergesújfalu, Hungary). One staple of CFs contained about 48,000 yarns with an average diameter of 7.4  $\mu\text{m}$  and a density of 1.78  $\text{g}/\text{cm}^3$ . The measured tensile strength and Young's modulus of the yarns were 412 MPa and 39 GPa, respectively.

#### Preparation of the PVC–CF composites

Sheets 0.5 mm thick were pressed from plasticized PVC granules with a warm press (MU-32 Fontyne, Vlaardingen, Nederland), the CFs were distributed evenly and parallel full length on one of the sheets and then pressed to join together (5 MPa) with another sheet at 150°C. The temperature and the relative humidity of the environment were 23°C and 52%, respectively. Samples were cut from the composite sheets corresponding in size and shape to ISO standards.<sup>15,16</sup>

Samples were also prepared with the same method from plasticized PVC powder by a cylinder press (Schwabenthan Polymix 150u, Berlin, Germany).

A composite with short CFs (10 mm) was prepared from plasticized PVC granulate in a Brabender-type mixing chamber (Duisburg, Germany): pure PVC was mixed for 2 min at 150°C, and then, the CFs were added and mixed again for 2 min.

#### Instruments

##### Mechanical testing

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

##### Scanning electron microscopy (SEM)

An Amray 1830 I scanning electron microscope (Bedford, MA) was applied to study the surface failure of the composites after break.

##### Hardness testing

The Shore A hardness was determined with a Zwick 3114.01 hardness tester (Leicester, England) according to Hungarian standards (MSZ ISO 868).<sup>17</sup>

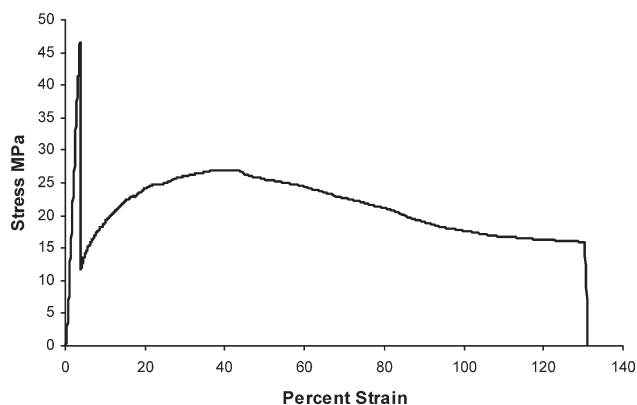
##### Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was used to determine the glass-transition temperature ( $T_g$ ) of the PVC–CF composites. A Rheometric DMTA MK-III instrument (Epsom, England) was applied at a frequency of 1 Hz frequency and a heating rate of 2 K/min heating rate. An oscillating sinusoidal strain was applied to the sample, and the resulting stress developed in the sample was measured as a function of the temperature.

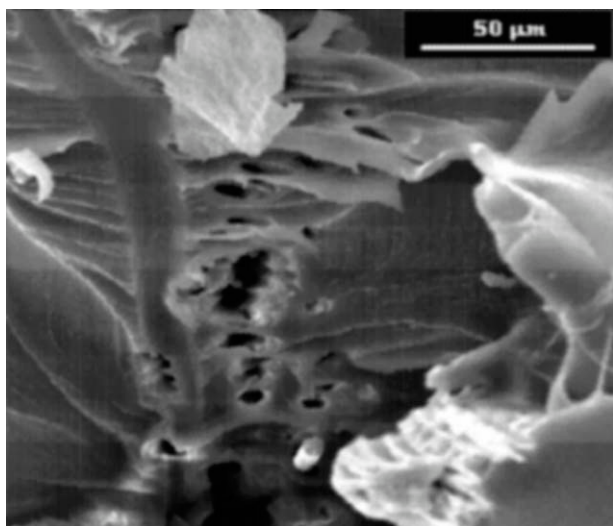
## RESULTS AND DISCUSSION

The plasticized PVC reinforced with unidirectional continuous CF showed improved mechanical properties (stiffness and strength), even at low CF contents, compared to those of the PVC matrix, as shown by the stress–strain curves (Figs. 1 and 2).

As shown in Figure 2, the initial slope of the stress–strain curves, that is, the Young's modulus for the PVC–CF composites ( $E_{\text{comp}}$ ) was significantly higher than that for the PVC matrix. On the other hand, the maximum stress value for the PVC–CF composite ( $\sigma_{\text{max,comp}}$ ) was also higher (2–3 times) compared to that of the PVC matrix as a result of reinforcement. The stress–strain curves of the pure PVC matrix did not display a yield point and possessed only one monotonous region, whereas the curves of the PVC–CF composites showed different regions: elastic, yielding, strain-softening, and strain-hardening regions. The first section of the curves, with a high slope, is typical in the case of stiff, brittle materials such as CFs, so

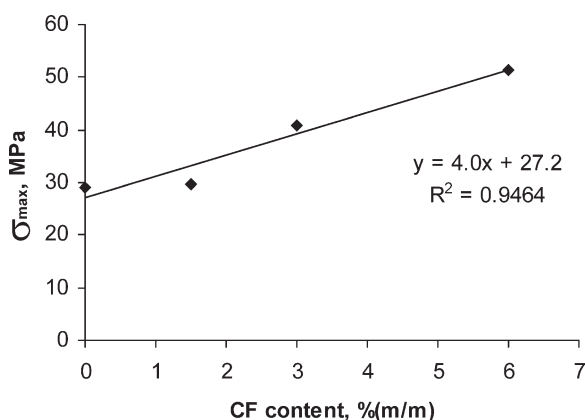


**Figure 2** Stress–strain curves for the PVC–CF composite with 3% CF content and 62% plasticizer content prepared by a warm press.



**Figure 3** SEM image of the PVC-CF composite on the surface failure (after break), (CF content = 3%, plasticizer content = 62%, warm press).

we concluded that the adhesion of CFs to the matrix was appropriate. The sharp maximum on the stress-strain curves could be explained by breaking of the CFs and/or by their partial slippage within the matrix. After the dramatic stress drop, the stress-strain curves showed a strain-hardening region. The last section of the curves were relatively flat, like the rigid PVC stress-strain curve after yielding. The breaking stress at the PVC matrix and at the PVC-CF composite did not differ significantly, the elongation at the break of the PVC matrix was about 500%, and in the case of the PVC-CF composites, it was about 100%. In comparison, we found a difference of one order of magnitude at the ultimate elongation between the PUR matrix and the PUR-CF composites.<sup>18</sup>



**Figure 4** Variation of  $\sigma_{\max}$  as a function of the CF content for the PVC-CF composite (30% plasticizer content, cylinder press). The solid line represents the fitted curve.

**TABLE I**  
Expected and Determined Values for the Slope of  $\sigma_{\max}$  versus the CF Content Function for Different PVC-CF Composites

Plasticizer content	Theoretical value (MPa)	Fitted value (MPa)
30%, cylinder press	301	402
50%, cylinder press	307	461
70%, cylinder press	311	433

To confirm that the matrix was bound to the surface of the CFs, SEM investigations on the surface failure after breaking were performed (Fig. 3).

As shown in Figure 3, the surface of the CFs were completely covered by the matrix. The fibers were broken into sections, not pulled out from the matrix; this indicated a strong adhesion of the matrix to the fiber.

The mechanical properties, such as  $\sigma_{\max, \text{comp}}$  and  $E_{\text{comp}}$ , as a function of the CF content were thoroughly investigated.

In Figure 4, the value of  $\sigma_{\max, \text{comp}}$  is plotted as a function of the CF content. Figure 4 shows that the values of  $\sigma_{\max, \text{comp}}$  changed linearly with the CF content. A similar dependency was observed for the other PVC-CF composites with various plasticizer contents. In a previous report, we showed that the values of the maximum stress ( $\sigma_{\max}$ ) changed linearly with the CF content for the PUR-continuous CF composites<sup>18</sup> according to eq. (1):

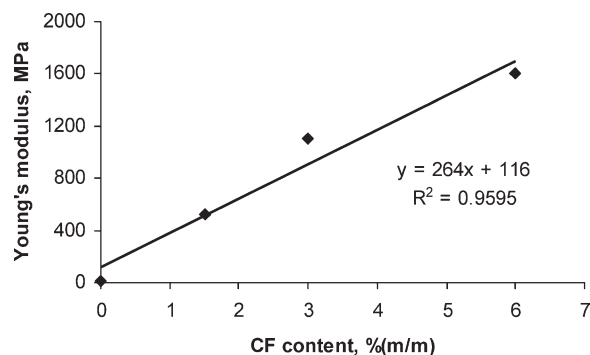
$$\sigma_{\max, \text{comp}} = w_{\text{CF}}(\sigma_{\max, \text{CF}} - \sigma_{\max, m})\rho_m/\rho_{\text{CF}} + \sigma_{\max, m} \quad (1)$$

where  $w_{\text{CF}}$  is the CF content of the composite expressed in weight percentage,  $\sigma_{\max, \text{CF}}$  and  $\sigma_{\max, m}$  are the maximum stresses of CF and the matrix, and  $\rho_{\text{CF}}$  and  $\rho_m$  are density of CF and the matrix, respectively.

Equation (1) could also be applied for the PVC-CF composites. On the basis of eq. (1), the slopes of the fitted lines in Figure 4 were close to those of the theoretical ones with values of  $\sigma_{\max, \text{CF}} = 412$  MPa,  $\rho_m = 1.4$  g/cm<sup>3</sup>, and  $\rho_{\text{CF}} = 1.78$  g/cm<sup>3</sup>. Table I shows the expected values for the slope and the values determined from the slope in Figure 4 for the different PVC-CF composites. The difference in the theoretical and experimental results may have been due to the uncertainty of  $\sigma_{\max, \text{CF}}$  obtained from the manufacturer specifications.

The variation of  $E_{\text{comp}}$  with the CF content is plotted in Figure 5. As shown in Figure 5, the Young's modulus also changed linearly with the CF content. The variation of  $E_{\text{comp}}$  with the CF content<sup>18</sup> could also be rationalized with eq. (2), similarly to eq. (1):

$$E_{\text{comp}} = w_{\text{CF}}(E_{\text{CF}} - E_m)\rho_m/\rho_{\text{CF}} + E_m \quad (2)$$

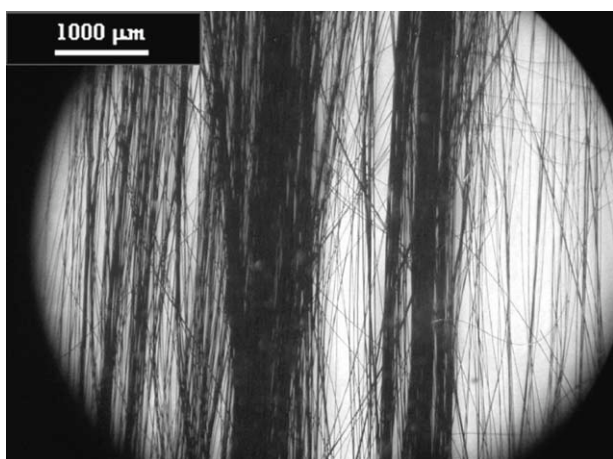


**Figure 5** Variation of  $E_{\text{comp}}$  with the CF content (50% plasticizer content, cylinder press). The solid line represents the fitted curve.

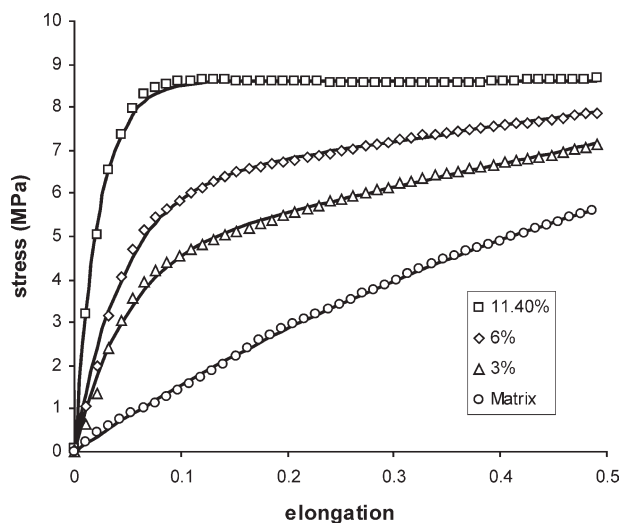
where  $E_{\text{comp}}$ ,  $E_{\text{CF}}$ , and  $E_m$  are the Young's modulus values of the composite, CFs, and matrix, respectively.

As Figure 5 shows, the slopes of the fitted curves were lower than that of the theoretical curve predicted according to eq. (2) ( $E_{\text{CF}} = 39$  GPa). At the highest CF content (6%)—as we realized during the sample preparation—the layered CFs covered the entire sample surface, and thus, this was the maximum fiber density that could be reached under laboratory circumstances. At higher CF contents, the surface of the CFs was not completely covered by the matrix. As Figure 5 shows, the Young's modulus value at the highest CF content was below the fitted curve. A similar effect was observed for the other PVC–CF composites with various plasticizer contents.

Figure 6 shows the parallel but uneven arrangement of CFs caused by the manual laying down of the fibers. Densely packed parts reduced the binding of the matrix to the CF surface and resulted in a weaker improvement in the mechanical properties. Automated feeding could be used to achieve a uniform layout of CFs.



**Figure 6** Light microscope image of the transparent PVC–CF matrix.



**Figure 7** Stress–strain curves for the pure PVC matrix and PVC–CF composites with 3, 6, and 11.4% CF contents and 62% plasticizer content, prepared by a warm press. The solid lines represent the fitted curves. (The fitted parameters were  $a_1 = 0.304$  MPa,  $a_2 = 32.2$ , and  $a_3 = 1.68$  for the matrix;  $a_1 = 5.29$  MPa,  $a_2 = 0.864$ , and  $a_3 = 21.1$  for the composite with a 3% CF content;  $a_1 = 3.47$  MPa,  $a_2 = 1.78$ , and  $a_3 = 22.1$  for the composite with a 6% CF content; and  $a_1 = 0.0189$  MPa,  $a_2 = 457$ ,  $a_3 = 44.0$  for the composite with an 11.4% CF content.)

In the next series of experiments, we investigated the mechanical properties of the PVC–CF composites with randomly oriented short (10 mm) fibers. The  $\sigma_{\text{max,comp}}$  values were very close to that of the PVC matrix itself. This observation indicated that the fibers become separated from the matrix at large strains. On the other hand, at low deformations, the stiffness of the composites increased with increasing CF content, and the Poynting–Thomson model [eq. (3)] could be applied to describe the stress–strain curves of these composites:

$$\sigma = a_1[\varepsilon + a_2(1 - e^{-a_3\varepsilon})] \quad (3)$$

where  $\sigma$  is the stress;  $a_1$ ,  $a_2$ , and  $a_3$  are parameters including the Young's modulus of the Hookien springs and the viscosity coefficient of the viscous liquid in the model; and  $\varepsilon$  is the strain.

**TABLE II**  
Shore A Hardness Testing of Plasticized PVC–CF Composites with Randomly Oriented Short (10-mm) Fibers

CF content (%)	Shore A hardness
0	77
3	87
6	89
12	93



**TABLE III**  
 $T_g$  Values of Plasticized PVC–CF Composites with Randomly Oriented Short (10-mm) Fibers

CF content (%)	$T_g$ (°C)
0	14.74
3	19.94
6	20.14
12	23.34

The stress–strain curves for the pure PVC matrix and PVC–CF composites with different CF contents, together with the calculated curves by eq. (3), are plotted in Figure 7. As shown in Figure 7, the initial slope of the stress–strain curves, that is,  $E_{comp}$ , was significantly higher than that of the PVC matrix, and it increased with the CF content. On the other hand, as is also evident from Figure 7, the stress–strain properties of the PVC matrix and the PVC–short CF composites could be adequately described by the Poynting–Thomson model.

The hardness of the composites was also examined. Table II shows that the Shore A hardness increased with increasing CF content of the composites.

Dynamic mechanical analysis (DMA) was used to determine the  $T_g$  values of the PVC–CF composites. Because the CFs could be treated as inactive fillers in point of molecular movements, no  $T_g$  increase was expected with increasing CF content. Table III shows a gentle  $T_g$  increase, which was presumably caused by the interactions between the polymer matrix and some residual surface treatment material on the CFs. Nevertheless, we deduced that the high increase in the Young's modulus entailed only a mild  $T_g$  increase.

### CONCLUSIONS

Significant improvements in the mechanical properties, that is,  $\sigma_{max}$  and the Young's modulus of plasti-

cized PVC were achieved with continuous CFs. A linear dependence of  $\sigma_{max}$  and the Young's modulus on the CF content of the PVC–CF composites was observed; this will allow simple control in the preparation of PVC–CF composites with desired mechanical properties. The adhesion of the CFs to the PVC matrix was appropriate. PVC–CF composites with randomly oriented short fibers were also investigated. When the CF content of the matrix was increased, significant increases in the Young's modulus and hardness were observed, whereas the highest stress did not change. With a remarkable improvement in stiffness, only a mild increase in  $T_g$  was measured.

### References

- Koenczoel, L.; Hiltner, A.; Baer, E. *Polym Compos* 1987, 8, 109.
- Nguyen, P. X.; Moet, A. *Polym Compos* 1987, 8, 298.
- Yuan, J.; Hiltner, A.; Baer, E. *Polym Compos* 1986, 7, 26.
- Termonia, Y. *J Mater Sci* 1992, 27, 4878.
- Parsons, M.; Toyoda, P. *J Vinyl Addit Technol* 2002, 8, 202.
- Kamel, S. *Polym Adv Technol* 2004, 15, 612.
- Grossman, R. F. *J Vinyl Addit Technol* 2006, 12, 124.
- Djidjelli, H.; Boukerrou, A.; Founas, R.; Rabouhi, A.; Kaci, M.; Farenc, J.; Martinez-Vega, J.-J.; Benachour, D. *J Appl Polym Sci* 2007, 103, 3630.
- Leblanc, J. L.; Furtado, C. R. G.; Leite, M. C. A. M.; Visconte, L. L. Y.; de Souza, A. M. F. *J Appl Polym Sci* 2007, 106, 96.
- Gong X. Y. *Polym Adv Technol* 1996, 7, 141.
- Correa, R. A.; Nunes, R. C. R.; Franco, W. Z. *Polym Compos* 1998, 19, 152.
- Karger-Kocsis, J.; Czigány, T.; Mayer, J. *Plast Rubber Compos* 1996, 25, 109.
- Czigány, T.; Karger-Kocsis, J. *Polym Polym Compos* 2001, 9, 491.
- GuoQuan, W.; Peng, Z. *Polym Eng Sci* 1997, 37, 96.
- Hung. Standard MSZ ISO 527-1, 527-2 (1999).
- Hung. Standard MSZ ISO 527-3 (1996).
- Hung. Standard MSZ ISO 868 (1991).
- Borda, J.; Kéki, S.; Ráthy, I.; Bodnár, I.; Zsuga, M. *J Appl Polym Sci* 2007, 103, 287.