JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 8, August 2007, p. 2524 - 2528

Properties of composite materials from polyethylene and cellulose microfibrils

D. M. PANAITESCU*, P. V. NOTINGHER[a], M. GHIUREA, F. CIUPRINA[a], H. PAVEN, M. IORGA, D. FLOREA
National Institute of Research and Development in Chemistry and Petrochemistry ICECHIM,
202 Splaiul Independentei, 060021, Bucharest, Romania,
[a]*Politehnica University of Bucharest, 313 Splaiul Independentei, 060042, Bucharest, Romania*

Composites from polyethylene and cellulose microfibrils are perceived as a viable alternative over traditional filled polymers in electrical insulation applications, biomedicine, packaging and construction. This interest arises from the remarkable mechanical properties of such microfibrils. Some experimental aspects regarding the preparation and the characterisation of polyethylene composites with cellulose microfibrils are presented in this paper. Morphological changes of polyethylene matrix when microcrystalline cellulose is added are pointed out by electronic microscopy, by mechanical and dielectric characterisation. Polymer composites from polyethylene and cellulose microfibrils show improved mechanical and dielectric properties compared to polyethylene and traditional organic composites.

(Received February 10, 2007; accepted April 27, 2007)

Keywords: Polyethylene, Cellulose microfibrils, Polymer composites

1. Introduction

Cellulose fibbers originating from wood or annual plants were used for reinforcing polymers for some decades [1-2]. They were used to replace glass fibbers as reinforcing component in polymers for low and medium price technical applications because of their lower density, lower cost and lack of abrasion to the processing equipment. Environmental advantages were considered too. Wood fibber and wood flour reinforced polymer composites have already found their application in construction and automotive industry [2-3].

Over the last few years the use of cellulose microfibrils with micron (nano)-sized diameters as reinforcing elements in polymer composites gained considerable attention [4-6]. Polymer composites with cellulose microfibrils are materials characterised by high specific strength, formability and geometrical complexity at very small scale, low density and abrasivity, dielectric properties and reciclability. The interest for polymer composites with cellulose microfibrils is growing up in the last decade as a result of the new environmental regulations and of the remarkable mechanical properties of such microfibrils. Composites from polymers and cellulose microfibrils are friendly environmentally products that could be applied in electrotechnics, automotive industry, biomedicine, packaging and construction.

The dimensions of cellulose microfibrils, especially the length/diameter factor, have influenced their dispersion capacity in polymer matrix, the adhesion at polymer/filler interface and the mechanical characteristics of composites. Cellulose microfibrils are characterised by a higher toughness and reactivity and therefore better adhesion to the polymer compared to cellulose fibbers with larger diameters. Physical and chemical treatment of microfibrils and the addition of compatibilizers improve the interface characteristics [5-8].

The advantage of microcrystalline cellulose for the reinforcement of polymers by compounding with thermoplastic resins has already been recognized [4-6, 9]. Composite materials from polystyrene and microcrystalline cellulose with a diameter of 20-50 μm, have been realized [10] The tensile strength at break for a composite with 40% microcrystalline cellulose was found to be double then that of polystyrene matrix. A significant increase in the stiffness was reported for a composite polypropylene / wood cellulose microfibers (40x20 μm^2) containing a compatibilizer. The modulus of elasticity for the composite (2060 MPa) was higher then that of polypropylene matrix (1490 MPa). [9]. For a low density polyethylene - microcrystalline cellulose composite the tensile stress grows approximately 1.2 times, while the relative elongation at break falls 40 times compared to polyethylene matrix [11]. The most drastic decrease in the relative elongation at break occurs when the filler content is increased at 10%.

The application of polymer composites with cellulose microfibrils in electrotechnics is restrained by the lack of information about morpho-structural aspects and the behaviour of such materials when mechanical or electrical stress are applied.

In this paper the use of cellulose microfibrils as reinforcements in polyethylene is explored. Some experimental aspects regarding composites preparation and characterisation are presented with special emphasis on mechanical and electrical behaviour.

2. Experimental

As polymer matrix a low density polyethylene type A-22-FMA-02 - PE (melt flow index 0.3…0.4 g/10 min. at 190 ^{0}C, 2.16 kgf) from Arpechim Romania has been used for the preparation of composites. Microcrystalline cellulose – MC (20 µm; bulk density 0.6 g/cm^3) was supplied by Sigma Aldrich. Polyethylene and microcrystalline cellulose were mixed in a Brabender Plasticorder, in the following conditions: temperature 155-160^{0}C, rotors speed 75 rpm/75 rpm, processing time 10 min. The samples used in mechanical and electrical measurements were prepared by hot pressing in an electrically heated press at 160^{0}C for 10 min with a force of 50 kN. After pressing, the samples were cooled to room temperature under pressure.

The morphology of the composites was investigated with a Quanta Scanning Electron Microscope 200. Modulus of elasticity of the composites was determined according to SR EN ISO 527:2000 on specimens type IB with 2 mm/min.

Ultrasonic measurements were performed using an ELPAN-543E measurement system according to ASTM E 494. Dynamic modulus of elasticity (E_L) at ultrasonic frequency (1 MHz) was calculated from the propagation speed of longitudinal waves (v_L) with the formula:

$$E_L = \rho\, v_L^2 \qquad (1)$$

where ρ is the density of the material.

Conductivity measurements were carried out using a Keithley 6517 electrometer with a measurement cell connected to PC-Pentium III computer, as described in [9].

Permittivity and dielectric loss factor measurements were carried out using a RLC Hewlett Packard Pont (4623B).

3. Results and discussion

3.1. Morphological aspects

Microcrystalline cellulose used in polymer composites has a diameter in the range 10-20 µm as shown by SEM image (Fig. 1).

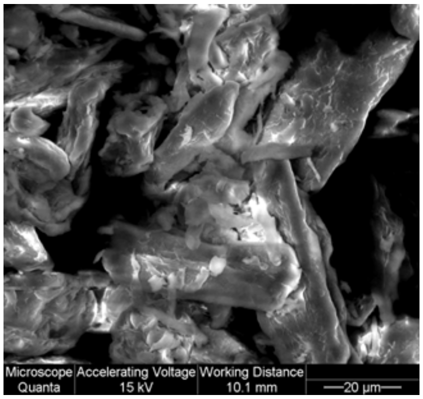
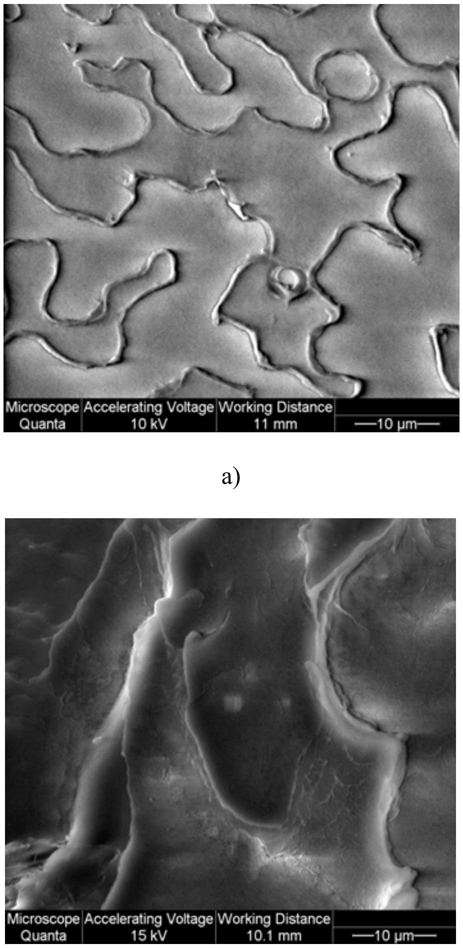


Fig. 1. SEM image of microcrystalline cellulose, x500

Morphological changes of polyethylene matrix in PE/cellulose composites were investigated by scanning electron microscopy. Experiments were performed for neat PE, sample 1 and PE composites with 5%, 10%, 15% and 20% MC, samples 2 – 5. Samples were fractured in liquid nitrogen.

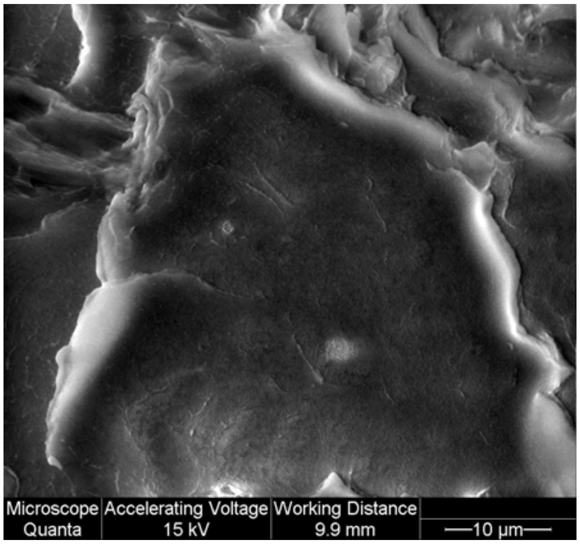
SEM micrographs of fracture surfaces of PE, PE/10% MC and PE/20% MC (Fig. 2) pointed out the morphological changes of polyethylene when microcrystalline cellulose is added, the changes being more important with the increase of cellulose concentration in the composite. It is difficult to differentiate microcrystalline cellulose from the polyethylene matrix, which may suggest that the cellulose particles are coated by the matrix and that the failure occurs in the matrix. It can be seen that matrix fracture occurred in various ways in sample 1 (PE) compared to sample 3 (PE/10% MC) or 5 (PE/20%MC) as shown in Fig. 2.

SEM images suggest a great influence of MC on the fracture mechanism at cryogenic temperatures: PE fracture surface seems to be relatively smooth but PE/MC composite presents an uneven fracture surface with many "hills" and "valleys" which suggest a significant matrix deformation. The failure edges observed in the case of the composite (sample 5) suggest possible bond between microcrystalline cellulose and polyethylene matrix.



a)

b)



c)

Fig. 2. SEM images of fractured samples of PE (a), PE/10% MC (b) and PE/20% MC (c).

3.2. Mechanical properties

The mechanical characteristics of polyethylene composites with microcrystalline cellulose are presented in Figs. 3 – 5. Relative tensile strength (the ratio between the tensile strength of the composite σ and of the unfilled polymer σ_0) of PE composites with different concentrations of microcrystalline cellulose is presented in Figure 3. The addition of 5% microcrystalline cellulose in polyethylene determines a small increase of the tensile strength but at higher concentrations of MC no significant effect is observed.

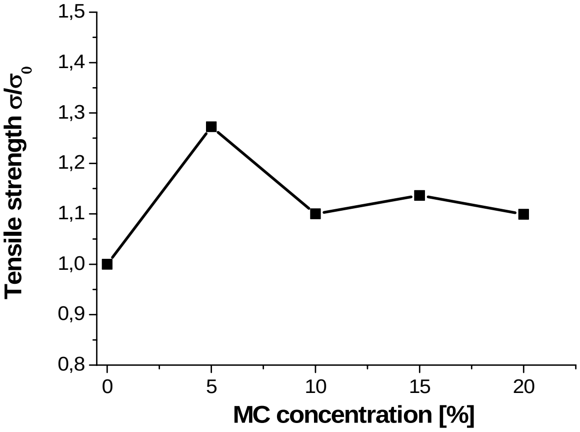


Fig. 3. Relative tensile strength of PE – MC composites versus MC concentration

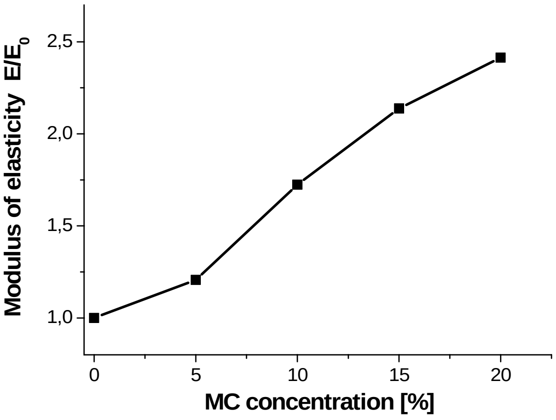


Fig. 4. Relative tensile modulus of PE – MC composites versus MC concentration.

Fig. 4 shows the variation of relative tensile modulus of the composites (E/E_0, E - modulus of elasticity of PE composite and E_0 - modulus of elasticity of PE) against the concentration of microcrystalline cellulose. The modulus increases with the increase of MC concentration, up to a value 2.4 times that of unfilled polyethylene for 20% of MC, indicating a reinforcing action of the filler. The increase of relative tensile modulus of polyethylene composites is determined by an increase in the rigidity of the matrix because of the restrictions of macromolecules mobility and deformability imposed by the presence of MC.

Fig. 5 shows the values of relative dynamic modulus (E_L/E_{L0}, E_L – dynamic modulus of PE composite at ultrasonic frequency and E_{L0}- dynamic modulus of PE at the same frequency) for different concentrations of MC.

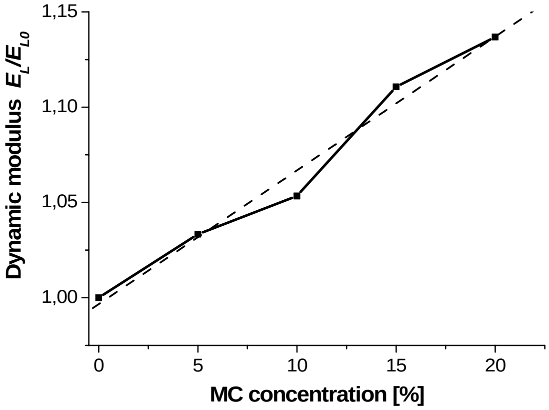


Fig. 5. Relative dynamic modulus of composites (ultrasonic measurements) versus MC concentration.

Ultrasonic experimental data can be approximated by the mathematical relation (dashed line in Fig. 5):

$$E_L = 0.997 + 0.007c \quad (2)$$

where c is MC concentration.

The almost linear increase of the dynamic modulus is less important then that of static modulus (E_L increases with 15% for sample 5 compared to PE matrix). This is an expected behaviour for dynamic conditions.

The reinforcing effect of microcrystalline cellulose in PE is pointed out by the significant change of static modulus of elasticity of the composite and by the slight increase of dynamic modulus. These results are supported by the morphological features observed in SEM micrographs of fracture surfaces.

3.3. Electrical properties

DC electrical measurements were performed by applying a voltage of 1000 V for a long period of time (an hour) on PE – MC samples of 100 mm x 100 mm x 2 mm, containing different concentrations of MC (samples 1…5). Volume resistivity of composite samples (ρ) depending on the time of voltage application t is presented in Figure 6.

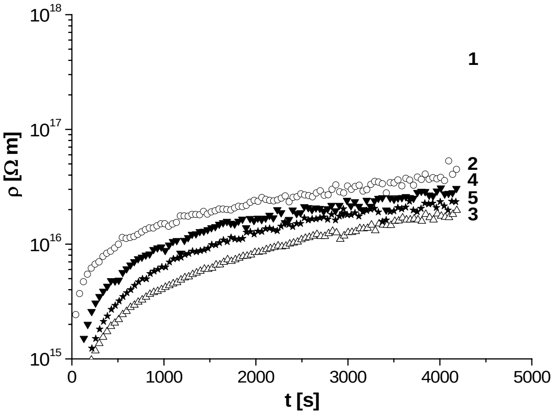


Fig. 6. Volume resistivity of composites, ρ, versus voltage application time t (samples 1...5)

The resistivity of composites samples (samples 2 – 4) increases in time but the increase slope is smaller than for polyethylene matrix (sample 1). A similar tendency of resistivity increase in time is presented in [13] for low density polyethylene and micro-sized TiO_2 composites. The resistivity of samples (after an hour of voltage application) in function of cellulose concentration is presented in Figure 7. The resistivity of composites (samples 2 – 4) is smaller then that of polyethylene matrix (sample 1), but the differences do not exceed an order of magnitude. For 5% till 20% MC in polyethylene the volume resistivity does not change significantly. The same resistivity dependence upon filler concentration was observed at epoxi/TiO_2 microcomposites [14]. The increase of composites conductivity compared to polyethylene matrix can result from the increase of traps concentration and of spatial charge density.

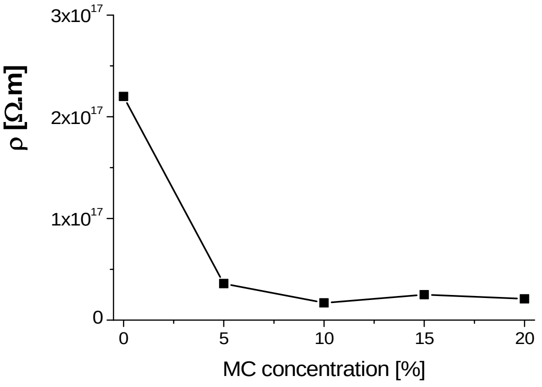


Fig. 7. Volume resistivity of composites samples versus cellulose concentration.

The relative permittivity (ε_r) of samples 1 – 5 is presented in Figures 7 against the frequency of the electric field (f).

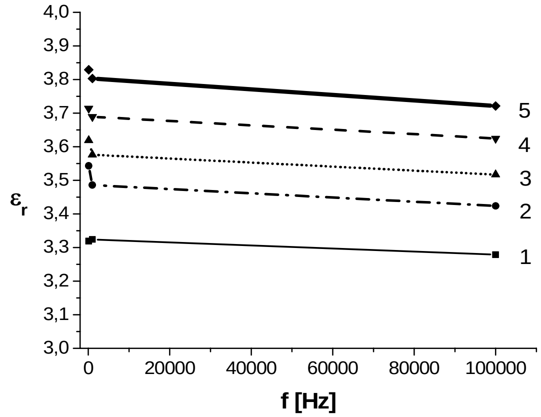


Fig. 8. Relative permittivity of polyethylene composites with microcrystalline cellulose ε_r versus frequency f (samples 1...5).

The variation of the permittivity with the frequency in the domain 0 - 10^5 Hz is not important but a slight decrease could be observed. The same tendency of slight decrease of the permittivity with the increase of the frequency is presented in [15] for polyethylene composites with 5% microsilica. The dielectric constant ε_r is influenced by cellulose concentration, the changes being proportional with the concentration of microcrystalline cellulose in polyethylene matrix as it can be seen in Fig. 9.

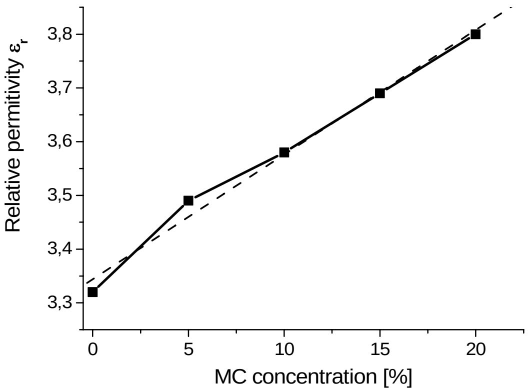


Fig. 9. Variation of relative permittivity of composites in function of cellulose concentration (f = 1000 Hz).

Relative permittivity increases rough linear when cellulose concentration in composites is increased. Relative permittivity results can be approximated by the mathematical relation (dash line in Figure 9):

$$\varepsilon_r = 3.344 + 0.023\,c. \qquad (3)$$

The increase of the permittivity with the increase of cellulose concentration in the composite could be explained by the higher permittivity of the organic filler ($\varepsilon_r \sim 4.5$ for cellulose) and the presence of double space charge at polymer/cellulose interface [16, 17]. The increase of cellulose concentration induces an increase of the total area of polyethylene – microparticles interfaces and, therefore, an increase of the charge at interfaces. As a result, the interfacial polarisation and the equivalent permittivity of the composite are higher [18].

4. Conclusions

Polyethylene composites with microcrystalline cellulose are polymer composites with interesting properties. The use of cellulose of micron size like filler in polyethylene causes important morphological changes of the matrix. The organic filler has reinforcing effect on polyethylene determining an important increase of the modulus of elasticity.

Volume resistivity of polymer composites is lower than that of polyethylene matrix but the difference did not exceed an order of magnitude.

The permittivity changes to a little extend with the frequency in the tested domain and with the concentration of microcrystalline cellulose in polyethylene matrix.

Dielectric properties (volume resistivity and permittivity) of polymer composites with cellulose (max. concentration 20 %) recommend these materials for electrical insulation applications.

References

[1] J. Ganster, H. P. Fink, Cellulose, **13**, 271 (2006).
[2] A.K Bledzki., J. Gassan, Prog. Polym. Sci., **24**, 221 (1999).
[3] K. Oksman, Appl. Compos. Mater. **7**, 403 (2000).
[4] A. Chakraborty, M. Sain, M. Kortschot, Holzforschung, **59**, 102 (2005).
[5] W. Gacitua, A. Ballerini, J. Zhang, Ciencia y tecnología **7**, 159 (2005).
[6] A. N. Nakagaito, S. Iwamoto, H. Yano, Appl. Phys. A, Mater. Sci.& Proces., **80**, 93 (2005).
[7] M. Abdelmouleh, S. Boufi, M. Belgacem, A. Duarte, A. Gandini, Int. J. Adhes. Adhesives, **24**, 43 (2004).
[8] P. V. Notingher, D. Panaitescu, Z. Vuluga, M. Iorga, H. Paven, D. Florea, J. Optoel. Adv. Mater. **8**, 687 (2006).
[9] A. Amash, P. Zugenmaier, Polymer Bulletin **40**, 251 (1998).
[10] M. G. Laka, S. A. Chernyavskaya, Mech. Compos. Mater., **32**, 381 (1996).
[11] M. Maskavs, M. Kalnins, M. Laka, S. Chernyavskaya, Mech. Compos. Mater., **37**, 159 (2001).
[12] P. V. Notingher, D. Panaitescu, H. Paven, M. Chipara, J. Optoel. Adv. Mater., **6**, 1081 (2004).
[13] R. J.Fleming, T. Pawolowski, A. Ammala, P. S. Casy, K.A.Lawrence, IEEE Trans. Dielectr. Electr. Insul., **12**, 745 (2005).
[14] J. K. Nelson, Y. Hu, J. Phys. D: Appl. Phys. **38**, 213 (2005).
[15] M. Roy, J. K. Nelson, R. K. MacCrone, L. S. Schadler, C. W. Reed, R. Keefe, W. Zenger, IEEE Trans. Dielectr. Electr. Insul. **12,** 629 (2005).
[16] T. J. Lewis, IEEE Trans. Dielectr. Electr. Insul. **11**, 739 (2004).
[17] T. J. Lewis, J. Phys. D: Appl. Phys. **38**, 202 (2005).
[18] C. T. O'Konski, J.Phys. Chem. **64**, 605 (1960).

---

*Corresponding author: panaitescu@icf.ro