STRUCTURE AND PROPERTIES OF THE NANOCOMPOSITES DEVELOPED ON THE BASIS OF RECYCLED POLYESTERS

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Abstract

Secondary polycarbonate (SPC) is modified with various amounts (5, 10, 30 wt. %) of ethylene vinyl acetate copolymer (EVAc) by melt blending in order to reduce its brittleness. It is observed that at optimal EVAc weight content maximum tensile strength σ_M and impact strength A_I increase by 14 % (ω_{EVAc}=5 wt. %) and 450 % (ω_{EVAc}=10 wt. %) in comparison to neat SPC, respectively. Addition of EVAc, however, reduces resistance to creep as well as decrease thermal stability of the investigated compositions. Addition of montmorillonite nanoclay (MMT) allows further increase of elastic modulus E and strength of the investigated SPC blend with 10 wt. % of EVAc. Besides it creep resistance and thermal resistance of the investigated system is increased to certain extent.

1 Introduction

Accumulation of solid waste is one of the most important environmental problems nowadays. More than 25 million tons of plastic wastes are generated in EU member states annually [1]. Recycling rates of this huge amount of waste in EU are still low, especially in waste electrical and electronic equipment (WEEE), construction and end of life vehicles (ELV) sectors [2]. Therefore incentives promoting recycling of plastic waste are important.

Secondary polymers, derived from post-consumer waste streams, can serve as suitable matrix materials for development of advanced composites with unique set of properties by using nanotechnologies. Up to know majority of investigations on polymer nanocomposites have been focussed on the use of primary polymers. Thus it is challenging to develop advanced nanocomposites for high-value markets on the bases of secondary engineering polymers, which is the topic of this research.

Secondary polycarbonate, derived from post-consumer DVDs, is modified with nanolevel modifiers in order to obtain multifunctional hybrid composites with the set of unique properties. Organically modified montmorillonite nanoclays are chosen to improve thermal, mechanical and solvent barrier properties of the nanocomposites. Specific organic modifiers

in its turn are chosen to reduce brittleness of the secondary polymer as well as to optimize processability of the nanocomposite.

2 Materials and testing methods

2.1. Materials

Secondary polycarbonate (SPC) was derived from post-consumer DVDs. Aluminum and lacquer were removed from DVD scrap mechanically. In order to aid removal process DVD scrap was treated with alkaline solution. After alkaline treatment purified polycarbonate was washed with distilled water until washing solution showed neutral reaction. Finally DVDs, purified in such a way, were grinded up to particle sizes suitable for extrusion. Before extrusion SPC particles was dried in a convection oven at 105°C for 24 hours.

Commercial ethylene vinyl acetate copolymer with vinyl acetate content of 26 % (EVAc: trade name *11507-375*), was used as impact modifier of SPC. The content of EVAc in SPC matrix was 5, 10 and 30 wt. %. Before extrusion EVAc was dried in a convection oven at 60°C for couple of hours.

Commercial montmorillonite (MMT: *Dellite LVF* by *Laviosa Chimica Mineraria S.p.A.*) was used as inorganic modifier. The content of MMT in SPC matrix was 1, 2 and 5 wt. %. Before extrusion MMT was dried in a convection oven at 105°C for 24 hours.

2.2. Manufacturing

Initially various SPC blends with EVAc were obtained by melt-compounding in a co-rotating twin screw extruder with L/D ratio 16 (*Thermo ELECTRON CORPORATION PRISM TSE 16 TC*). Temperature profile during extrusion was in the range of 250 ^{o}C and 275 ^{o}C. SPC composition with 10 wt. % of EVAc was chosen for further treatment with MMT. Temperatures during extrusion were between 250 ^{o}C and 275 ^{o}C. In order to ensure better mixing of the components, systems were extruded for 2 times.

Specimens for quasistatic tensile, creep and instrumented *Charpy* impact tests were manufactured by using vertical injection molding machine (*Minijector Machinery Corp. Model 55*). Temperature profile during injection molding was 280-290-300 ^{o}C. Mold temperature was 70°C.

2.3. Testing

Tensile tests were performed at room temperature according to EN ISO 527-1&2 [3-4] by using *Zwick/Roell BDO FB-020FN* universal testing machine. Rate of the upper moving cross-head was 1 mm/min. for determination of Young's modulus and 50 mm/min. for determination of tensile characteristics at yield and break.

Charpy impact strength was determined at 23 +/- 2°C according to EN ISO 179-2 [5] by using instrumented *Zwick 5102* impact tester. Type A notched test specimens were used. Energy of the pendulum was 4 J.

Calorimetric properties were characterized by using *Mettler Toledo DSC1/200W* differential scanning calorimeter according to the manufacturer's manual. Measurements were made under N_2 flow. In order to eliminate the effects of thermal history samples of ~10 mg were heated, cooled and repeatedly heated in the temperature interval from 25 ^{o}C to 300 ^{o}C at a scanning rate of 10 ^{o}C/min.

Thermal resistance was characterized by using *Mettler Toledo TGA1/SF* thermogravimetric analyzer according to the manufacturer's manual. All measurements were made in oxidative environment (air); samples of ~10 mg were heated from 25 ^{o}C up to 800 ^{o}C at a scanning rate of 10 ^{o}C/min.

3 Results and discussion

SPC, used in this research was too brittle for any practical applications. Therefore it was modified with EVAc. The effect of EVAc modifier on its properties is shown in Fig. 1.
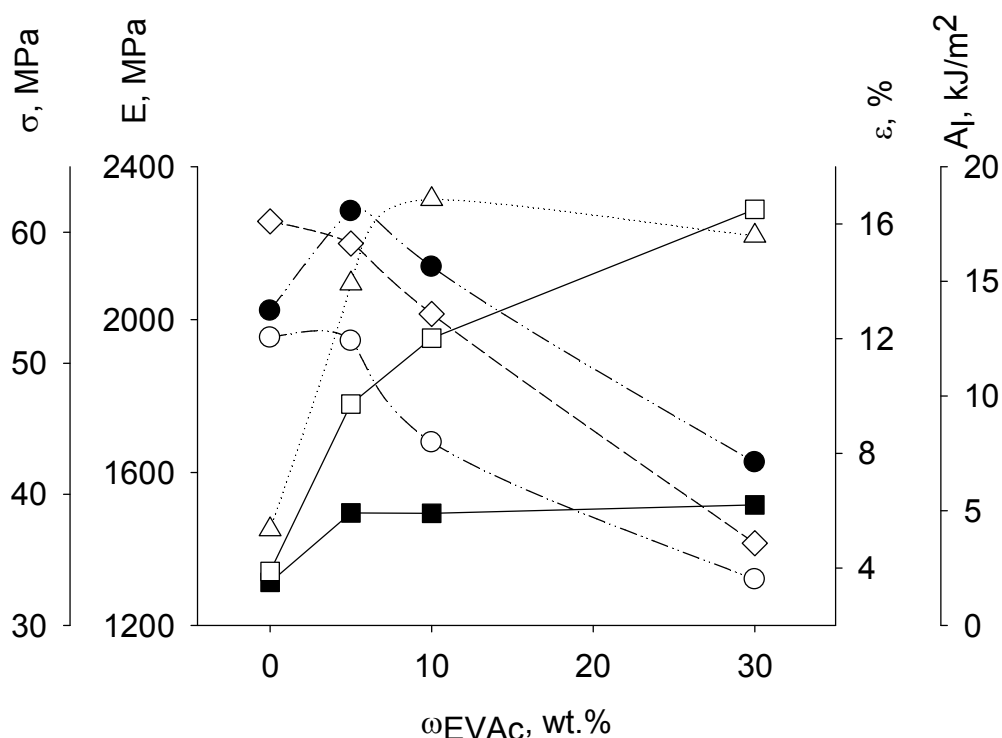

Figure 1. Young's modulus E ($\diamond$), maximum tensile strength σ_M ($\bullet$), relative elongation at maximum tensile strength ε_M ($\blacksquare$), tensile strength at break σ_B ($\circ$), relative elongation at break ε_B ($\square$) and *Charpy* impact strength A_I ($\triangle$) as functions of EVAc weight content ω_{EVAc}.

As one can see, addition of EVAc leads to considerable improvement of mechanical properties of SPC, especially at lower modifier content. The optimal content of EVAc modifier evidently is in the interval of 5-10 wt. %. In this region SPC/EVAc blends have highest values of tensile strength σ_M (increment by 14 % in comparison to neat SPC at EVAc content ω_{EVAc}=5 wt. %) and impact strength A_I (increment by 450 % in comparison to neat SPC at EVAc content ω_{EVAc}=10 wt.%), furthermore in this region growth rate of A_I and

relative elongations at maximum tensile strength and break (ε_M, ε_B) are the greatest. Reduced modification efficiency of EVAc at higher EVAc content most probably is attributed to the approaching phase inversion region, where mutual incompatibility between the blend ingredients start playing decisive role.

The results of creep of neat SPC and its composites are shown in Fig. 2 by dots, which are obtained by averaging the data of three parallel tests carried out under a constant tensile stress of 10 MPa.
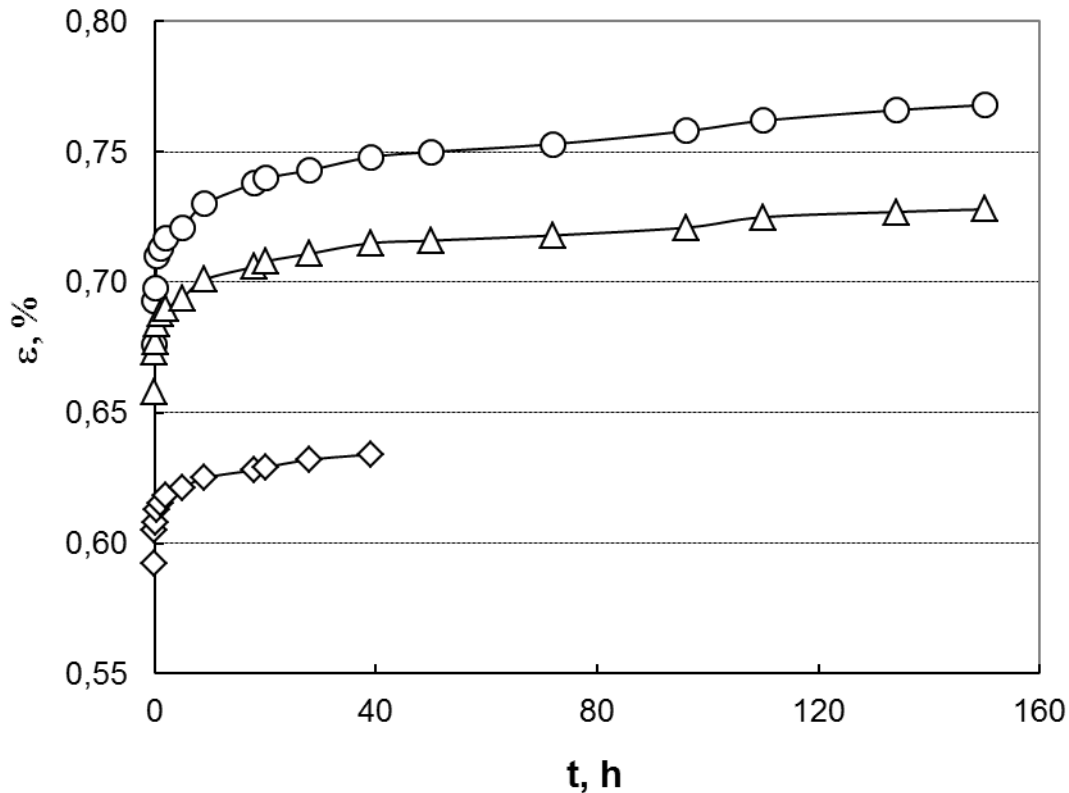

Figure 2. Creep strains ε of neat SPC ($\diamond$), SPC blend with 10 wt. % of EVAc ($\circ$) and SPC nanocomposite with 10 wt. % of EVAc and 2 wt. % of MMT ($\triangle$) as functions of time t.

The data obtained testifies that addition of 10 wt. % of EVAc considerably increases creep of the investigated materials.

For describing the experimental creep curves, we used the equation which is frequently called the *Findlay* power law of creep in the literature [6]

$$\varepsilon(t) = \varepsilon_0 + \varepsilon_c t^n \tag{1}$$

Under the action of a constant stress σ, the total strain $\varepsilon(t)$ in Eq. (1) consists of a time-independent instantaneous strain ε_0 and a creep strain growing with time in proportion to t^n, where t is time and n is a coefficient.

Expression (1) can be written as

$$\log(\varepsilon - \varepsilon_0) = \log \varepsilon_c + n \log t, \qquad\qquad (2)$$

which is the equation of a straight line with an inclination n in the axes $\log(\varepsilon - \varepsilon_0)$ and $\log t$.
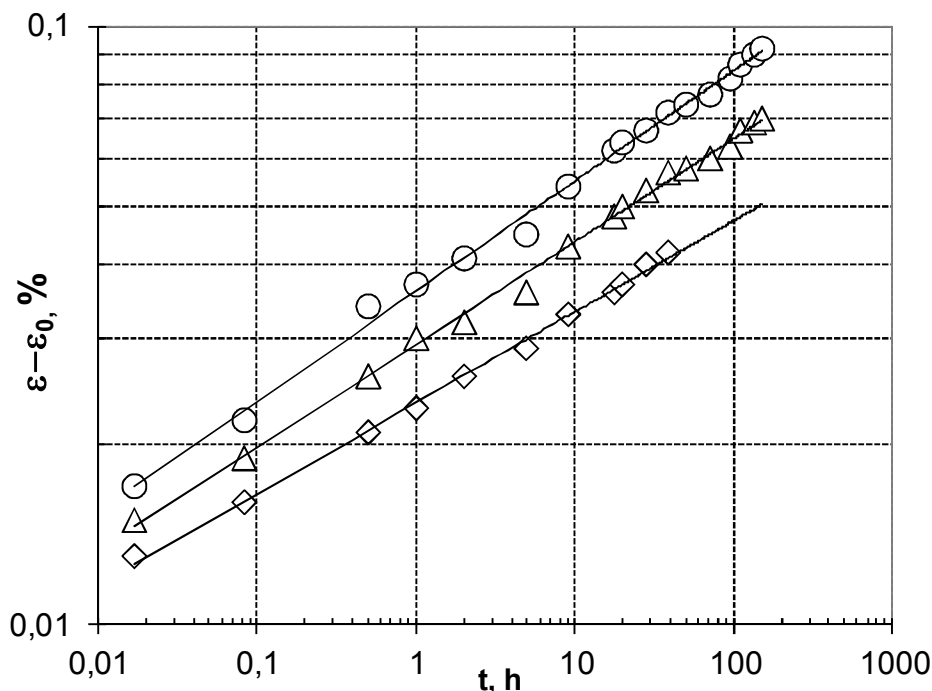

Figure 3. Creep strains of selected SPC/EVAc/MMT compositions (the total strains at a current instant of time ε minus the instantaneous ones ε_0) in logarithmic coordinates. Dots — experiment; lines — approximation according to Eqs. (1) and (2). Designations as in Figure 2.

Material	$\varepsilon_0 \cdot 10^2$	$\varepsilon_c \cdot 10^2$	n
SPC	0,592	0,023	0,149
SPC+10%EVAc	0,676	0,037	0,184
SPC+10%EVAc+MMT	0,658	0,030	0,172

Table 1. Values of the coefficients ε_0, ε_c, and n entering into Eq. (2), corresponding to creep at σ=10MPa

The experimental creep data in these axes are shown in Fig. 3, from which one can see that the experimental points are really arranged along straight lines. It should be noted that the time t in Eqs. (1) and (2) is regarded as a nondimensional ratio between the current time and a unit of time, assumed to be 1 h in our calculations. The straight lines in Fig. 3 are drawn by the method of least squares. The coefficients obtained are presented in Table 1. The average relative approximation error does not exceed 5%. Attention is drawn to the fact that introduction of EVAc has led to a marked increase in n, which describes the creep rate. The value of n for the SPC+10%EVAc exceeds that for the neat SPC by 23%.

Reduction of creep resistance, E, σ_M and σ_B, especially at higher ω_{EVAc} as shown in preceding figures most probably is attributed to the plastifying effect of EVAc on SPC, as confirmed also by DSC measurements, demonstrating decrease of glass transition temperature T_g of SPC by 7°C (from 143 °C to 136 °C) with rising of EVAc content from 0 to 30 wt. %.

Addition of EVAc modifier decrease also thermal stability of SPC. Thus for composition SPC+10%EVAc temperature of 10 % weight losses $T_{10\%}$, occurring close to 400°C, is ~12 % smaller than that of neat SPC.

In order to diminish negative effects of EVAc addition, various amounts of MMT are introduced in the composition SPC+10%EVAc. It has been already shown that addition of nanoclays allows increase of stiffness, strength, barrier and other characteristics of neat PC and EVA nanocomposites [7-15]. In these investigations, however, organically modified nanoclays and in most cases also additional compatibilizers are used. Organic modifier, used in nanoclays, however, can cause also some unwanted effects due to it decomposition, especially, if processed at high temperatures (generally above 200 ^{o}C). Decomposition of organic modifier in clays can lead to discoloration of polymers as well as reduction in modification efficiency, especially after multiple reprocessing steps. Therefore in this research attention is paid to the evaluation of the effect of less expensive unmodified MMT clays on the properties of secondary polymer systems.

The effect of MMT on the creep behaviour of SPC blend with 10 wt. % of EVAc is shown in Fig. 2 and Fig. 3 as well as Table 1. As one can see the effect of creep can be reduced to certain extent by addition of only 2 wt. % of MMT. At this nanofiller concentration the value of n is reduced by ~7% in comparison to unmodified SPC blend with 10 wt. % of EVAc.

Addition of MMT improves also thermal resistance of the investigated compositions. Thus $T_{10\%}$ is decreased by ca 5-6%, whereas greatest changes are observed at lower MMT weight contents (not exceeding 2 wt. %). One should mention here, that it is well known that improvement of thermal properties of polymer nanocomposites [16] is especially strongly influenced by the dispersion degree of the nanostructured filler in a polymer matrix. Evidently dispersion degree of MMT in SPS+10%EVAc matrix is considerable higher at lower nanofiller weight content.

Similarly addition of clay nanofiller improved quasistatic mechanical properties of the investigated SPC based systems, especially modulus of elasticity E and strength at break σ_B, which increased by ~10 % and ~15 % respectively. Simultaneously it should be mentioned that addition of nanoclay does not considerably reduce impact strength of the investigated compositions (A_I decrease from 18 to 15 kJ/m^2 at MMT wt. content 2 %) as it is characteristic for traditional microcomposites. Probably this could be attributed to certain interaction between the polymer matrix and MMT, as confirmed also by increment of T_g of SPC by a couple of degrees as well as narrowing of the melting peak of EVAc in respect to neat SPC upon introduction of MMT.

4. Conclusion

Results of the investigation testify that addition of certain amounts of EVAc (5-10 wt. %) allows reduce brittleness of SPC. Maximum tensile strength σ_M and impact strength A_I increase by 14 % (at ω_{EVAc}=5 %) and 450 % (at ω_{EVAc}=10 %) in comparison to neat SPC, respectively. Besides it up to EVAc concentrations of 10 wt. % growth rate of A_I and relative

elongations at maximum tensile strength and break (ε_M, ε_B) are the greatest. Decrease of Young's modulus E, σ_M, creep resistance and thermal stability $T_{10\%}$ of SPC blend with 10 wt.% of EVAc, associated with plastifying effect of the elastomer addition, can be compensated to some extent by addition of montmorillonite nanoclay (MMT), causing certain increase of these characteristics. This improvement could be attributed to certain interaction between the polymer matrix and MMT, as shown by increment of glass transition temperature T_g of SPC by couple of degrees as well as narrowing of the melting peak of EVAc in respect to neat SPC upon introduction of MMT.

Acknowledgement

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