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Recycled Polycarbonate Blend as Matrix for Development of Polymer Nanocomposite

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Summary: Secondary polycarbonate (SPC) is modified with various amounts (5, 10, 30 wt%) of ethylene vinyl acetate copolymer (EVAc) 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 increse by 14% ($\omega_{EVAc} = 5$ wt%) and 450% ($\omega_{EVAc} = 10$ wt%) in comparison to neat SPC, respectively. Addition of montmorillonite nanoclay (MMT) allowed further increase of elastic modulus E, strength and creep resistance of the investigated SPC blend with 10 wt% of EVAc.

Keywords: blends; clay; elastomers; mechanical properties; polycarbonates

Introduction

Thousands of tons of used polymer goods are introduced in the global waste stream annually. Post-consumer polymers therefore could serve as considerable source for the development of new materials, becoming more and more important in the light of depleting natural resources. Considering that secondary materials are usually with lower exploitation properties than primary ones, it is important to develop versatile modification system making possible to compensate this property drop, on the one hand, and enabling to assign specific features to the developed composite materials, on the other hand. In literature there are multiple evidences about embrittlement of the secondary polymers during their "life cycle",[1] requiring their toughening during recycling. Some of the materials used for these purposes with greater or smaller success are diene rubbers, ethylene copolymer elastomers, polyolefins, mixtures of rubbers with polyolefins and others.[2–6] One should, however, consider that addition of rubber or elastomer, negatively affects stiffness and strength of the base polymer. For increasing the stiffness and strength of the material one of the most widespread ways is its modification with anisometric inorganic fillers. In the literature there are many testimonials about use of layered silicates,[7] carbon nanotubes,[8] cellulose whiskers,[9] and other fillers for these purposes. Choosing the appropriate high-modulus modifier as well as determining optimal elastomer/nanofiller ratio could lead to the development of the multifunctional materials with unique set of properties. Consequently the aim of this research was investigation of the effects of ethylene vinyl acetate copolymer modifier and layered silicate nanofiller on the technological and exploitation properties of secondary polycarbonate (SPC).

Experimental Part

SPC was derived from DVD scarp. In order to aid removal of aluminium and lacquer admixtures DVD scrap was treated with alkaline solution. After alkaline treatment purified polycarbonate was washed with distilled water until washing solution showed neutral reaction. Before further processing SPC was dried in a convection oven at 105 °C for 24 hours. Ethylene vinyl

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acetate copolymer modifier with vinyl acetate content of 26% (EVAc: *11507-375*), was used as elastomeric modifier. Commercial montmorillonite (MMT: Dellite LVF by Laviosa Chimica Mineraria S.p.A.) was used as inorganic modifier.

SPC based composites containing various amounts of EVAc (in the concentration range up to 30 wt%) and MMT (in the concentration range up to 5 wt%) were obtained by melt-compounding in a co-rotating twin screw extruder.

Specimens for quasistatic tensile, creep, instrumented Charpy impact tests as well as differential scanning calorimetry measurements were manufactured by using vertical injection moulding machine.

Tensile tests were performed at room temperature according to EN ISO 527. 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. Tensile creep tests were carried out at room temperature under a constant tensile stress of 10 MPa. Charpy impact strength was determined at room temperature for notched test specimens according to EN ISO 179. Calorimetric investigations were made from 25 °C up to 250 °C at test speed 10 °C/min. Multiple scans were performed in order to exclude the effects of thermal history.

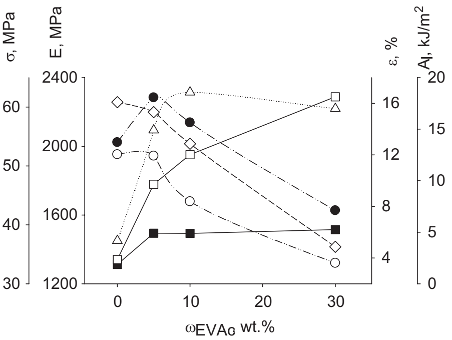

Figure 1.
Young's modulus E (◇), maximum tensile strength σ_M (●), relative elongation at maximum tensile strength ε_M (■), tensile strength at break σ_B (○), relative elongation at break ε_B (□) and Charpy impact strength A_I (△) as functions of EVAc weight content ω_{EVAc}.

Results and Discussion

SPC, derived in this research, appeared to be too brittle for practical applications. Therefore the effect of EVAc modifier on its properties was initially evaluated. As shown in Figure 1, addition of EVAc modifier leads to considerable improvement of its mechanical properties, especially at lower EVAc content. The optimal content of EVAc modifier seems to be 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 $\omega_{EVAc} = 5$ wt%) and impact strength A_I (increment by 450% in comparison to neat SPC at EVAc content $\omega_{EVAc} = 10$ 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 Figure 2 by dots,

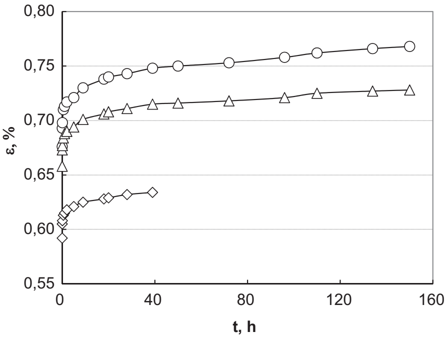

Figure 2.
Creep strains ε of neat SPC (◇), SPC blend with 10 wt% of EVAc (○) and SPC nanocomposite with 10 wt% of EVAc and 2 wt% of MMT (△) as functions of time t.

which are obtained by averaging the data of three parallel tests carried out under a constant tensile stress of 10 MPa.

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:[10]

$$\varepsilon(t) = \varepsilon_0 + \varepsilon_c t^n \qquad (1)$$

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:

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

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

The experimental creep data in these axes are shown in Figure 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 Figure 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%.

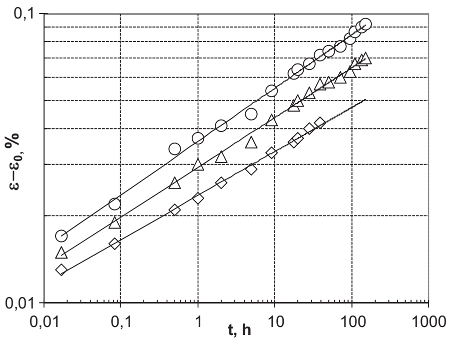

Figure 3.
Creep strains of selected SPC/EVAc/MMT compositions (the total strains at a current instant of time ε minus the instantaneous ones ε_0) in logarithmic coordinates. Dots — experiment; lines — approximation according to Eqs. (1) and (2). Designations as in Figure 2.

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

Material	$\varepsilon_0 \cdot 10^2$	$\varepsilon_c \; 10^2$	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

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%.

It has been shown that addition of nanoclays allows increase of stiffness, strength, barrier and other characteristics of neat PC and EVA nanocomposites.[11–19] 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 °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 great attention should be paid to the evaluation of the effect of less expensive unmodified montmorillonite 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 Figure 2 and Figure 3 as well as in 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. 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 2 wt% MMT content) 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.

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 $\omega_{EVAc} = 5\%$) and 450% (at $\omega_{EVAc} = 10\%$) 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 and creep resistance 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 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.

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