

Recycling and Reuse of Plastics Contained in Waste from Electrical and Electronic Equipment (WEEE)

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Abstract

In the present research, blending of polymers used in electrical and electronic equipment and, more specifically, blending of acrylonitrile-butadiene-styrene terpolymer (ABS) with polycarbonate (PC) or polypropylene (PP), was performed in a twin-screw extruder, in order to study the effect on the mixture properties and to establish a procedure for appropriate waste management. The addition of PC in ABS matrix seemed to increase its thermal stability. Also, the addition of PP in ABS matrix facilitates its melt processing, whereas the addition of ABS in PP matrix improves its mechanical performance. Moreover, upgrading of the above blends by incorporating 2 phr organically modified montmorillonite was attempted. The prepared nanocomposites exhibit greater tensile strength, elastic modulus and storage modulus, as well as, higher melt viscosity, compared to the unreinforced blends. The incorporation of montmorillonite nanoplatelets in PC-rich ABS/PC blends turns the thermal degradation mechanism to a two stages process. Alternatively to mechanical recycling, energy recovery from the combustion of ABS/PC and ABS/PP blends was estimated by measuring the gross calorific value (GCV). Comparing the investigated polymers, PP presents the higher gross calorific value, followed by ABS and then PC. The above study allows a rough evaluation of various methodologies for treating plastics from WEEE.

Key words: acrylonitrile-butadiene-styrene terpolymer, blending, calorific value, extrusion, organoclay, polycarbonate, polypropylene, WEEE

Introduction

With continuous growth for more than 50 years, global production of plastics in 2012 rose to 288 million tones – a 2.8% increase compared to 2011. However in Europe, in line with the general economic situation, plastics production decreased by 3% from 2011 to 2012 reaching 57 million tones. In 2012, demand in Europe decreased by 2.5% and reached 45.9 million tones. The electrical and electronic equipment sector covered the 5.5% of the european plastics demand in 2012.

Furthermore, 25.2 million tones of plastics ended up in the waste stream in 2012. That year, the landfill disposal of plastics was 38.1% (9.6 Mtone) and the plastics recycling and energy recovery reached 61.9% (15.6 Mtone). For specialty plastics, the recycling was 26.3% (6.6 Mtone) and the energy recovery was 35.6% (8.9 Mtone). The total recovery of plastics increased by 4% and this growth shows a continuously strong trend. At the same time, there was a reduction of 5.5% of landfilled plastics, which also shows a general positive development. Collection for mechanical recycling shows a growth of 4.7%, while feedstock recycling even on a lower level of 86 thousand tones increased by 19.4%. Energy recovery also increased by 3.3%. Since 2009, the total amount of post-consumer plastics waste has been increasing in Europe but since 2011 it

has remained at more or less the same level with 25.2 million tones generated in 2012 [plasticseurope].

The waste coming from WEEE represents an about 8% of the total municipal waste internationally [The Economist, 2005]. In European Union, 12-20 kg WEEE/habitant is produced each year and their overall, annual production varies between 6.5-7.5 million tones [HSWMA], whereas in Greece, 170.000 tones WEEE are produced per year.

In Greece, the annual aim until 2015 is the collection of 4 kg WEEE/habitant. After 2016, the minimum yearly percentage of WEEE collection must be the 45% of the average amount of EEE disposed in the market during the previous three years. Since 2019, this percentage will be increased at 65%. In 2012, 36021 tones or 3.33 kg/inhabitant of WEEE, were collected from the domestic sector and from them, 33411 tones were further processed [EOAN]. During 2005-2013 (1st semester), the 87.73% of EEE was treated, whereas the 12.27% was led to landfill in Greece [electrocycle].

The WEEE are consisted mainly of iron and steel (47.9%), whereas the polymers hold the second position in the composition of WEEE, as they are met at 20-21% [HSWMA]. The polymers and plastic technical components used by the involved industries are estimated to amount to some 15-20 % of the total value of plastics used in Europe, or about 60-80 billion € [plasticsconverters].

The materials used for technical parts in the above industries are very numerous, and often very advanced. The most common plastics are polystyrene, acrylonitrile-

butadiene-styrene terpolymer (ABS), polycarbonate (PC) and blends of them. These are widely used for equipment housings and enclosures and, in the case of PC, for optical storage media (CDs). Polybutylene terephthalate (PBT) is growing fast, especially for connectors. Polyethylene (PE-LD and PE-HD) and cross-linked polyethylene are used increasingly in applications such as cable sheathing, as an alternative to polyvinyl chloride (PVC). Thermosetting resins also play a major part in E&E products [plasticsconverters].

There are several researches dealing with the recycling of ABS/PC blends. Eguiazábal and Nazábal (1990) concluded that recycling of PC/ABS blends produces a change in the rubbery phase of ABS as it becomes crosslinked/oxidized. The effect of reprocessing in the properties has two stages. After one or two processing cycles all the high-strain mechanical properties show only a slight change in the usual condition. However, after more than two processing cycles, the decrease in these properties is very significant. Also, Balart et al. (2005) investigated the effect of previous degradation and partial miscibility of ABS/PC blends to their mechanical performance. Liang and Gupta (2002) mixed virgin ABS with virgin and recycled PC and examined the rheological and mechanical behavior of the blends. Khan et al. (2007) concluded that recycled polycarbonate can be used as an additive for virgin or recycled ABS, as a mean of giving flame resistance to ABS in high-value applications. Liu and Bertlsson (1999) blended recycled ABS and PC/ABS (70/30) with a small amount of methyl-

methacrylate-butadiene-styrene core-shell impact modifiers and observed better impact properties for the mixture than any of its individual components. Mahanta et al. (2012) studied the effect of the addition of two compatibilizers (maleic anhydride-grafted polypropylene and solid epoxy resin) and the effect of incorporating organically modified nanoclays to the thermomechanical properties of recycled ABS/PC blends.

The aim of this research was the treatment of blends used in electrical and electronic equipment by incorporating to them organically modified montmorillonite, in twin screw extruder or by recovering the energy which is liberated from their combustion.

Materials and methods

Materials

The terpolymer poly(acrylonitrile-butadiene-styrene) (ABS) was supplied by BASF, under the trade name Terluran[®] GP-35 and polycarbonate (PC) by Bayer under the trade name Makrolon[®] 2805. The polypropylene (Ecolen[®] HZ40P) was donated by Hellenic Petroleum. Commercial montmorillonite clay, Cloisite[®] 30B was purchased by Rockwood Clay Additives GmbH.

Preparation of blends

ABS/PC and ABS/PP blends with compositions 100/0, 70/30, 50/50, 30/70 and 0/100 w/w were prepared by melt mixing, in a co-rotating twin-screw extruder, with

L/D=25 and 16 mm diameter (Haake PTW 16). All materials were dried before processing, in order to avoid hydrolytical degradation. After melt mixing, the obtained material in the form of continuous strands was granulated using a Brabender knife pelletizer.

Characterization

The melt flow index (MFI) was determined in a Kayeness Co. model 4004 capillary rheometer at 260 °C with 2.16 kg load for ABS/PC blends and at 230 °C with 2.160 kg load for ABS/PP blends.

Mechanical testing of the injection molded specimens was run according to ASTM D 638, in an Instron tensometer (4466 model), operating at grip separation speed of 50 mm/min. Injection moulding was performed with an ARBURG 221K ALLROUNDER machine.

DMA measurements were performed in an Anton Paar analyzer, MCR 301, at a frequency of 1 Hz, with a heating rate of 5 °C/min between -120 to 200 °C for ABS/PC blends and between -120 to 160 °C for ABS/PP blends, in N₂ atmosphere. Samples prepared by injection molding were studied by this technique.

TGA measurements were accomplished in a thermal gravimetric analyzer (Mettler Toledo, TGA-DTA) from 25 to 800 °C for ABS/PC blends and from 25 to 600 °C for ABS/PP blends, at rate of 10 °C/min, in N₂ atmosphere.

Results and Discussion

From Fig. 1, it is observed that the incorporation of organoclay into the ABS/PC blends results in an increase of the system's viscosity. Confinement of polymer chains motion, caused by the organoclay platelets and tactoids in the ABS/PC matrix and the interactions between the polar groups of ABS and oxygen containing groups of Cloisite 30B, may be responsible for this behavior (Aalaie 2007). According to the bars shown in Fig. 2, ABS exhibits higher viscosity than PP and ABS/PP blends presents melt behavior closer to that of PP. Moreover, the melt viscosity of ABS/PP blend drops by increasing PP content and tends to increase by incorporating organically modified montmorillonite.

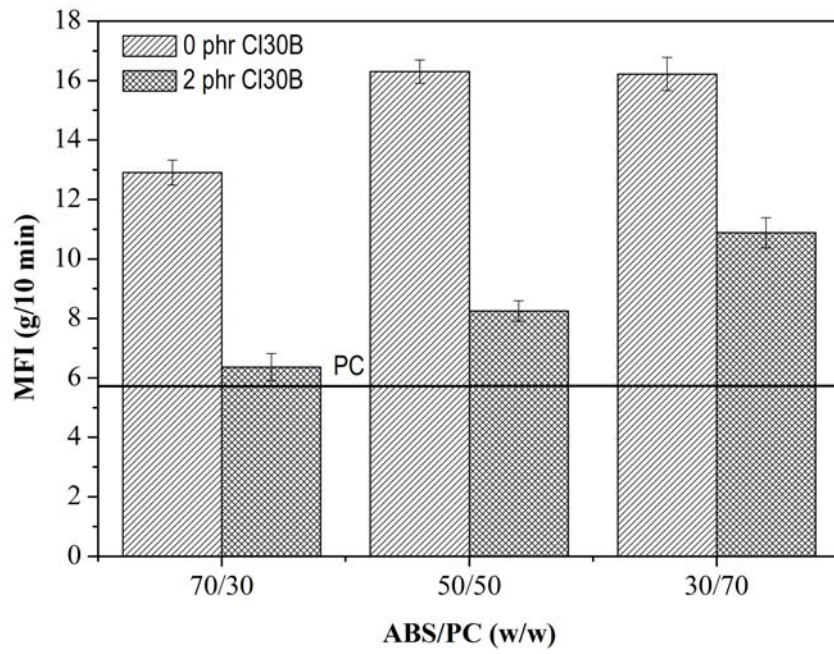


Figure 1: Melt Flow Index (MFI) of ABS/PC blends and their nanocomposites at 260 °C, with a load of 2.160 kg.

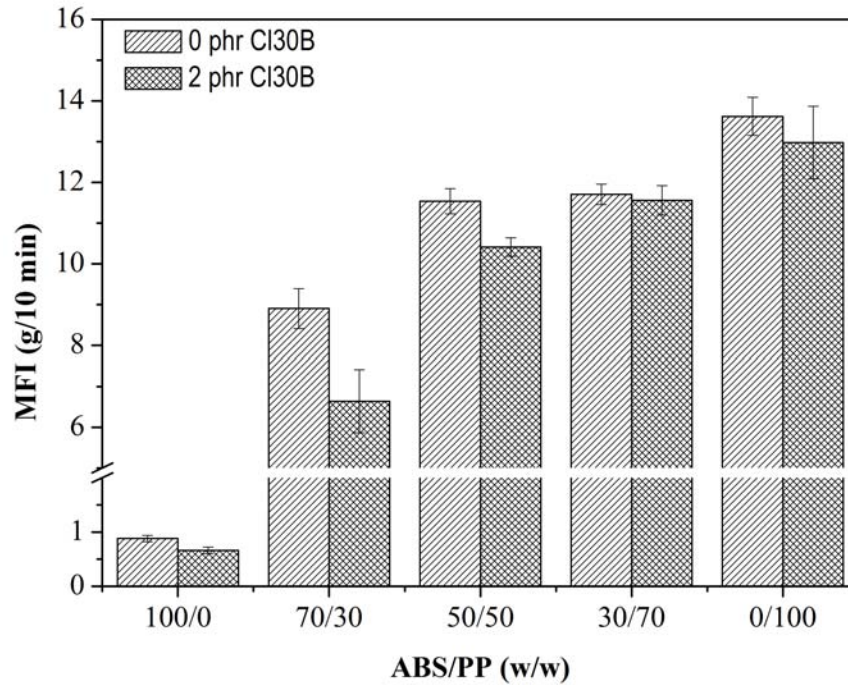


Figure 2: Melt Flow Index (MFI) of ABS/PP blends and their nanocomposites at 230 °C, with a load of 2.160 kg.

Regarding the mechanical properties, the tensile strength of ABS is increased by the addition of PC and this increase seems to follow the rule of mixture (Fig. 3). On the other hand, the tensile strength of ABS is reduced significantly by the addition of PP. The tensile strength of ABS/PP blends is closer to that of PP.

As far as the Young's modulus is concerned (Fig. 4), a synergic action between ABS and PC is observed. The highest improvement of Young's modulus is recorded for composition 50/50 w/w. A significant enhancement of modulus is clear, since the

contribution of PC leads to an increase of the rigidity of ABS and limits the plasticizing effect of the rubber phase. In ABS/PP blends, the Young's modulus is decreased as the PP concentration is increased.

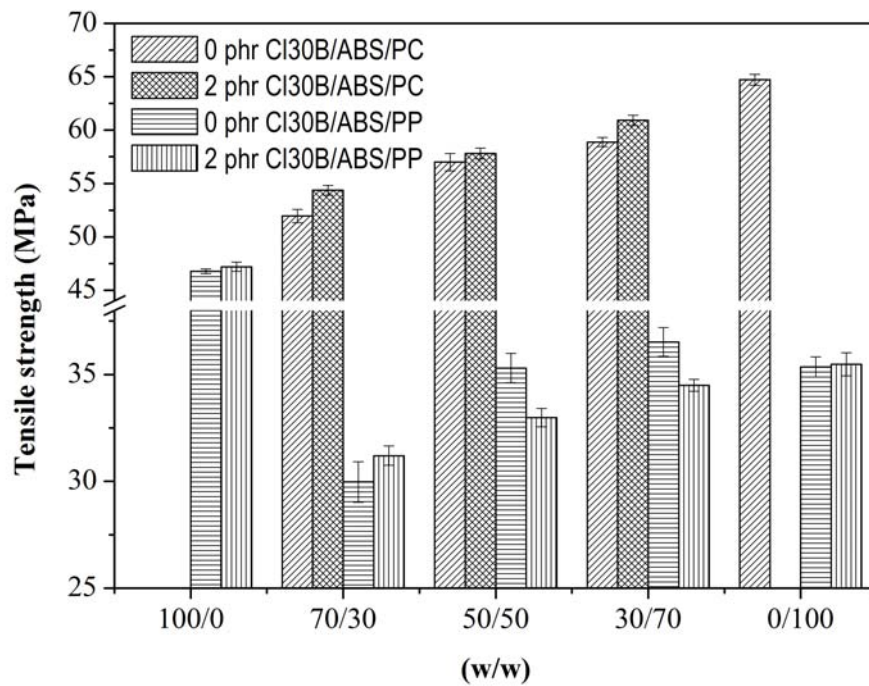


Figure 3: Tensile strength of ABS/PC and ABS/PP blends and their nanocomposites.

The incorporation of nanofillers in ABS/PC blends seems to cause a slight increase in the tensile strength. In ABS/PP blends, the addition of organoclay increases the tensile strength in ABS-rich blends, whereas it reduces this property at PP-rich blends.

On the other hand, the addition of nanofiller significantly improves the Young's modulus of the examined blends.

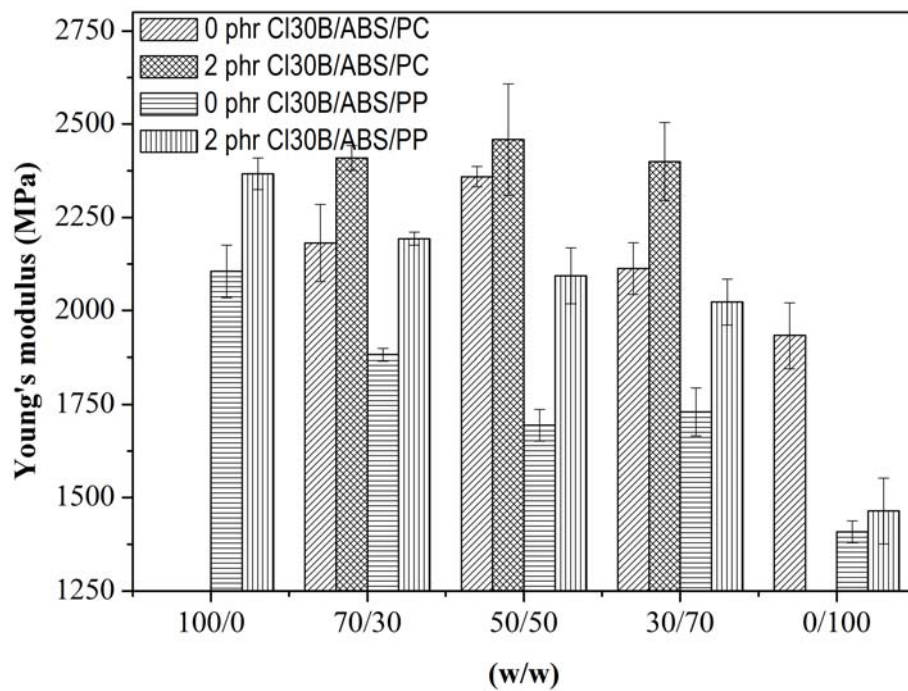


Figure 4: Young's modulus of ABS/PC and ABS/PP blends and their nanocomposites.

The increase of tensile strength can be attributed to the strong adhesive bonding at the filler–matrix interface, which facilitates the stress transfer from the matrix to clay. The enhancement of stiffness is interpreted by the higher modulus of organically modified clay and by the low deformability of polymeric chains penetrating the silicate galleries (Lim 2010). Xiang-Fang et al. (2009) prepared PP/ABS/OMMT

nanocomposites and recorded a small decrease of their tensile strength and an increase of the tensile strain and modulus, in comparison with unreinforced blends. The van der Waals force played a large role on the overall interaction between the OMMT particles and the PP/ABS matrix and formed an interface layer due to physical entanglement. Thus, the faint effects between layers hardly resisted the load, resulting in cracks in the matrix and decreased strength.

The storage modulus, G' , is one of the most important parameters determined by DMA, relevant to the elastic response during the sample's deformation. From Fig. 5 it is observed that the G' of ABS drops sharply with increasing temperature, starting from the temperature range of $\sim 70^\circ\text{C}$ and approaches zero at 110°C , while PC drops sharply at $\sim 130^\circ\text{C}$ and approaches zero at 150°C . A synergistic effect is observed for ABS/PC blends and the greatest value is recorded for 50/50 w/w composition.

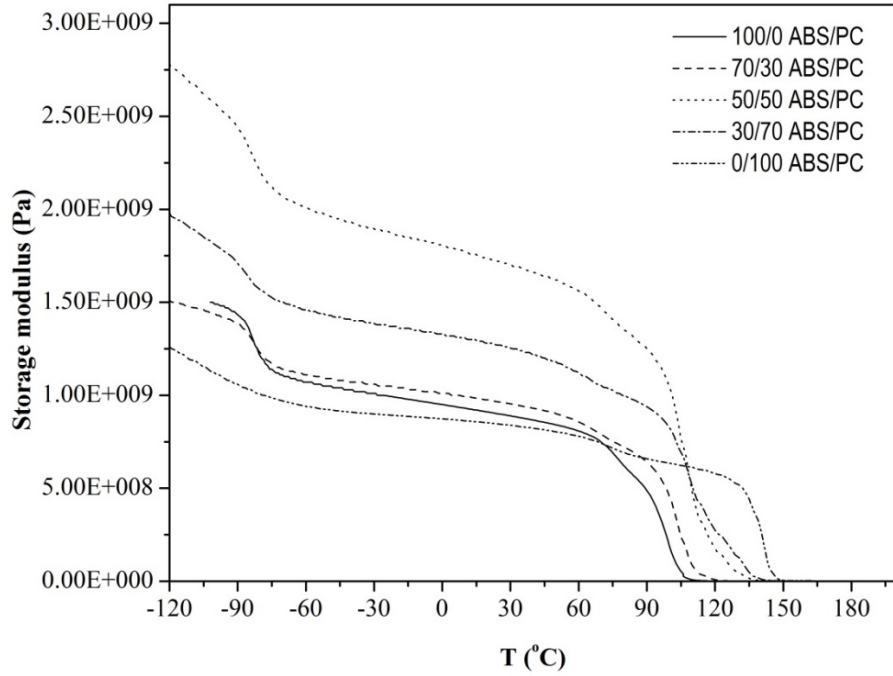


Figure 5: Storage modulus versus temperature of ABS/PC blends.

The storage modulus, G' , of PP starts to drop at $\sim(-20)$ °C and then sharply decreases approaching zero at 150 °C (Fig.6). A change in the behavior of storage modulus of ABS/PP blends is recorded at about 10 °C. In particular, below 10 °C, the ABS/PP blends present higher storage modulus than that of neat ABS and lower than or equal to that of neat PP. On the contrary, over 10 °C, the G' of ABS/PP blends is higher than that of neat PP and lower than that of neat ABS. A return to the initial behavior can be observed at 110 °C.

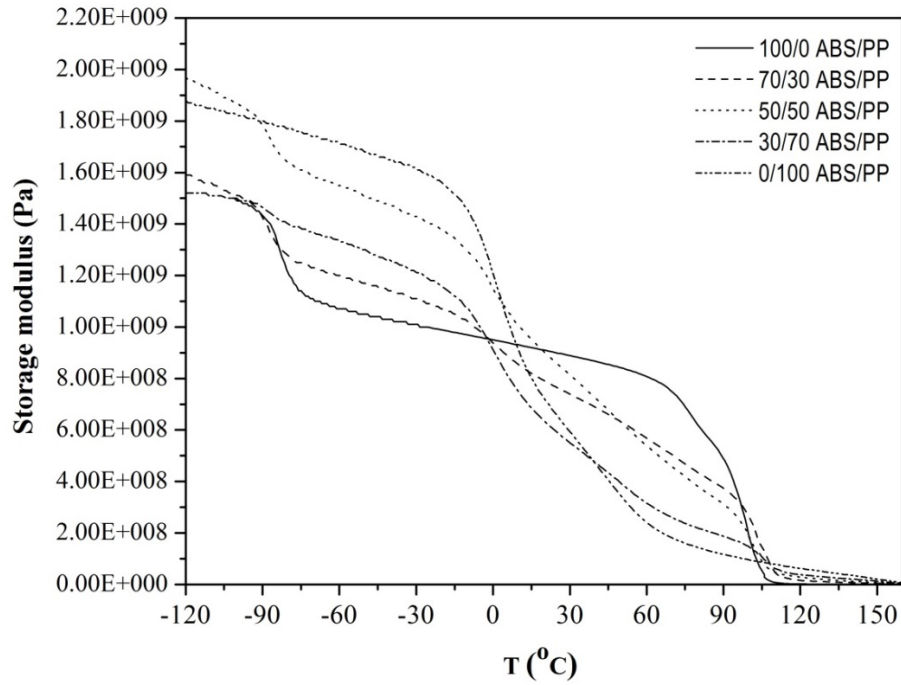


Figure 6: Storage modulus versus temperature of ABS/PP blends.

From Fig. 7, it can be seen that the incorporation of nanoparticles leads to an impressive increase of storage modulus, in comparison with this corresponding to unreinforced blends. Cai et al. (2010) found that the incorporation and efficient dispersion of silicate clays increases remarkably the storage modulus of ABS nanocomposites.

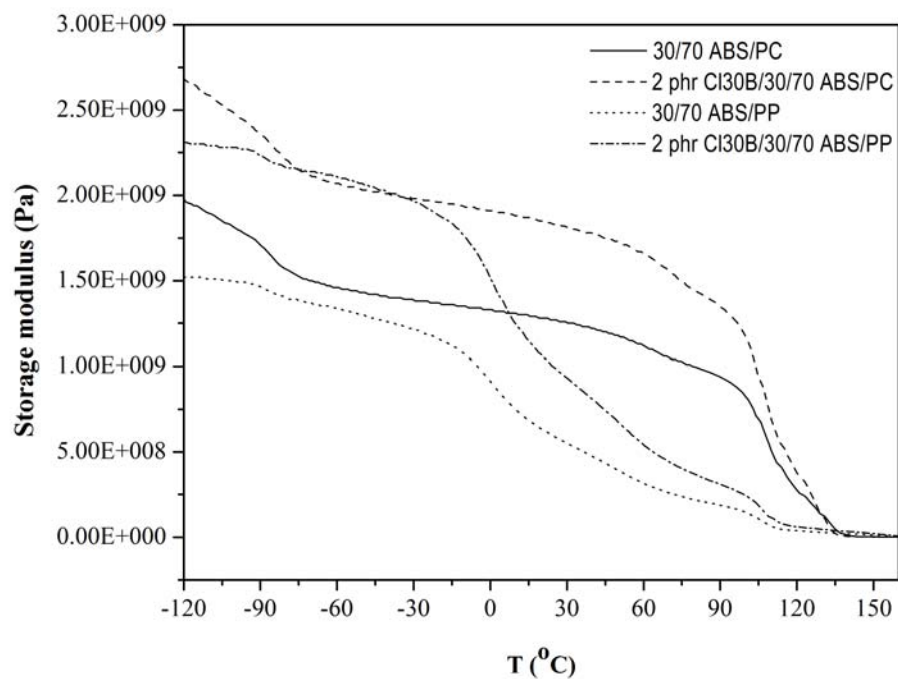


Figure 7: Storage modulus versus temperature of ABS/PC and ABS/PP blends and their nanocomposites at 30/70 w/w.

Regarding the thermal stability, it increases with the following order: ABS<PP<PC. In ABS/PC blends, the thermal degradation mechanism takes place in one stage (Fig. 8), whereas in ABS/PP blends it involves two stages (Fig. 9).

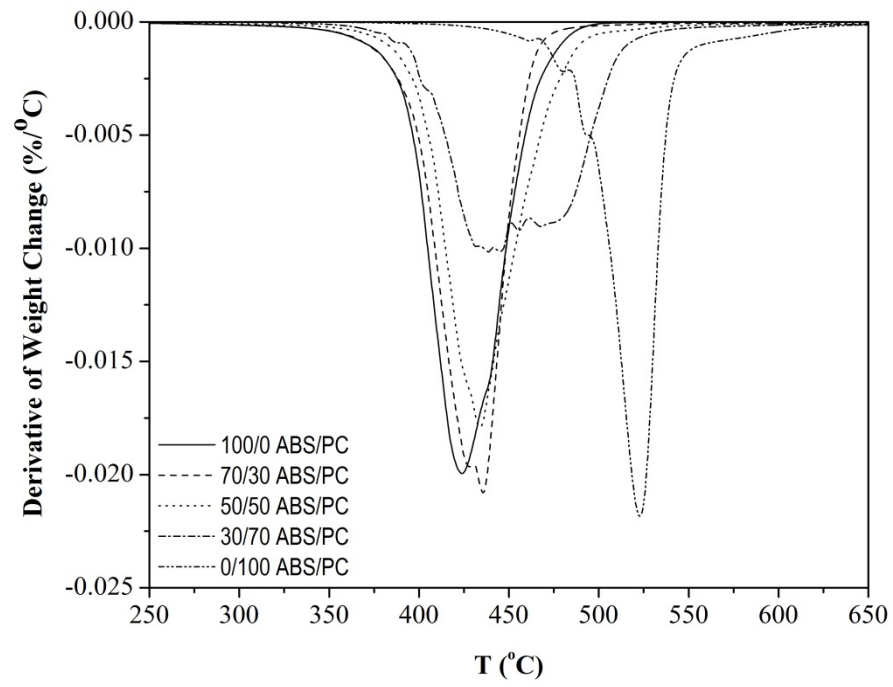


Figure 8: Derivative of weight change versus temperature for ABS/PC blends.

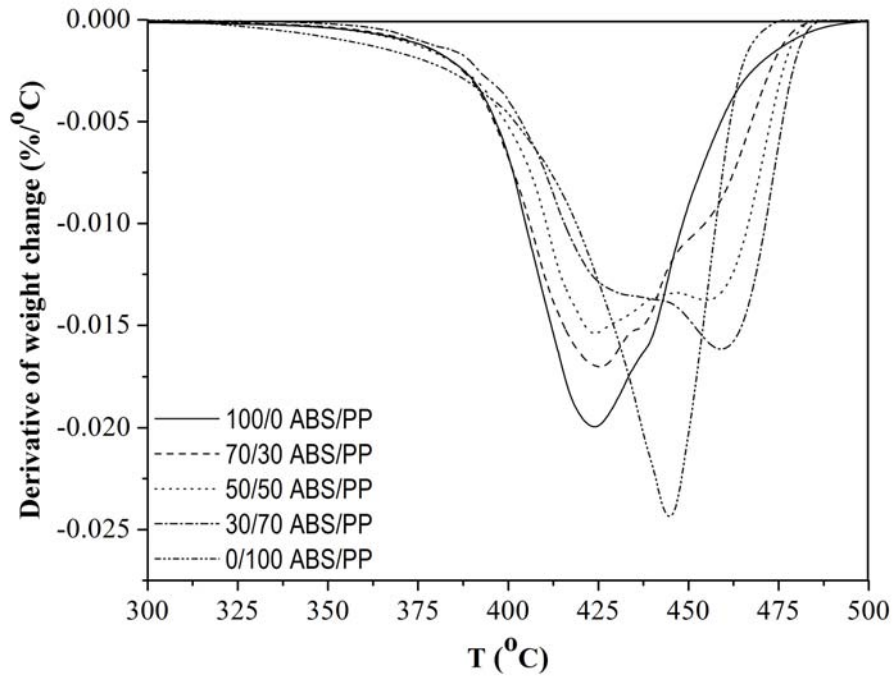


Figure 9: Derivative of weight change versus temperature for ABS/PP blends.

However, the incorporation of clay platelets in PC-rich ABS/PC blends turns the thermal degradation mechanism to a two stages process (Fig. 10), creating a “broadening” of the peak towards the high temperatures area in 50/50 w/w and splitting the degradation peak in 30/70 w/w ABS/PC blend. Wang et al. (2003) observed that the addition of OMMT to PC/ABS alloys causes the decomposition of alloys at two stages. Therefore, the OMMT seems to inhibit thermal degradation of the PC phase, which might be due to the creation of new paths of the degradation reaction and to the formation of a protective layer of nanoclay at the ABS/PC interface.

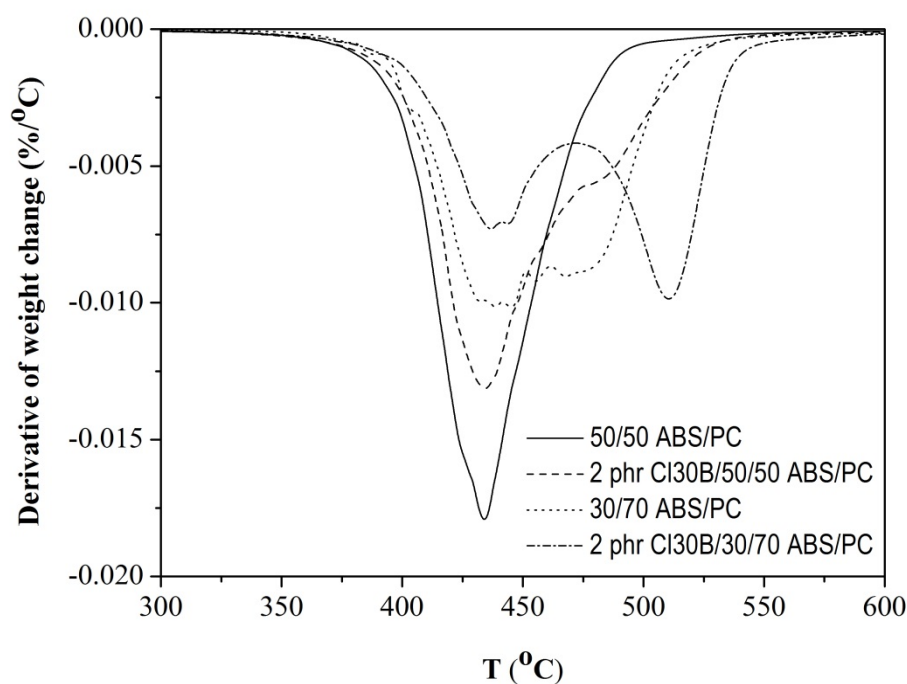


Figure 10: Derivative of weight change versus temperature for 50/50 and 30/70 w/w ABS/PC blends and their nanocomposites.

As PC concentration in ABS/PC blends increases, the thermal characteristics are improved, but this dependence is not consistent with the “rule of mixtures”. The incorporation of organoclay nanofillers does not essentially affect the onset degradation temperature (T_{onset}) and the temperature of maximum degradation rate (T_{peak}), but enhances the resistance of polymers against thermal degradation, leading to higher values of char residue. Wang et al. (2002) discovered that after pyrolysis carbonaceous-

silicate char builds up on the surface during burning; this insulates the underlying material and prevents the escape of the volatile products generated during decomposition.

In ABS/PP blends, the incorporation of nanofiller does not essentially affect the T_{onset} . Furthermore, it tends to increase the T_{peak} corresponded to ABS phase in ABS-rich ABS/PP blends, whereas decreases slightly the T_{peak} corresponded to PP phase in PP-rich ABS/PP blends.

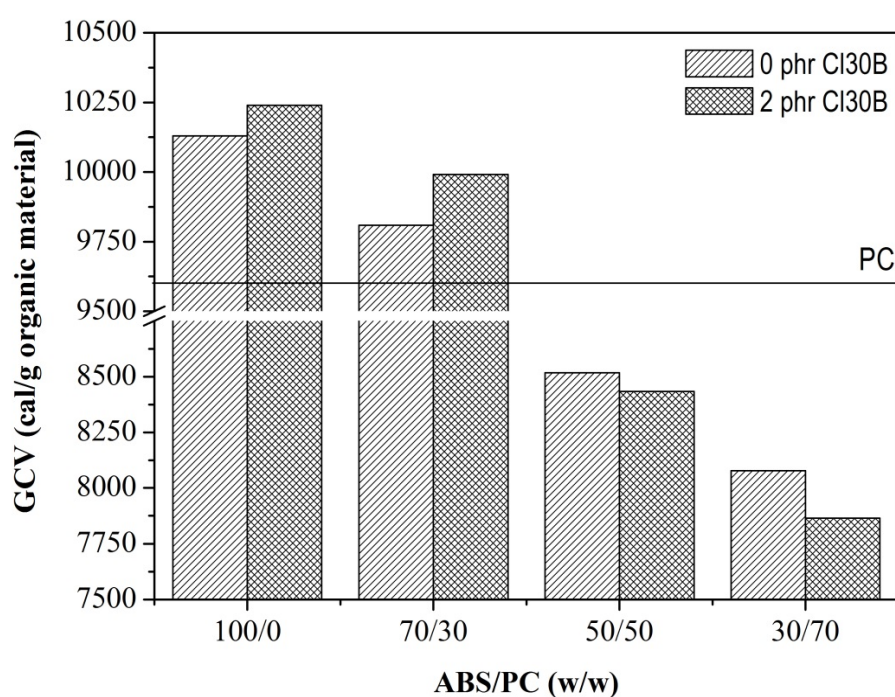


Figure 11: Gross calorific value of ABS/PC blends.

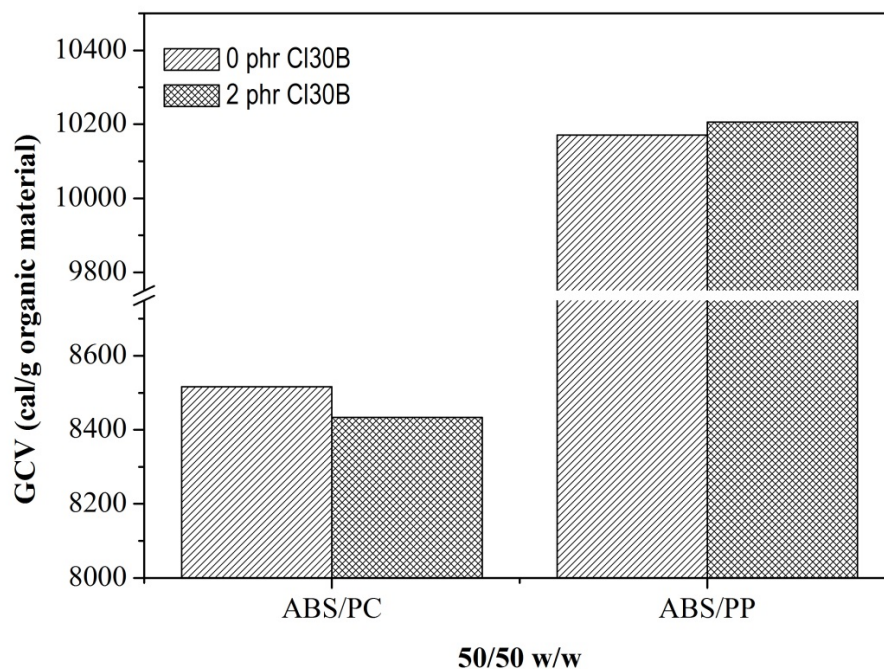


Figure 12: Gross calorific value of 50/50 w/w ABS/PC and ABS/PP blends and their nanocomposites.

Regarding combustion properties, polypropylene presents the higher gross calorific value (11377 cal/g) and then follows ABS terpolymer (9539 cal/g), whereas the last is the polycarbonate (7694 cal/g). According to Fig. 8, as the PC content in ABS/PC blends increases, a reduction of gross calorific value (GCV) is observed, due to the poor burning characteristics of PC as compared with ABS.

The incorporation of organically modified montmorillonite to ABS and ABS/PC 70/30 w/w blend increases slightly their gross calorific value up to 2 phr. However, in

blends with high PC content (ABS/PC 50/50 and 30/70 w/w blends) a decrease occurs as the clay loading increases. In 50/50 w/w ABS/PP blend, the addition of nanoparticles tends to increase its gross calorific value.

Conclusions

The blending of polymers used in WEEE is an appropriate procedure for their common management, which eliminated the time consuming and costly phase of sorting. Regarding the effect on properties, the addition of PC in ABS matrix improves its thermomechanical properties. Furthermore, the addition of PP in ABS matrix decreases its melt viscosity making easier the processing and increases its thermal stability, whereas the addition of ABS in PP matrix improves its mechanical behavior.

The incorporation of organically modified montmorillonite to ABS/PC blends leads to an increase of their melt viscosity, improves significantly the Young's modulus and the storage modulus and, moreover, protects the PC phase during the thermal decomposition. In ABS/PP blends, the addition of nanoplatelets causes a slight increase of their melt viscosity, increases sensibly the elastic and the storage modulus and tends to increase the T_{peak} corresponded to ABS phase in ABS-rich ABS/PP blends, whereas it slightly decreases the T_{peak} corresponding to PP phase in PP-rich ABS/PP blends. It seemed, therefore, that the incorporation of organically modified clay to WEEE blends is a promising technique for their upgrading.

On the other hand, the investigated blends present lower gross calorific value in comparison with the mean fraction of polymers, used for energy recovery by burning and therefore is not a recommended treatment.

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