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Electrical and thermal properties of recycled polypropylene-carbon black composites

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Summary

In the last decade the recycling of different types of waste has become a worldwide necessity. A large amount of polymeric material is generated in the health care sector and nowadays, due to a lack of technology and stiff government regulations, most of this material is incinerated thereby causing other type of problems. In this paper, a study of the degradation and possible reutilization of the polypropylene used in the fabrication of disposable syringes is done. The main idea is to use this polymer as the matrix and carbon black as the filler in an electrically conductor composite with proper a thermal properties for applications such as a heating material.

Introduction

Post-consumer plastics waste has become the focus of legislation and environmental concerns. The major polymeric component of these plastic waste streams are polyethylene, polypropylene, styrenics, polyvinyl chlorides and polyethylene terephtalate. Separation of the plastic waste into a particular single polymeric type by various methods is costly and complete sorting is economically nonviable and sometimes impossible. In particular, polymeric waste material produced in the health care system is considered by government regulations, as hazardous material, thereby, they cannot be disposed off as in any municipal waste dump site nor recycled. Some of these products used in the health care system are manufactured using high quality polymeric resins and they are, from the recycling point of view, excellent candidates if a disinfecting process is used. Different companies in several countries have developed systems to perform a selection process and subsequently they sanitize the material in order to use hem. One advantage in the utilization of these materials from the health sector is that sorting and collection is performed on site, thereby resulting in a considerable cost reduction.

In this paper, we explore the use of polypropylene obtained from disposable syringes together with carbon black in the production of a composite material with specific thermal properties. Such composites could be used as house-heating sources in template and cold climates. The properties of the disposables-syringe-polypropylene-carbon black composites are compared with those of a composite material produced using pristine polypropylene and carbon black. The effect of several cycling processes on the matrix properties is also studied.

Experimental

Two types of polypropylene were used in this study, pristine extrusion grade polypropylene from PEMEX and recycled polypropylene. Carbon black was Black Pearls 2000 obtained from Cabot Corporation. Its surface area was 254 m^2/g and the primary particle size was 30 nm and a density of 0.27 g/cm^3.

The carbon black/polypropylene conductive composites were prepared using a Brabender bambury type mixer Model PLE330 at a temperature of 200 °C. The mixture process was carried out in three stages and, for each of them, the speed and time of mixture was different. For the first stage, they were 10 rpm for 2 minutes, which were increased to 40 rpm and kept for two minutes. For the last stage they were further increased to 15 rpm for 15 minutes. Prior to mixing, the carbon black was dried in an oven at 120 °C for 24 hours to eliminate any trace of humidity and to avoid the formation of lumps. The materials obtained were laminated using a 12 x 12 cm square-shaped mold to a thickness of 0.7 mm. After filling the mold, the temperature was increased in the laboratory press (Carver Laboratory Press, model C) to 200 °C until thermal equilibrium was achieved. The load was applied in several steps, from an initial value of 454 Kg for 4 minutes, up to 1360 Kg for 4 minutes and then, to 2268 Kg for 10 minutes. At this point, the plate was cooled using circulating water while the load was still applied to avoided any residual stress deformation. The carbon black content in the composite was varied from 0 % (w/w) to 30 % (w/w).

For the electrical and thermal characterization, 60 mm long and 10 mm wide samples were cut from the laminates. The electrical resistivity of the carbon black/polypropylene composites was measured using a ohmmeter. A special fixture was devised to clamp the specimen to the power supply. To insure good electrical contact, the ends were coated with a silver paint. The temperature change was recorded using a J-type thermocouple attached to the specimen surface. An adiabatic chamber was constructed using a thermal insulating material and cooled to an initial temperature of -40 °C.

The mechanical properties of the composite were determined using an Instron universal testing machine, model 1125 equipped with a 50 Kg load cell, a crosshead speed of 20 mm/min. The samples for tensile testing were cut from the same laminates to dimensions of 60 mm x 10 mm using a pneumatic cutter from CEAST using the DIN-53445 norm.

The morphology of the composites was studied using an optical microscope from ZEISS, model Axioplan MC80. Thin sections (1 μm thick) were prepared by a microtome from samples previously embedded in an suitable epoxy resin.

Results and Discussion

Effect of the recycling in the polypropylene

The loss of molecular weight as a function of the number of recycling processes is shown in Table 1. As it can be seen, the largest weight loss occurs after the first processing cycle. However, in spite of such molecular weight loss that occurs even after the second processing cycle, it can be said that the polymer is still a material suitable to be used as a matrix in a composite material. After the fourth or subsequent processing cycles, some cross linking is observed, most likely because of the resulting free radicals formed by the rupture of molecular chains. It can also be observed that

the polydispersity tends to decrease with an increasing number of processing cycles. This could be attributed to the fact that the continued scission suffered by the molecular chains leads to a homogeneous molecular size, but the presence of the free radicals also makes the crystalline face to become more imperfect with increasing processing cycles.

Table 1 Polypropylene molecular weight data for different step recycling.

No. Recycled Processes	Mw	Mn	Mw/Mn
0	141900	39200	3.6
1	119000	36400	3.3
2	102900	29900	3.4
3	91100	27300	3.3
4	90500	28900	3.1
5	81000	25700	3.1

The heat flow for both, pristine and recycled polypropylene during fusion is shown in figure 1. It should be noticed that there is a slight difference in the shape and size of the peak of the enthalpy during fusion. For the pristine polypropylene, the enthalpy of fusion is equal to 78.5 J/g and for the recycled polypropylene is 83.7 J/g. This difference in the enthalpy of fusion is attributed to a decrease in the molecular weight because of the degradation process and to the lower polydispersity of the polymer as mentioned before. There is also a difference between the temperature of fusion for the pristine and recycled polypropylene and the lowest value is attributed to the decrease in the molecular weight resulting from the degradation. It should be remembered that for a lower molecular weight there corresponds a higher mobility thus resulting in a higher crystallinity, but the resulting crystals will have more imperfection. As mentioned before such imperfections are mainly due to the formation of free radicals during rupture of the molecular chains. The little humps that are observed for each peak are attributed to the existence of two crystalline phases with different degrees of imperfection. In this case, the imperfection of the crystalline phases is attributed to the cooling rate and the scale rate of the thermal history of each polymer. Also, some authors have mentioned [1, 2] that the carbon black will be attracted by the crystalline phase and for this reason, any change in the crystallinity will have an effect on the electrical conductivity of the material. Figure 2 shows the mass loss and its derivative as a function of temperature. It is noticed again that the pristine polypropylene exhibits a higher thermal stability than the recycled polymer. This difference in thermal behavior is attributed to the degradation suffered by the recycled material. From the derivative, it can be observed that the kinetics of degradation is the same for both polymers because both peaks have the same shape and size. This is an indication that the degradation suffered by the polymer is only due to rupture of chains and that there is no formation of a different molecular structure which could lead to a different kinetics of degradation. It is reasonable to assume that the number of free radicals, which are formed after the first recycling process, is too low to have an influence on the kinetics of degradation.

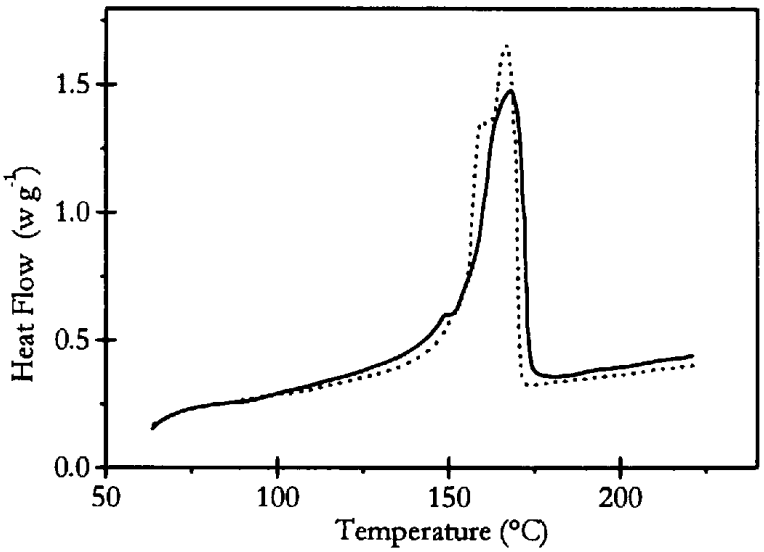

Figure 1. Fusion enthalpy; (·····) recycled, (——) pristine polypropylene.

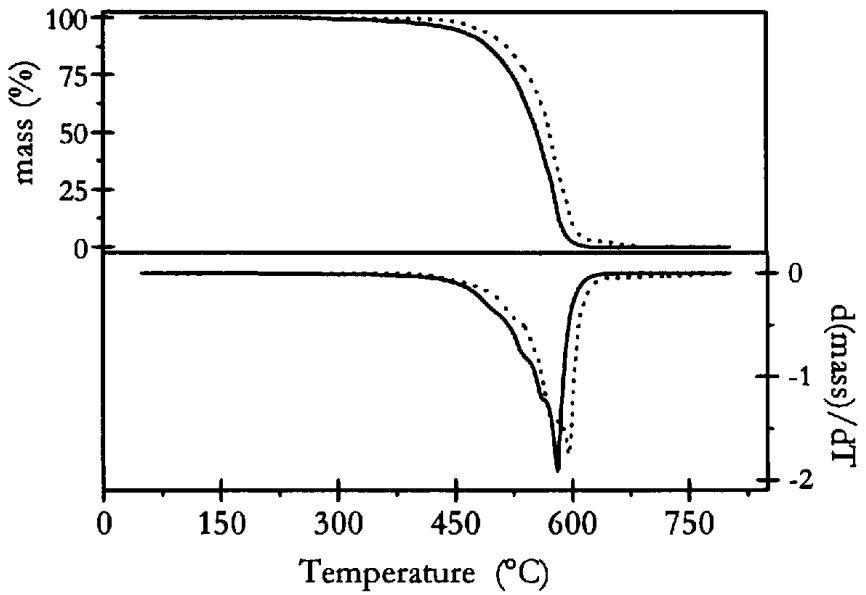

Figure 2. Loss weigh and its derivative as a function temperature; (·····) recycled (——) pristine polypropylene.

Effect of carbon black on the electrical conductivity

The conductivity of the carbon black/polypropylene and carbon black/recycled polypropylene composites as a function of carbon black content is illustrated in figure 3. The electrical conductivity of these composites increases dramatically when the carbon black content reaches the percolation threshold. However, small differences in the percolation threshold are noticed. For the recycled polypropylene, such threshold is obtained at a 10 % carbon black content, while for the pristine polypropylene the threshold is obtained for a 15 % content. These threshold values were obtained from the intersection of lines drawn tangent to the curve on both sides of the inflexion point. From a closer analysis, it can be observed that for a 5 % carbon black content, (see the insert in figure 3) there is already an electrical conductivity in both materials as it has been reported in the literature [3].

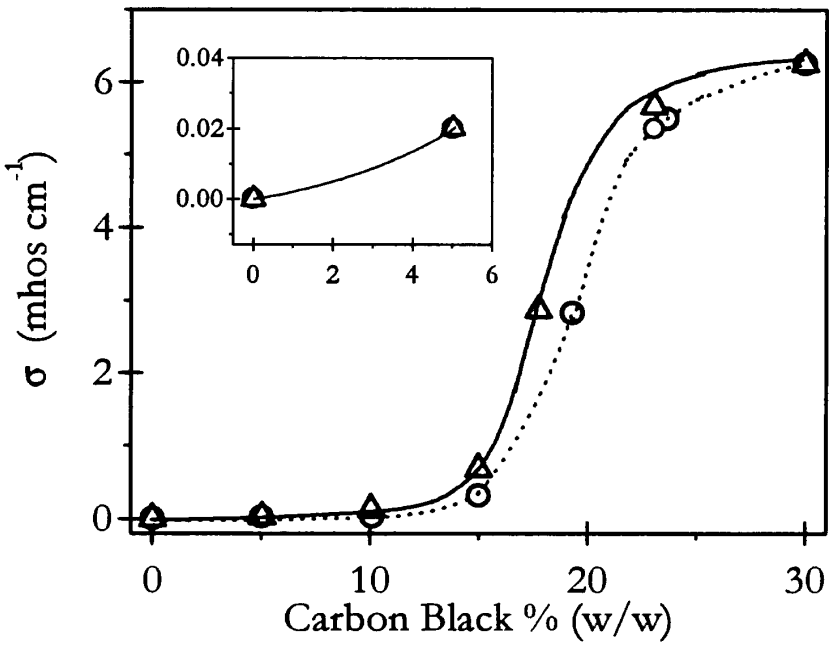

Figure 3. Electric conductivity as a function of carbon black content; (∝) recycled, (Δ) pristine polypropylene/carbon black composites.

For increasing carbon black content there is an abrupt change in the conductivity but it is also noticed that the conductivity remains the same for both the pristine and recycled materials for carbon black contents of 30 % and higher. The only other noticeable fact is that despite the reduction of molecular weight of the recycled polypropylene of approximately 27.5 %, as compared with the pristine material, the conductivity for both composites reaches the same value. It is also noticed that the electrical conductivity obtained for the composite with a 30 % carbon black content is of the order of 6 Mhos-cm^{-1}, similar to that reported for conductive composites of HDPE and the same carbon black content [4].

Figure 4 shows optical microscopy micrographs of the carbon black/polypropylene composite for concentrations of 1 % and 5 % respectively. It should be noticed that

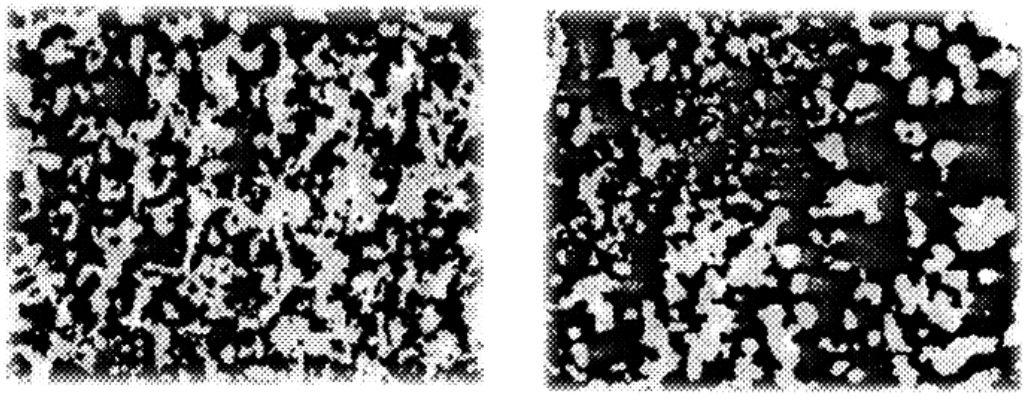

Figure 4. Optical micrographs of polypropylene/carbon black composite 99/1 w/w (left) and 95/5 w/w (right), for recycled polypropylene. The black zones correspond to carbon black and the white zones correspond to polypropylene.

for the higher carbon black content percolation the carbon particles are interconnected in a network thereby indicating that there is already percolation. The change in conductivity as a function of the applied voltage is shown in figure 5, and it is observed that these materials do not obey Ohm's law for low values of applied voltage (0-10 V). Also, the electrical conductivity shows an asymptotic behavior and this means that for a higher applied voltage, there is a tendency to follow Ohm's law. This non-linearity at low values of applied voltage could be attributed to the mechanisms of electrical percolation, which even nowadays are not fully understood. Generally, the electrical percolation threshold in these materials is reached before the conducting particles get in contact between each other [3]. It is also observed that because of the high electrical conductivity of the carbon black particles, the electrical conductivity of

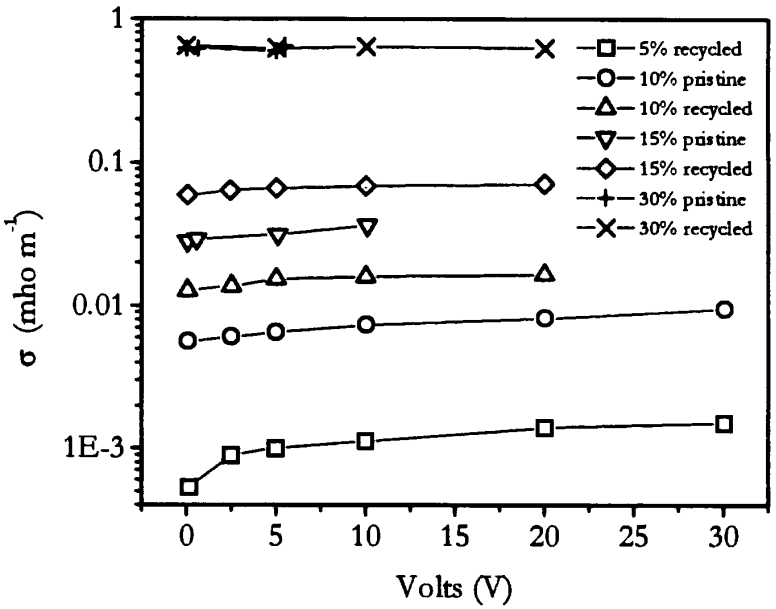

Figure 5. Conductivity as a function of the applied voltage, for different compositions of carbon black.

both pristine and recycled polypropylene composite materials is high. It should also be observed that Ohm's law is fully satisfied by both 30% carbon black content composites.

The change in temperature with respect to time (up to 30 seconds) for two different applied voltages for a 30 % carbon black content composite made from recycled polypropylene, is shown in figure 6, with respect to the time of voltage application. The slope of the lines represent the heating rate of these materials. This value is used to control the heating speed as a function of the applied voltage. The energy dissipated by the material is given as the energy dissipation of any electrical resistance, that is, the product of the applied voltage times the resulting electrical current. Indeed the electrical current will depend on the material properties, specifically the electrical resistivity. This means that the higher the resistivity the higher the amount of energy to be dissipated. This will be true up to a certain value of the electrical resistivity, because for very high resistances the value of the circulating current will be so low that the energy dissipation will also be low. A sudden change of the energy dissipation is observed between 5 and 10 volts. Also, it is noticed that after application of 10 volts, the behavior of this material obeys Ohm's law as shown in figure 5.

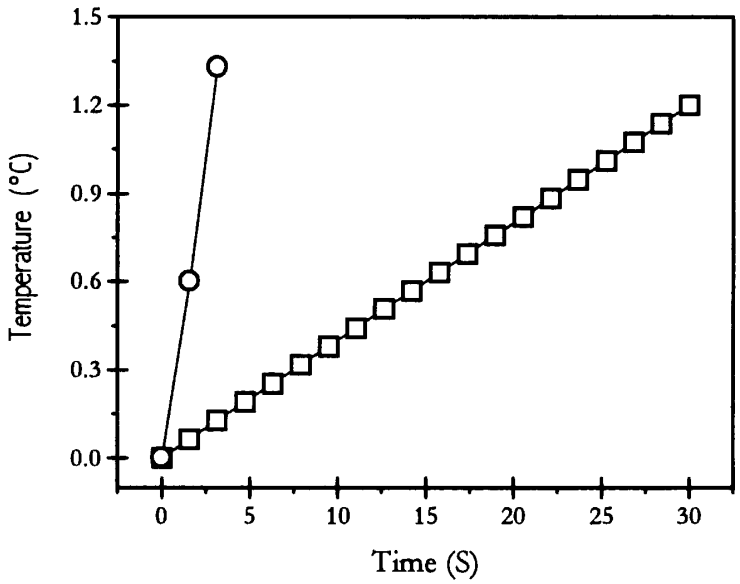

Figure 6. Increase in temperature as a function of time, for tow level of applied voltage; (ϖ) 5 V, ( ) 10 V, recycled polypropylene.

It can be observed that there exists a voltage value, between 5 and 10 volts for which such heating rate increases from 0.04 °C/s to 0.46 °C/s. With this heating rate, it is possible to heat the composite material and any surrounding space to, say 30 °C in a relatively short time and low energy consumption.

Effect of carbon black on the mechanical properties

Figure 7 shows the effect of the inclusion of carbon black on the mechanical

properties of the pristine and recycled polypropylene composites. It is noticed that for the pristine, the elastic modulus increases for carbon black contents above a 3% w/w polypropylene. However, the elastic modulus such increase for the recycled v polypropylene is noticed after carbon black contents above 8% w/w.

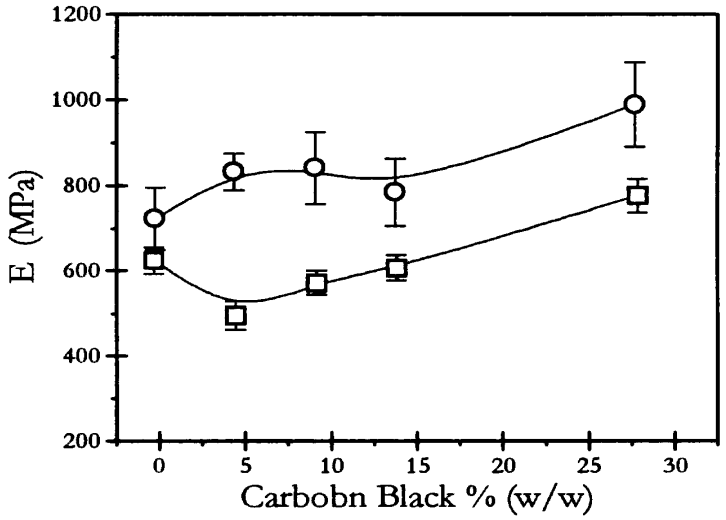

Figure 7. Elastic modulus of polypropylene/carbon black composite as a function of carbon black content; (○) pristine and ( ) recycled.

Conclusions

No noticeable effects on the thermal properties of polypropylene are noticed even after two recycling processes. This means that it is possible to use it after that number of processing cycles.

Electrical conductivity is observed for both the pristine and the recycled polypropylene even at a low carbon black content, approximately 5% (w/w).

The crystallinity of the polypropylene decreases in a 4.5 %, and this decrement results in a higher value of the percolation threshold.

For both the pristine and recycled materials, a filler content above 30 % results in the same electrical conductivity of both materials. The resulting heat generated is high enough to increase the temperature of the material and its surroundings with a relatively low applied voltage, (~30 V).

Reference

1 Lux F (1993) J Mat Sci 28:285
2 Gubbels F, Jérôme R, Teyssié P, Vanlathar E, Deltour R, Calderone A, Parenté V and Brédas J (1994) Macromolecules 27:1972
3 Sherman R, Middleman L and Jacobs S (1983) Polym Eng Sci 23:36
4 Yang G, Teng R and Xiao P (1997) Polym Com 18:477