

Compatibilization of Commingled Plastics with Maleic Anhydride Modified Polyethylenes and Ultraviolet Preirradiation

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ABSTRACT: The improvement of the properties of commingled plastics was carried out with a prototype blend of Mexican municipal plastic waste with and without poly(vinyl chloride) (PVC). Compatibilizing agents such as high-density, low-density, and linear low-density polyethylenes modified with maleic anhydride were used. The agents were prepared in the laboratory with peroxide, and their usefulness was compared with that of a commercially modified linear low-density polyethylene. The blends with PVC were preirradiated with ultraviolet radiation for 12, 24, or 48 h to create oxidized groups to help *in situ* compatibilization during the

blending step of the reactive extrusion process. Compatibilized materials showed a markedly more homogeneous morphology with improved mechanical properties: the elongation at break and impact strength increased with the compatibilization level. The presence of PVC in commingled plastics significantly reduced the beneficial effect of the maleic anhydride modified polyethylene as a compatibilizer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2597–2603, 2008

Key words: blends; compatibilization; graft copolymers; radiation; recycling

INTRODUCTION

During the last decades, the plastics industry has been growing at a significant rate. Part of this growth has come from the substitution of plastic materials for traditional paper and glass materials in packages and bottles for food products.¹ These plastics are causing a problem in municipal solid waste (MSW), in which the percentage of plastics is increasing rapidly, creating serious damage to the environment. The amount of plastic in MSW is generally higher in industrialized countries of North America (8.5–11%), Eastern Asia (11–14%), and Northern Europe (11–13%), in contrast to developing countries in Central America (4–6.7%), South and Western Asia (4–7.2%), Eastern Europe (5–6%), and Africa (3–5%).^{2–6}

On the other hand, the types of plastics in MSW change from one country to another. In general, the plastics found in municipal waste consists of three types of polyethylenes [high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and low-density polyethylene (LDPE)], polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), and others

in small amounts; certainly, polyethylenes have the highest concentration of 50% or more.^{3–9} The separation of these polymers for recycling is expensive; therefore, the possibility of processing such a mixture collected directly from waste has industrial and economic interest, although the great heterogeneity of these thermoplastics involves several difficulties, primarily their incompatibility and differences in melting points.

The recycling of mixed plastic waste by extrusion requires temperatures high enough to melt PP and PET that can induce dramatic degradation in other polymers such as PVC, PS, and some polyethylenes with low antioxidant contents. In addition, the incompatibility of these polymers results in the creation of the same number of phases as polymers in the mixture, and this leads to poor mechanical properties of the mixture.

Since the 1970s, when the introduction of a compatibilizing agent was first visualized, there have been many studies reported in the literature devoted to the problem of recycling mixed plastic waste. The first material used for this purpose was chlorinated polyethylene,^{10,11} and after that came polymers modified with polar and carboxyl groups; styrene block copolymers were popular for this use.^{12–21}

All the compatibilizing agents act at the interface between the polymers, increasing the interactions between the phases and helping to produce materials with better mechanical properties and more homoge-

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neous morphologies. On the other hand, there is also a reported method^{22–24} in which the compatibilization of this kind of mixed plastic waste is achieved with the generation *in situ* of free radicals on the surfaces by the fracture of materials during a pulverization process in a corotating twin-screw extruder (solid-state shear pulverization), and the compatibilization is obtained when radicals react with other polymer radicals, forming copolymers that promote a better interaction between the phases.^{22–24}

In this work, prototype blends of commingled plastics prepared with virgin polymers were compatibilized with grafted maleic anhydride (MA) modified polyethylenes prepared in our laboratory. MA was selected as the compatibilizer because of its low cost, accessibility, wide applicability with most polymers, and popularity. The mixtures were compared to a commercial maleic anhydride grafted linear low-density polyethylene (LLDPE-g-MA), and the effect of PVC in the mixtures was also evaluated. Moreover, these prototype blends were exposed to ultraviolet (UV) radiation for some time intervals and compared to those without UV exposure.

EXPERIMENTAL

Materials

The materials used in this work were commercial resins: LDPE 20020 and HDPE 60003 from PEMEX (Coatzacoalcos, Mexico), LLDPE 2045A from Dow (Midland, MI), PET IMPET 100 from Celanese (Querétaro, Mexico), crystal PS from Polidesa (Tlalpantra, Mexico), PVC compound Iztablend from Elf-Atochem (Puebla, Mexico), and PP Valtec HP423M from Indelpro (Altamira, Mexico). A Dupont (Wilmington, DE) LLDPE-g-MA known as Bynel was also acquired as a commercial compatibilizer.

Compatibilizing agents

Three compatibilizing agents were prepared, and they basically consisted of polyethylenes modified with MA. One of them was LDPE, another was HDPE, and the last was LLDPE; all of them were prepared in our laboratory by the addition of a peroxide initiator, as published previously.²⁵ The melt index, grafting level, and gel content were evaluated for each compatibilizer material prepared (including the commercial one).

Blend preparation

A physical mixture of resin pellets of the acquired materials, including a 5% (w/w) concentration^{18,19} of the corresponding compatibilizing agent, was fed to the extruder for an appropriate molten mixing step. The mixture prototype consisted of HDPE, LDPE, LLDPE, PET, PVC, PP, and PS in the weight percent-

age ratio of 69.41/7.015/7.015/8.20/4.92/1.20/2.24, respectively, and was prepared to correspond to the currently reported proportions of these polymers in urban plastic waste for Mexico.⁷

The blend was prepared in a W&F ZSK-30 corotating twin-screw extruder (Ramsey, NJ) with the temperature in five heating zones set at 250°C and the screw speed set to 400 rpm. Finally, the pellets from extrusion were used to obtain specimens for determining mechanical properties by injection molding in a 75-ton Battenfeld machine (Koltingbrum, Austria).

Material characterization

Melt index

The melt flow indices for the compatibilization agents were evaluated in a Kayeness model 7053 melt index instrument (Morgantown, PA) according to ASTM D 1238 (temperature = 190°C, load = 21,600 g). This evaluation was carried out under such conditions that differences in the flow properties of the agents could be observed.

Grafting and gel content

The unreacted MA was removed by the extraction of 1 g of the compatibilizing agent under 250 mL of hot xylene for 8 h according to the described apparatus in ASTM D 2765. The xylene-insoluble portion corresponded to the gel percentage, whereas the soluble part was precipitated and washed with acetone and finally dried at room temperature. The grafting percentage was determined by the acid number according to a literature-reported procedure.²⁶

Mechanical properties

The specimens were tested with ASTM standard methods. After injection molding, they were conditioned in a room for 40 h according to ASTM D 618 before the mechanical evaluations. Tensile properties were evaluated with a United model STM-10 mechanical testing machine (Huntington Beach, CA) and with specimen type IV with a thickness of 3.2 mm and a testing speed of 51 mm/s according to ASTM D 638. The Izod impact strength was determined with notched specimens with a thickness of 3.2 mm and with a CSI model CS-137 pendulum apparatus (Cedar Knolls, NJ) with an impact capacity of 2 J; ASTM D 256 was followed. The reported values for all properties were averages of five evaluations.

Scanning electron microscopy (SEM)

The blend morphology was examined with a Topcon (Osaka, Japan) SM-510 scanning electron microscope. The samples were fractured under liquid nitrogen

TABLE I
Compatibilization Agents

Compatibilizer	Grafted MA (%)	Melt flow index	Gel (%)
HDPE-MA-PXD	1.01	34.5	0.40
LDPE-MA-PXD	1.88	15.3	0.48
LLDPE-MA-PXD	0.56	38.1	0.28
Bynel	0.3	22.7	0.15

PXD, peroxide as initiator.

and then vapor-coated with Au/Pd for microscopy. The samples were observed at a magnification of 2000 \times , and microphotographs were taken.

RESULTS AND DISCUSSION

Compatibilizing agents

The agents used as compatibilizers were characterized before their use; the results are shown in Table I. It can be seen that the level of grafted MA has the same trend as the generated gel content during the modification reaction. The latter is corroborated by the melt fluid index, which in turn depends on the polymer, because it is well known that polyethylene gets high levels of crosslinking through the formation of macroradicals. The LDPE presented the highest level of grafting and gel generation, followed by HDPE; the lowest grafting level was obtained for LLDPE.

Processing and mixing

During processing and mixing, a change in color from white to yellow was observed, as well as a characteristic odor of HCl, indicating that degradation of PVC was occurring at the processing temperature of 250°C. Degradation of PVC under such conditions was studied by La Mantia,²⁷ who found that the dehydrohalogenation of this material, when present in a municipal plastics waste prototype blend, is not as important for effects on the mechanical properties of the mixture. The apparent stability of PVC was attributed to the short time of residence during processing, for which the thermal stabilizers and antioxidants were efficient enough for protection.

Considering our results from the processing of the blend, we prepared a second blend including HDPE, LLDPE, LDPE, PET, PP, and PS without PVC with the final weight percentage ratio of 73.00/7.375/7.375/8.63/1.27/2.35, respectively. The behavior of this blend was completely different because the material did not yellow or produce any odor.

Mechanical properties

The tensile strengths at yield and break of blends with and without PVC and with and without a com-

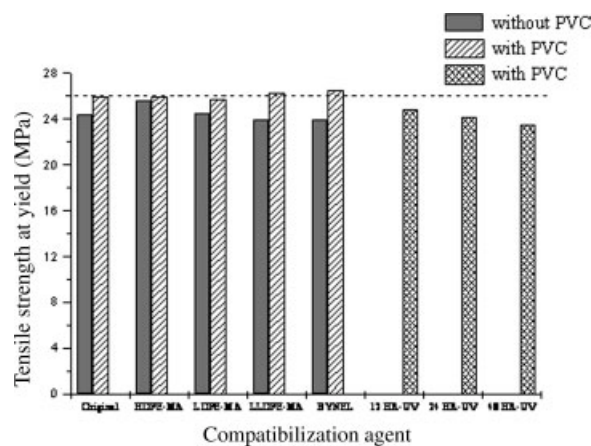


Figure 1 Tensile strength at yield of compatibilizing blends with and without PVC and irradiated blends with PVC.

patibilization agent, including the UV-irradiated blends, are reported in Figures 1 and 2. The strength at yield did not show important changes with the addition of the compatibilization agents, and the same was observed for the irradiated blends. This behavior indicates that the elastic limits are not altered with the compatibilization. Xanthos et al.²⁸ observed the same compatibilization of a municipal plastic waste (MPW) blend with styrene ethylene butadiene styrene block copolymer (SEBS) at 5 wt %; no significant changes were observed until a 10 wt % concentration of this copolymer was added to the blend. This indicates that the yield strength behavior of MPW is defined by the toughness and content of the components.

On the other hand, the tensile strength at break shows major changes mainly in the blends containing PVC and a compatibilization agent, which apparently have higher tensile strength than those without PVC and a compatibilization agent; this is because the fracture occurs prematurely after yield without the plastic strain being reached, and a frag-

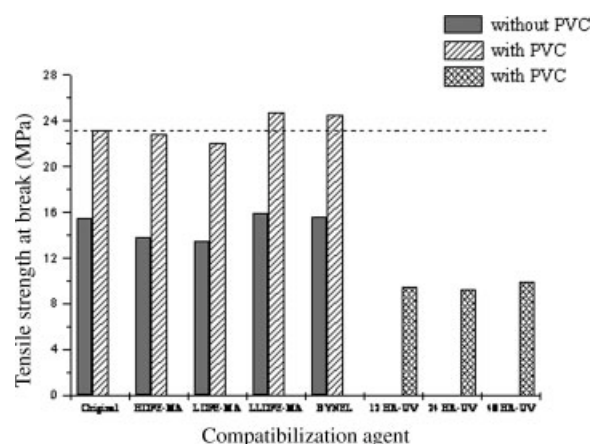


Figure 2 Tensile strength at break of compatibilizing blends with and without PVC and irradiated blends with PVC.

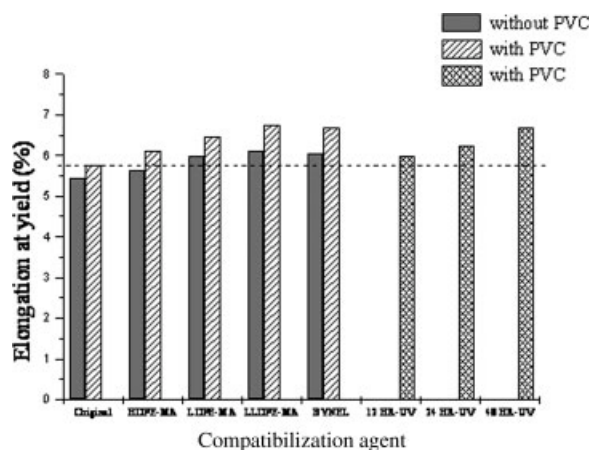


Figure 3 Elongation at yield of compatibilizing blends with and without PVC and irradiated blends with PVC.

ile fracture is produced. This is the reason that the values of the tensile strength at break are very similar to those obtained at yield for these blends with PVC. The more significant changes in the tensile strength at break were observed in blends without PVC and a compatibilization agent, which had lower values for this mechanical property as a result of ductile fracture during the plastic strain.

This behavior indicates an increment in the adhesion at the interface of the components with no PVC in the blends. On the other hand, the blends with PVC irradiated with UV at different doses did not show significant differences among them, although they all had lower values. The fracture occurred during the plastic strain, and this showed that the interface adhesion increased more for this blend than the no-PVC blend.

Figures 3 and 4 show the elongation at yield and break, respectively. In the case of the elongation at yield, there was a tendency to increase according to the toughness of the compatibilization agent, this

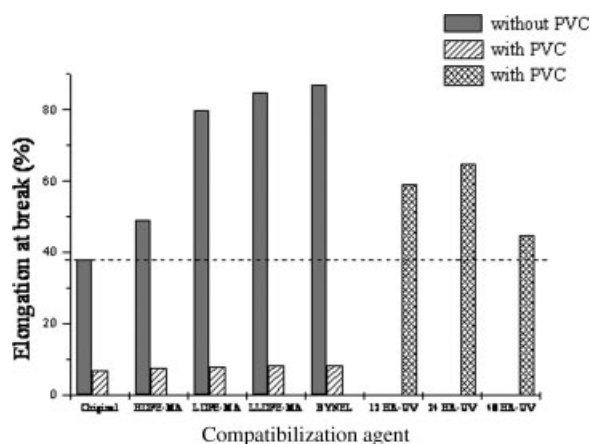


Figure 4 Elongation at break of compatibilizing blends with and without PVC and irradiated blends with PVC.

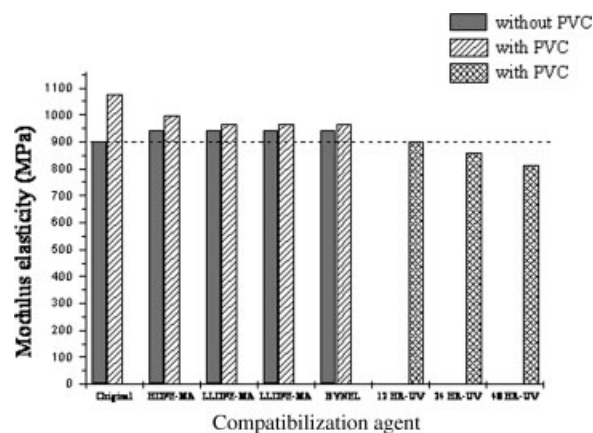


Figure 5 Modulus of elasticity at break of compatibilizing blends with and without PVC and irradiated blends with PVC.

being more important for those blends of LLDPE-g-MA and less important for maleic anhydride grafted high-density polyethylene (HDPE-g-MA). The increase also indicates better interphase adhesion. In the UV-irradiated blends, this increasing tendency was observed with an increase in the irradiation time, and this could be mainly due to crosslinking of the polyethylenes through a degradation mechanism and the interaction between phases within components. The elongation at break (Fig. 4) of the blend with PVC presented the lowest values, with a small tendency to increase for the compatibilized blends. This highlighted the low efficiency of the polyethylenes grafted with MA.

However, the blends without PVC presented a completely different behavior: high elongation was obtained for the blend free of compatibilization, and even higher elongation was obtained for the compatibilized ones. The increase became more than 100% for those blends containing LDPE and was only 25% for HDPE-g-MA; in these blends, the compatiliza-

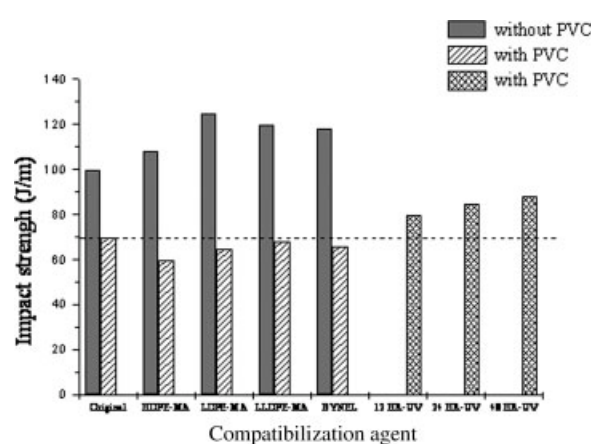


Figure 6 Impact strength of compatibilizing blends with and without PVC and irradiated blends with PVC.

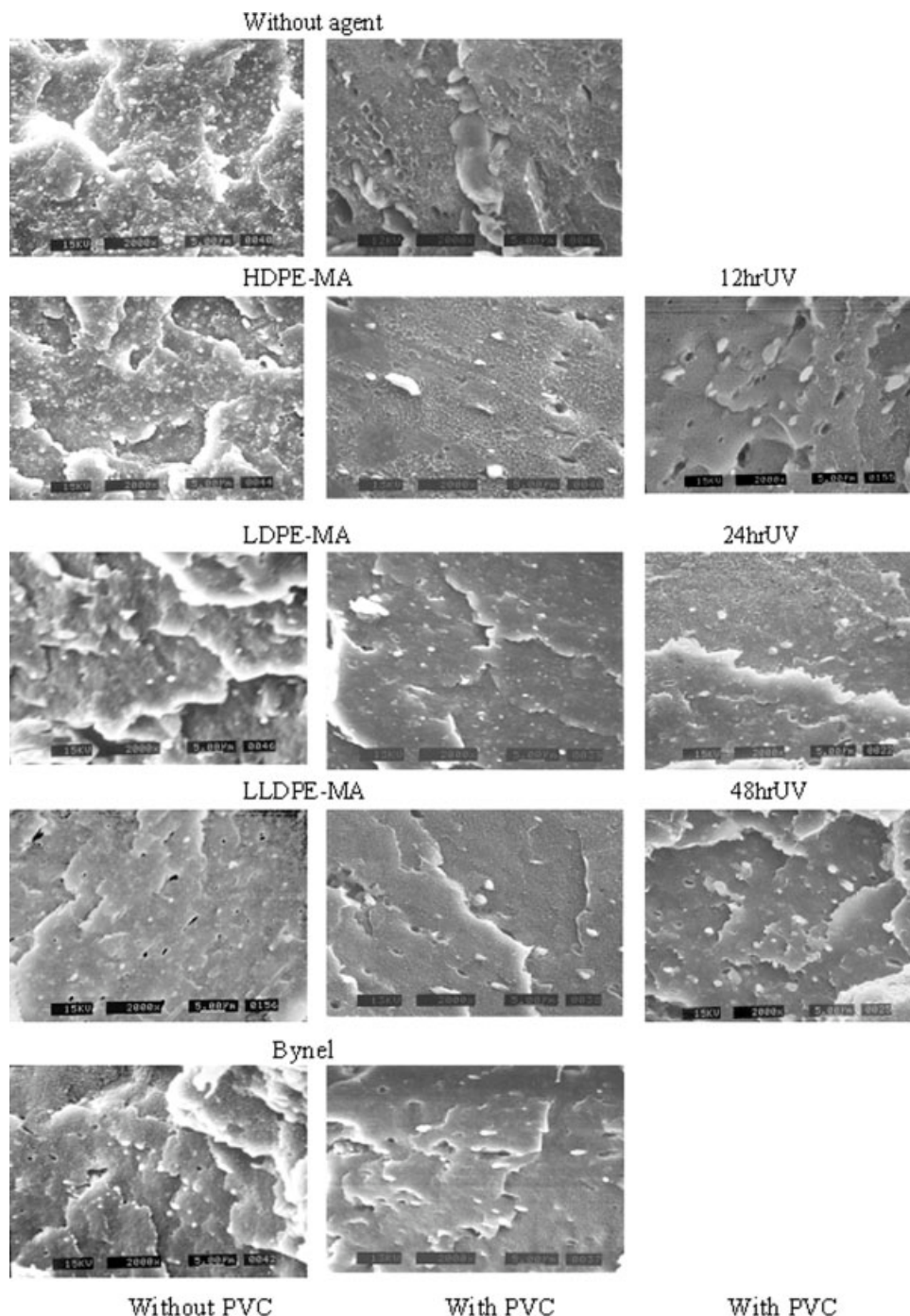


Figure 7 SEM microphotographs of compatibilizing blends with and without PVC and irradiated blends with PVC.

tion agents were more efficient than in blends containing PVC. Such behavior in the strain of the blends indicates that PVC inhibits the action of modified polyethylenes because the MA group can interact with the chlorine of PVC and produce HCl during the processing step; furthermore, such an interaction could be responsible for the lack of compatibilization.

For blends with PVC, the strain was also lower because of the presence of HCl produced during the processing step, which increased the incompatibility

of the blends while decreasing the adhesion between phases.

On the other hand, the irradiated blends showed behavior similar to that of the blends without PVC, and this indicated that oxidized groups which formed during the irradiation step reacted during processing, producing macroradicals, which in turn reacted with others to form copolymers. The latter improved interactions among phases, and apparently the presence of PVC and HCl did not affect such

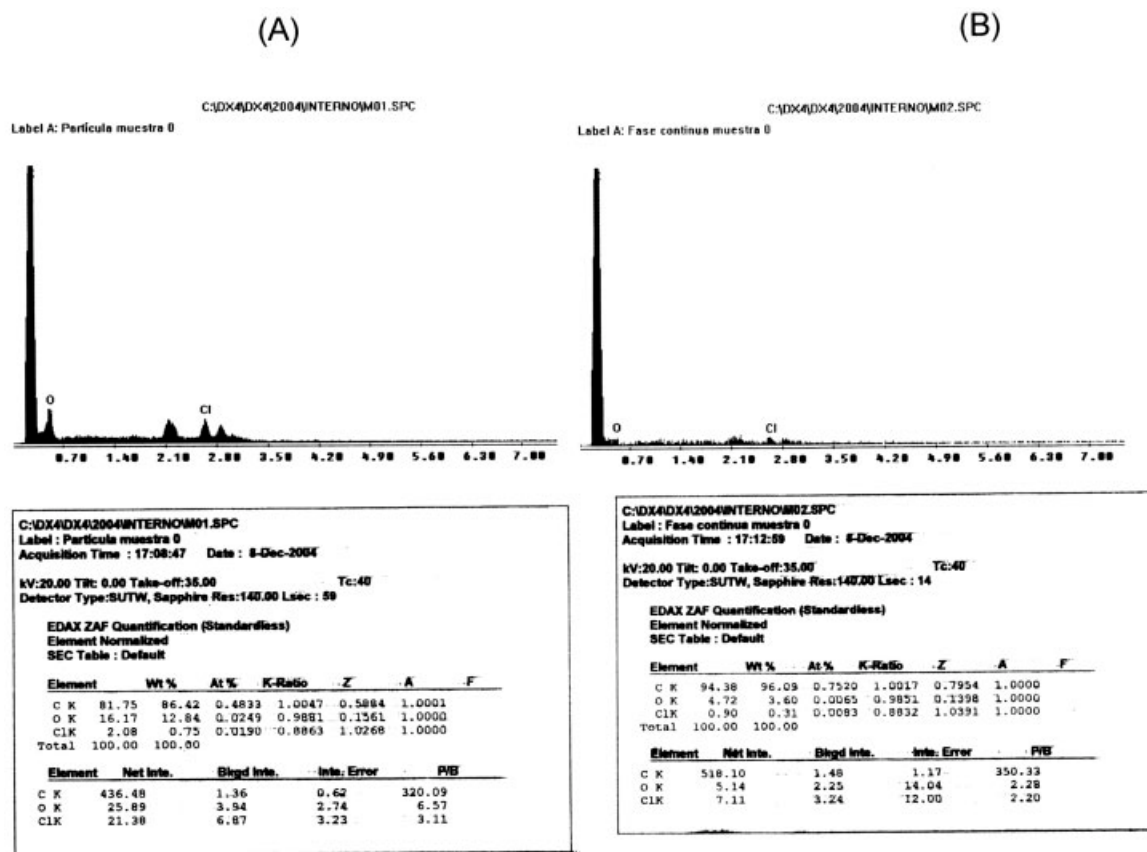


Figure 8 Spectrum and semiquantitative elemental analysis by SEM-EDX of (A) the disperse phase (particle) and (B) the continuous phase.

reactions, as in the compatibilized blends with MA-modified polyethylenes.

Figures 5 and 6 show the behavior of the modulus and impact strength, respectively. The trend of the modulus was similar to the trend of the tensile strength at yield, for which the changes were minimal. In the irradiated blends, one could distinguish a small decrease in rigidity as a function of the irradiation time. This was due to the increased number of interactions created during the processing step among oxidized groups, which decreased the surface tension and increased adhesion among the phases. Blends with and without PVC did not show changes in rigidity.

The impact strength (Fig. 6) showed a performance similar to that of the elongation at break, for which big changes could be observed. The blends without PVC showed an important effect of the compatibilization agents, as well as the irradiated blends with PVC: the creation of copolymers during the processing step was another form of compatibilization of this kind of multicomponent blend.

SEM

The microphotographs obtained by SEM for fractured surfaces of blend samples with and without

PVC, compatibilized and uncompatibilized, and for UV-irradiated blends are shown in Figure 7. The microphotographs show continuous and disperse phases. The polyethylenes and PP were the main components of the continuous phase. The dispersed phase became more homogeneous and smaller in size with the presence of compatibilization agents or with UV-irradiation exposure. This was indicative of a reduction in the surface tension. The blends compatibilized with modified polyolefins with PVC consisted of big particles in a dispersed phase, noticeably more than those blends without PVC, and this was the reason for the lower mechanical properties.

On the other hand, a semiquantitative elemental analysis was carried out with a dispersive-energy X-ray (EDX) accessory of SEM for both continuous and dispersed phases for the blends with and without PVC. Figure 8(B) shows the spectrum and results of the analysis in the continuous phase, in which oxygen and chlorine were present, and Figure 8(A) shows the spectrum and results of the analysis in a particle (dispersed phase), in which oxygen and chlorine were present in increased concentrations. This indicates that the dispersed phase was formed mainly of PET and PVC, and the interactions of chlorine and HCl (the blend presented an odor) of PVC

and the oxidized groups of PET were confirmed with these results. Therefore, the efficiency of compatibilization agents in this type of blend was inhibited by this interaction and especially by the free HCl. This was the reason for the low values of the mechanical properties of the compatibilized blends with PVC.

CONCLUSIONS

During the blending and extrusion of commingled plastics, PVC gave a yellow coloration and some odor of HCl to blends when processing was carried out at a high temperature (250°C); this was indicative of some degree of degradation. Furthermore, it inhibited the action of modified polyethylenes used as compatibilization agents and accelerated the hydrolytic degradation of PET. This was also the reason for the lower mechanical properties obtained for the compatibilized blends containing PVC. The commercially modified LLDPE used as a compatibilization agent showed behavior similar to that of the modified LLDPE made in our laboratory. The UV-irradiated materials before the blending and extrusion step showed some improvement in the compatibilization of the blends because of the reactive oxidized groups produced during the UV exposure, which generated some copolymers during processing, increasing the interactions between phases of these multicomponent blends.

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