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High-energy mechanical alloying of thermoplastic polymers in carbon dioxide

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Abstract

High-energy ball milling was performed on low density polyethylene (LDPE) and isotactic polypropylene (*i*PP) as well as on 20/80 binary mixture of both polymers. Mechanical alloying was carried out at high pressure with carbon dioxide for a short period. The presence of CO_2 avoids oxidative mechano-chemical degradation of polymers and enhances the effectiveness of the milling. The effects of the mechano-chemical treatment on the molecular and physical properties of both single polymers and blends of intrinsically incompatible polymers were explored by FTIR spectroscopy, thermal analysis, intrinsic viscosity determination and solvent fractionation. Structural changes on PP and PP/LDPE blend were observed and have a strong dependence on the milling time. Mechanical tests confirm an overall improvement in blend properties by mechanical alloying. Experimental evidences are presented to suggest that CO_2 high-energy ball milling causes a self-compatibilization of the blend LDPE–*i*PP by breaking *i*PP polymer chains and allowing them to recombine with the neighboring LDPE chains.

Keywords: Mechanical alloying; Self-compatibilization; Grafting

1. Introduction

Mechanical milling (MM) and mechanical alloying (MA) refers to high-energy ball milling (BM) technique employed to process solid-state single or multiple phase materials, respectively. Starting from the late sixties, applications of BM in the synthesis of stable and metastable inorganic materials have been extensively studied [1]. Recently several workers demonstrated that solid-state MM and MA of polymeric materials carried out at cryogenic temperatures represent a strategy for producing polymer blends with acceptable mechanical properties. Pan and Shaw [2] applied MM to polyamide, polystyrene, polyethylene and found out this mechanical treatment resulted in considerable alteration of both crystal structure and microstructure of these polymers. In order to increase the degree of dispersion of polyisoprene (PI) into poly(methyl methacrylate) (PMMA), Smith et al. [3] applied MA on the polymeric mixture. Bay et al. [4] published a complete study of the effects of MM on physico-chemical properties of poly(ethylene terephthalate) (PET). Nesarikar et al. [5] achieved in situ compatibilization of polymer blends through solid-state shear pulverization. High-energy ball milling is effective to co-pulverize shredded polymer films, promoting a substantial size reduction and also creating chemical effects on the material. The combination of mechanical effects, such as impact, compressive and shear forces is expected to induce radical chain scissions within polymer particles. Reaction of macromolecular free radicals from different chain species of intrinsically incompatible polymers could couple and produce a more stable blend by grafting.

Although former works addressing the mechano-chemistry of polymers have been focused on milled induced structural and chemical changes in semi-crystalline polymers and their blends, the molecular physico-chemical changes that occur as a result of milling need to be elucidated in details. A full understanding of processing parameters and structure–property relationship in polymers increases the options available in achieving specific chemical and mechanical properties in new materials.

A novel BM technique, operating at near room temperature, requires the use of liquid CO_2 in the milling vial to enhance the mechano-chemical effect induced by BM on polymeric materials [6]. Using CO_2 assisted BM process (CBM hereafter), pulverized particulate can be obtained in a very short milling time (~10 min). In the present work, we describe the application of CBM technique at traditionally incompatible polymers, such as polypropylene (*i*PP) and

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polyethylene (LDPE). Our emphasis is on showing how a self-compatibilization of *i*PP/LDPE blend can be accomplished by such a mechano-chemical process. Infrared spectroscopy, thermal analysis, intrinsic viscosity determination, selective dissolution of milled blends, as well as mechanical tests, were performed in order to ascertain the in situ compatibilization and to investigate structural and chemical modifications induced by milling into *i*PP and PE solid phases.

2. Experimental section

2.1. Materials

Isotactic polypropylene (*i*PP) and low density polyethylene (LDPE), both commercial grade additive free, were used without further purification. Viscosity average molecular weights of LDPE ($M_v = 18\,000$) and *i*PP ($M_v = 350\,000$) were determined in decaline (reagent grade, from Carlo Erba) at 135 °C. Thermal analysis was performed with Perkin–Elmer DSC 7 calorimeter. Infrared spectra were recorded by a Perkin–Elmer FTIR series 2000 spectrometer equipped with microscope. Thin films of LDPE and *i*PP were prepared by molding (Struers Prontopress). Mechanical tests were performed with a Testometric Micro 350 apparatus. Intrinsic viscosity of polymers, in xylene (reagent grade, from Carlo Erba), was measured with suspended flow viscometer.

2.2. Sample preparation

Mixed samples were obtained milling 0.5 g of polymers. The composition of blends was fixed at a weight ratio of 80/20 *i*PP/LDPE. All the materials were placed in a suitable high pressure, 60 cm^3, cylindrical stainless steel vial with 150 g WC balls (measuring 8–15 mm in diameter) and 20 g of solid carbon dioxide. To make CO_2 manipulation easy, the vial was filled with dry ice and immediately closed after its filling. After a few minutes, measured values of pressure and temperature were 5×10^6 Pa and -10 °C, respectively. The vial assembly was placed in a SPEX 8000 apparatus and agitated for milling time up to 70 min to produce a powder which was removed and stored. To avoid overcoming of critical temperature of CO_2, the apparatus was air cooled. In addition, every 10 min of milling were followed by an equivalent period of rest. During the process, a thermocouple was fixed on the vial wall and the measured temperature never exceeded 30 °C.

2.3. FTIR measurements

Infrared spectra were recorded with a resolution 1 cm^{-1}, for each spectrum 16 scans were signal averaged. For IR measurements, thin films were obtained by hot pressing in cylindrical mould ($\phi = 24$ mm, $F = 18$ kN). LDPE films, with a constant thickness of 13 μm, were prepared at 140 °C and *i*PP, as well as *i*PP/LDPE mixture films, 25–50 μm thick, were molded at 185 °C. In the case of *i*PP and *i*PP/LDPE films, the absorption at 1167 cm^{-1} arising from CH_3 units have been used as internal reference band. Both the ethene and propene contents of the graft polymers fractions, obtained from selective solvent fractionation (described later), using ASTM D3900 procedure, were determined by infrared spectroscopy. The applicability of this IR test method for the determination of the proportion of ethylene and propylene units in ethylene–propylene copolymer holds over the range from 35 to 85 mass% ethylene and it is reasonable to apply such a method to our system. The ratio of the absorbance of methyl groups from propylene units at 1377 cm^{-1} versus the absorbance of methylene sequences from ethylene units at 719 cm^{-1} was measured. A calibration curve, made by mixing known amounts of LDPE and *i*PP in the explored composition range, correlated the spectral data to the *i*PP/LDPE composition of the sample to be studied. Curve fitting of the complex infrared absorption of the CH_2 rocking vibration (760–690 cm^{-1}) was obtained by summation of Lorentzian peaks which properly describe the infrared absorption pattern [7].

2.4. Dissolution test

Solvent fractionations were carried out on 100 mg of polymer mixture milled for 30 and 50 min and 100 mg of pure polypropylene milled for 50 min, with 20 ml of xylene at 80 °C for 2 h. The soluble polymer fractions were filtered, recovered by precipitation in methanol and dried. The insoluble fraction were dried and weighted.

2.5. Viscosity and thermal properties measurements

Values of intrinsic viscosity for mechanically treated samples were determined in xilene at 80 and 120 °C, respectively, by using a Ubbelhode capillary viscometer. Calorimetric characterizations were carried out over the temperature range 5–250 °C using a Perkin–Elmer DSC 7 purged with argon at a scanning rate of 10 °C min^{-1}. Samples were mounted, heated up to 200 °C and then slowly cooled before running spectra. Test cylinder specimens for punch strength measurements, measuring 24 mm in diameter and 1–2 mm in thickness, were prepared by melt pressing the compound at 130 °C and 30 kN.

3. Results and discussion

3.1. CO_2 enhanced high-energy ball milling

Recently many efforts have been addressed to employ mechanical alloying as a means of blending different types of polymers [8]. BM techniques can be easily applied on fragile materials and therefore the process is generally carried out below the glass transition temperature, T_g, of polymeric materials. Usually cryogenic condition and long

milling time (12–24 h) are needed to obtain the final material. The energy transfer from the milling device to the milled powder occurs during a single hit event between balls and between ball and vial walls. As result of the hit, the kinetic energy of the ball is transferred to the trapped powder. The trapped material can accumulate the transferred energy (in forms of surface and interfacial energies after breaking of particles, defect energy in crystalline materials, etc.) increasing its energy content. In such a way, repeated hits can produce an almost continuous energy increase in the milled material and the system can stabilize in consecutive processes, as phase transformation and/or chemical reactions. The described behavior needs an essential condition that the milled material is unable to release the energy transferred by the hits in other ways. If the material can easily recover its initial energetic state, a continuous energy accumulation mechanism cannot operate. In this case, to produce a mechano-chemical reaction in the trapped powder the energy transferred during the single hit must be large enough to overcome the activation barrier of the reaction. At a temperature above T_g, plastic materials can easily change their conformational state. In this way when a polymer is mechanically activated by a hit, it easily increases its conformational energy and immediately relaxes in the more stable starting conformation, transferring heat to the system. In ordinary BM processes of polymers, liquid nitrogen cooling inhibits the chains mobility and in this way the described energy accumulation effect can occur. The CBM process uses liquid CO_2 as energy transfer medium, overcoming the necessity to operate below glass transition temperature. In this way, very short milling time (10 min) is enough to pulverize shredded polymeric films and to obtain a blend. Unlike the traditional BM process, when a single hit occurs, the kinetic energy of the ball can be transferred not only at the trapped polymeric powder but also to the liquid CO_2. Estimated time of a single hit is about 10^{-4} s [9] and the energy released in our experimental conditions is of the order of 10^{-2} J/h [10]. The transfer of 0.01 J to the liquid CO_2 in the vial is able to promote the evaporation of about 0.2 mg of liquid in a time of the order of 10^{-4} s. In other words microexplosions of CO_2 are induced in a single hit. The microexplosive phenomenon is fast enough to inhibit material relaxation. A substantial physical reduction (250–500 μm) in the scale of dispersion is obtained within the polymeric system by CBM and mechano-chemical reactions can be activated. Interface bonds arrangements, such as grafts or crosslinks can be envisaged and compatibilized polymeric blend can be produced.

3.2. FTIR spectroscopy and intrinsic viscosity determination

To ascertain in situ compatibilization of the polymeric blend promoted by CBM, the presence of grafted polymer component has to be verified. The presence of this polymeric fraction is quite difficult to determine, because it is likely to be present at the level of few percent of the whole sample as well as because of its chemical similarity to the other components of the mixture. As *i*PP is more likely reactive than LDPE, the composition of binary mixture was fixed at 80/20 (w/w) to put in evidence the grafted polymer component. IR spectroscopy was used for determining whether the grafting or branching has occurred within PP or LDPE chains. FTIR spectra of these two compounds, having separately undergone a high-energy ball milling, were recorded to evidence differences between pure and treated starting materials, before studying mechanically treated blend of PP/LDPE. Characteristic peaks of PP and LDPE were assigned according to Ref. [11]. Short chain branches of polyethylene can be qualitatively identified [12] by the presence of a band at approximately 890 cm^{-1} assigned to a methyl rocking mode for branches larger than ethyl such as butyl or hexyl branches, and a band at 770 cm^{-1} attributable to the methylene rocking mode of ethyl branches. When a polymer is subjected to a mechanical stress, the presence of oxygen may promote a mechano-chemical degradation, in particular polypropylene with its oxidation-sensitive tertiary carbons oxidizes more easily than polyethylene. Due to oxidation process, the first products of degradation are hydroperoxide groups whose decomposition leads to chain scission with formation of carbonyl or carboxyl groups at the chain ends. As it is shown in Fig. 1, the CBM process does not cause any degradation phenomenon, not even after 50 min of milling. In fact no peaks in the carbonyl region (1700–1800 cm^{-1}) are observed neither in the case of milled *i*PP nor in the case of milled LDPE. An important feature is shown in the absorbance FTIR spectra reported in Figs. 2 and 3. Whereas in the

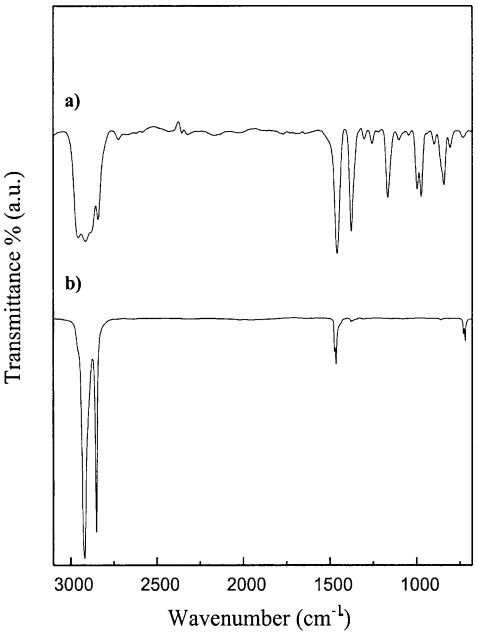

Fig. 1. FTIR spectra of CO_2 mechanically treated (50 min) (a) *i*PP and (b) LDPE.

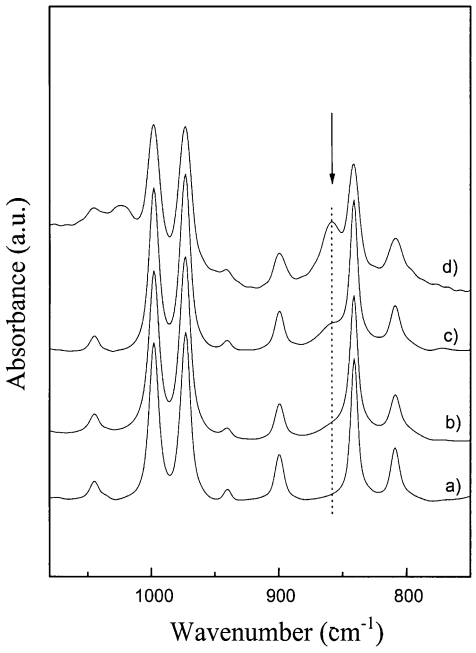

Fig. 2. FTIR spectra of *i*PP samples milled for different periods: (a) 0 min, (b) 10 min, (c) 30 min, (d) 50 min.

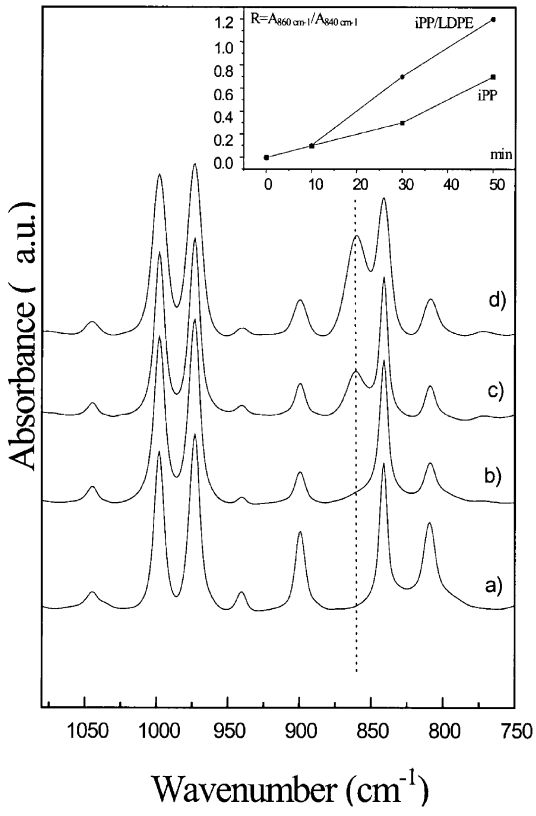

Fig. 3. FTIR spectra of PP/LDPE blend samples milled for different periods: (a) 0 min, (b) 10 min, (c) 30 min, (d) 50 min. Insert: time dependence of the absorbance intensity ratio (860 cm^{-1}/840 cm^{-1}) calculated by deconvoluting the peaks.

case of polyethylene, usual infrared bands were found and no discernable changes were observed in the spectra, both milled PP (Fig. 2) and PP/LDPE (Fig. 3) samples exhibited a new peak at 860 cm^{-1} in their spectra. The absorption at 840 cm^{-1} is characteristic of rocking methylene vibration of the helix, the new peak is attributed to the rocking methylene vibration mode of the grafted polypropylene bearing short chains originated by CBM process.

In both single *i*PP and *i*PP/LDPE milled samples, the new band at 860 cm^{-1} grows as a function of milling time, however the increase of the new rocking band for the blend appears more dramatic. The absorbance intensity ratio (860/840 cm^{-1}) was calculated by deconvoluting the peaks for both milled samples and the achieved linear dependence (Fig. 3) of such ratio versus milling time exhibits an higher slope for *i*PP/LDPE spectra than for *i*PP spectra.

This behavior demonstrates that structural changes occurring on polypropylene chains involve polyethylene chains. To properly assign these new absorbance peaks, we examine the chain fracture process and subsequent reaction pathways of radicals produced in previous studies [13–15]. In analogy with molecular modification induced by gamma irradiation or reaction with peroxide in the polypropylene chains, we assume that the possible evolution of free radicals produced during the ball milling are: (i) β scission with molecular weight decrease and formation of double bonds, (ii) addition of free radicals to double bonds with chain branching or crosslinking formation and molecular weight increase, and (iii) termination. As there is no spectroscopic evidence of double bonds (vinylidene groups) or aldehydes and ketones, we expect mechanical stress not to produce decrease in PE and *i*PP molecular weights but joining of chain fragments to similar or different chains forms branched *i*PP or copolymers *i*PP/LDPE, respectively. Another possibility is that radicals react with unsaturated bond of another molecule and form grafts or branches. Moreover a close examination of 70 min milled PP/LDPE spectrum, Fig. 4, reveals milling-induced differences in the CH_2 rocking vibration band profile at approximately 725 cm^{-1}. According to previous studies [7], we are able to determine the number of bands in this region, and their assignments so far used for analytical determination on EP copolymers.

Peaks at 720 and 730 cm^{-1} are representative of the ethylene crystallinity and correspond to long ethylene chain sequences. Ethylene amorphous units appears at 722 cm^{-1}, whereas isolated $-(CH_2)_x-$ groups between tertiary carbon atoms of polypropylene have been assigned in the range 722–752, the band at 770 cm^{-1} is assigned to pendant ethyl groups. Following Ref. [7], summation of Lorentzians yields the shape of the peak (see Fig. 4), the range of interest being limited to 690–789 cm^{-1} to decrease fitting errors. Curve fitting of 0–30 min milled samples can be satisfactorily obtained by the sum of three amorphous and crystalline bands at 720, 730 and 722 cm^{-1}, respectively. In order to properly describe the band profile of 50–70 min milled samples, it was necessary to introduce a

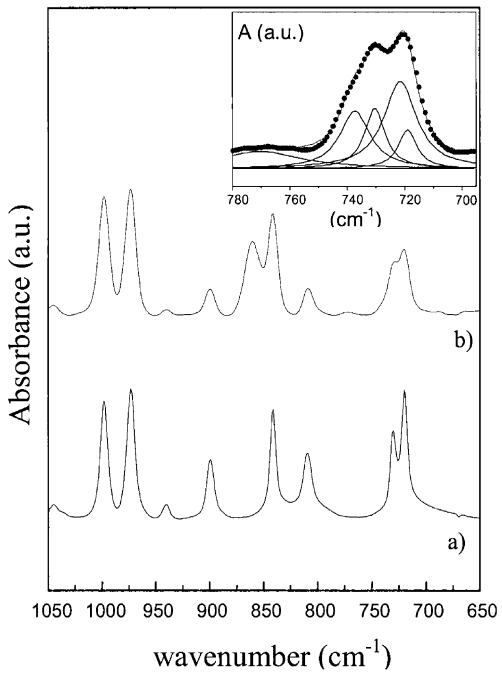

Fig. 4. FTIR spectra of PP/LDPE blend samples milled for (a) 0 min and (b) 70 min. Insert: curve fitting of the rocking vibration absorbance peaks in the range 780–690 cm^{-1}.

contribution at 737 cm^{-1}. This new peak was assigned to rocking vibration of $-(CH_2)_x-$ groups ($x \geq 3$) present between tertiary carbon atoms of polypropylene whose milling-induced macroradicals reacted with polyethylene chains.

Table 1 reports the intrinsic viscosity of milled LDPE, *i*PP and LDPE/PP blend at different milling times. Intrinsic viscosity of LDPE and LDPE/PP blend is unaffected by the extent of milling, data confirm the result achieved by infrared spectroscopy that chain degradation not even occurs after prolonged milling time. Indeed with increasing milling time the $[\eta]$ of polypropylene slightly decreases. Intrinsic viscosity measurements cannot be interpreted unambiguously for graft polymers. This is because polymers with long chain branching have a reduced volume compared to linear chains of the same molecular weight, hence, in comparing intrinsic viscosity of unmilled linear polypropylene with mechanically treated samples we can observe a decrease in the measured value due to the reduced volume of the branched chains even though the molecular weight may increase.

3.3. Fractionation of grafted copolymer

In order to prove the grafting reaction, between polyethylene and polypropylene that occurred during the milling process, selective dissolution was performed. The procedure was to extract the blend of the two polymers with xylene at 80 °C, (which does not dissolve PP) and then to show that the extract, recovered by evaporating the solvent, had IR

Table 1
Intrinsic viscosity measurements $[\eta]$, of LDPE, PP, and PP/LDPE samples milled for different periods

Milling time (min)	$[\eta]$ (dl/g)		
	LDPE	*i*PP	PP/LDPE
0	0.36	1.2	–
10	0.37	–	–
30	–	1.1	0.8
50	0.39	0.8	0.8

characteristic bands indicative of PP/PE grafting. Graft copolymer formed by the reaction of LDPE and PP are expected to have solubility intermediate between the constituent polymers to be present in the soluble fraction at the temperature 80 °C. Further the extent of solubility of the graft polymer in this fraction is an indication of the extent of the grafting reaction. Blank on milled pure polypropylene was used to check the insolubility under the same experimental conditions. The yield of the extraction of two samples, 30 and 50 min milled, was 34 and 40% (w/w), respectively. Both the fractions were studied by IR spectroscopy. In Fig. 5, the presence of graft polymer characteristic peaks at 860 cm^{-1} was observed in the soluble and insoluble fraction, although LDPE characteristic bands

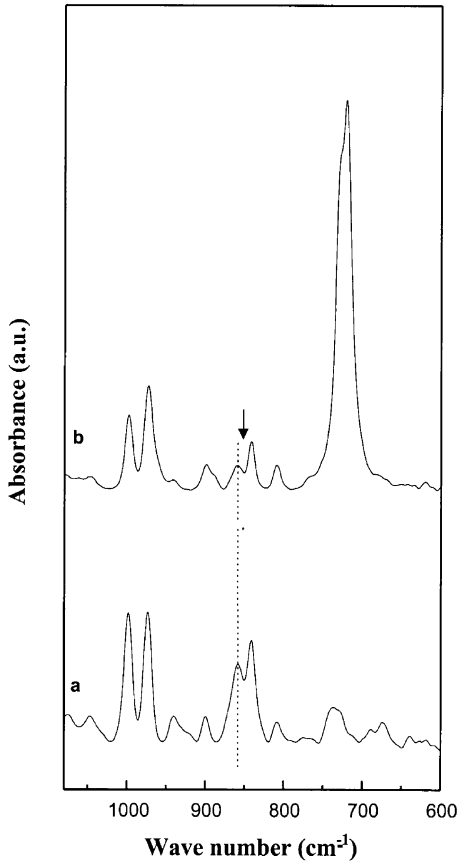

Fig. 5. FTIR spectra of (b) soluble and (a) insoluble, fractions obtained from selective extraction test of 70 min milled *i*PP/LDPE blend.

Table 2
Thermal behavior of unmilled and milled LDPE, *i*PP, and *i*PP/LDPE blend samples

Material	Milling time (min)	T_m (°C)	ΔH_f (J/g)	Crystallinity (%)
LDPE	0	111	130.1	45
	30	111	137.5	47
	50	110	113.3	39
*i*PP	0	164	86.5	44
	30	161	78.7	40
	50	161	58.2	29
LDPE in blend	30	110	12.8	22
	50	110	10.7	18
	70	110	4.5	8
*i*PP in blend	30	162	59.4	37
	50	162	51.0	32
	70	163	20.4	13

were present only in the soluble phase. The compositions of the soluble fraction of the two samples were determined by the method described in Section 2 using the calibration curve: $\ln(A_{1377\ cm^{-1}}/A_{719\ cm^{-1}}) = -0.032(\%PE) + 1.74$, and, respectively, 60 and 50% (w/w) of LDPE were measured against 40 and 50% of PP. The fact that no xylene-insoluble material was observed at 120 °C rules out the possibility that some crosslinked gel was formed during the mechanical alloying.

3.4. Differential scanning calorimetry analysis

Table 2 shows the detailed results obtained from differential scanning calorimetry (DSC) measurements. The endothermic peak temperatures of separately milled LDPE are quite stable whereas the separately milled PP thermograms indicate a decrease in the melting temperatures after ball milling. The melting enthalpies, as determined by DSC, tend to decrease as the milling time rises and this effect is especially observed for mechanically treated blend LDPE/PP. The crystallinity percentage, C (%), was calculated according to Eq. (1), the values for complete crystallinity ($\Delta H_{100\%\ crystalline}$) were given in the literature (290 J/g for LDPE; 198 J/g for *i*PP) [16] and ΔH_{melt} is the melting enthalpy recorded at the second heating scan:

$$C(\%) = [\Delta H_{melt}/\Delta H_{100\%\ crystalline} \times 100] \quad (1)$$

Samples exhibit a smaller melting enthalpy with the increase of milling time indicating an amorphization of the crystalline polymers. The comparison among crystallinity data reported in Table 2, shows that LDPE amorphization is strongly affected by the reactive PP macroradicals rather than the ball milling treatment itself. The compressive and shearing deformation generated by collisions is expected to produce breakage of chains mainly in amorphous phase so that although grafting and branching reactions takes place between the amorphous chain segments of polypropylene and polyethylene, the chemical modifications reduce the chain mobility and the extent of recrystallization occurring during the first calorimetric cooling step.

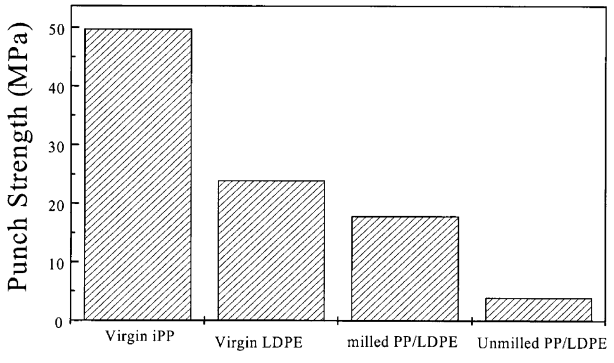

Fig. 6. Comparison of punch strength measurements performed on untreated polymers (LDPE, *i*PP), unmilled PP/LDPE mixture and 30 min milled PP/LDPE blend.

3.5. Mechanical properties measurements

To ascertain the effect of mechanical alloying on the physical properties of LDPE/PP blend, punch strength testing has been performed on specimens before and after milling. Results of these tests are displayed in Fig. 6 for unmilled mixture, 30 min milled blend and corresponding untreated polymer samples are included for comparison. As expected, the mechanical properties of an unmilled PP/LDPE mixture are significantly worse than that of the two pure polymers because of their intrinsic incompatibility. Nevertheless, the grafting between PP and LDPE produced by mechanical alloying leads to a sort of compatibilization of the blend with a significant improvement (350%) in the mechanical properties of the material. As it is well known, mechano-chemical effects act mainly on the particle surface and such a graft polymer works as interfacial agent to improve blend properties.

4. Conclusion

In this study, two different polymer, LDPE, *i*PP, and the blend LDPE/PP, have been subjected to CO_2 assisted high-energy ball milling, CBM, to investigate their response to this solid-state processing technique. Our findings suggest that CBM of polymers does not yield chains degradation but rather results in new bonds formation, namely the chains breakage forms free radicals and the free radicals recombine to form graft polymers and copolymers. FTIR spectra pointed out that structural changes induced by mechanical treatment have a strong dependence on the milling time. DSC analysis also provided evidence that CBM produces significant morphological and chemical changes and xylene fractionation of the total product of the polymeric reaction into its components demonstrated the presence of graft copolymers. Grafting of polypropylene chain segment on polyethylene leads to the formation of graft copolymers which acts as compatibilizer reducing the interfacial tension and increasing the adhesion at the interfaces between the two phases. The mechanical properties of the milled blends are consequently drastically improved compared to unmilled mixture. In conclusion, the present study has demonstrated that miscibility of LDPE and *i*PP by CO_2 assisted mechanical alloying begins to occur after a short period of ball-milling. One of the ways that carbon dioxide are believed to be effective is to speed up the mechanical alloying by its explosive evaporation.

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