A STUDY ON THERMAL AND MECHANICAL PROPERTIES OF MECHANICALLY MILLED HDPE AND PP

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Abstract: In this study, mechanical mixing of HDPE and PP was performed via ball milling. Prepared compositions were 75/25 , 50/50 , 25/75 w/w HDPE/PP. Milling time and ball to powder ratio (B/P) were kept constant and system was cooled by adding solid CO_2 to improve the milling efficiency. To compare these systems with traditional methods, mixtures were also melt mixed by Brabender Plasti-Corder. Both milled and melt mixed systems were examined with DSC for thermal properties and tensile testing for mechanical properties Results are discussed by comparing milled , melt mixed and as-received polymers. It is observed that, unlike ball milled systems, in melt mixed systems mechanical properties are composition dependent. In addition , ball milling results in amorphization of both polymers and very high amounts of PP (75wt %) creates very amorph HDPE structure.

Key words: Ball milling, HDPE, PP, polymer mixture.

1.INTRODUCTION

Polypropylene (PP) and high density polyethylene (HDPE) are the most commercial thermoplastic materials used in many applications. Elastic properties of PP makes it a good choice for structural applications. However, because its glass transition temperature (Tg) [1] is relatively high (-20°C), mechanical properties of PP gets worsen as temperature decreases. Low Tg (-110°C) [1] and 60-80 % crystallinity of HDPE makes it suitable when good impact and mechanical properties are required at low temperatures.

Low temperature mechanical properties of PP can be improved by blending it with HDPE. However, PP and HDPE are not miscible.[2] At molecular levels, phase separation is observed which leads to inferior mechanical properties. In the literature lots of additives are used for compatabilization of PE/HDPE blends [3]. These additives are incorporated into blends in low amounts to improve interfacial adhesion between polymer phases in melt state.

Recently, ball milling is employed to immiscible polymers to enhance compatibility of phases in solid state. Since the method involves more than one material, it is also referred as mechanical alloying. Apart from phase compatibility, decrease in molecular weight , grafting of polymer chains and amorphization of crystal polymers are also observed in some ball milled polymer mixtures [4,5,6] .Results of ball milling are strongly material and process dependent. Effect of ball milling on various polymer systems have been investigated such as PET-PBT [7], PMMA-PI and PMMA-PEP [8], LCP-PET [9].

In ball milling of polymers, process conditions are adjusted such that both polymer milling and phase miscibility are observed simultaneously. To achieve this, polymers should be crushed and diffused into each other. By their nature, at ambient temperatures most polymers are found to be above their Tg and behave in a ductile manner which prevents milling. Thus to obtain efficient milling, system, in which polymer is milled, should be cooled down near or below Tg. Solid CO_2 of which solid-gas transition temperature is – 78.5°C at 1 atm is can be used for this purpose.

The aim of current work is to examine the effect of ball milling on PP- HDPE systems in terms of mechanical and thermal behavior. For this purpose, ball milled and melt mixed polymers were compared with each other.

2. EXPERIMENTAL PROCEDURE

MH 418 PP, S 464 HDPE are commercial grade raw materials supplied from Petkim. Some physical properties of polymers are given in Table 1. Studied compositions are given in Table 2.

Table 1. Physical Properties of PP and HDPE

Polymer	Density (g/cm^3)	Melt Flow Index (MFI)[a]	Tg(°C)
PP	0.880	1.77	-20
HDPE	0.940	0.31	-110

a: 190°C, 2.16 kg

Table 2. Studied Compositions

Compositions	PP wt %	HDPE wt %
Pure PP	100	-
Pure HDPE	-	100
25 PP	25	75
50 PP	50	50
75 PP	75	25

To prepare melt mixed systems according to their percentage ratios , polymer granules were hand mixed and then melt mixed by Brabender Plasti-Corder .In all systems, mixing time, rotation rate and mixing temperature were 15 minutes, 45 rpm and 190°C, respectively. The working temperature was chosen such that both polymers are in molten state without any degradation during mixing. Solidified polymer mixtures were hot pressed in the form of sheets at 190°C and water cooled. Dumbbell shaped tensile test samples were prepared from them.

For milling, as received polymers were firstly grinded below 30 mesh (-590μm) to increase the efficiency of milling process. For each system, 1 gram of polymer mixture was milled with 30 g of stainless steel balls. (B:P=30.1).In each time , system was cooled by adding approximately 10 g of solid CO_2 into milling chamber just before start of the milling operation. Under these conditions ball milling was carried out for 15 minutes. Milled polymers were than hot pressed at 190°C and tensile specimens were prepared in a similar manner with melt mixed systems.

Specimens of both melt mixed and ball milled polymers were subjected to tension tests by Lloyd LR 5K with a rate of 50 mm/min. Thermal properties were studied by Dupont Thermal Analysis 2000 DSC 910 S. Samples were heated from room temperature to 200°C at 10°C/min heating rate.

3. RESULTS AND DISCUSSION

Tensile testing on 5 specimens of all compositions were averaged and the results discussed for both melt mixed and ball milled systems. Young's Modulus , strain at break and work to break values were measured to investigate the mechanical behavior of mixtures. Obtained data are given in Figure 2.

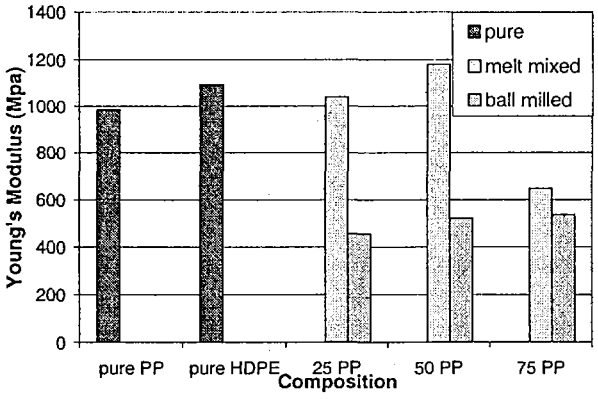

Figure 2a. Young's Modulus Values of Pure, Melt Mixed and Ball Milled Systems

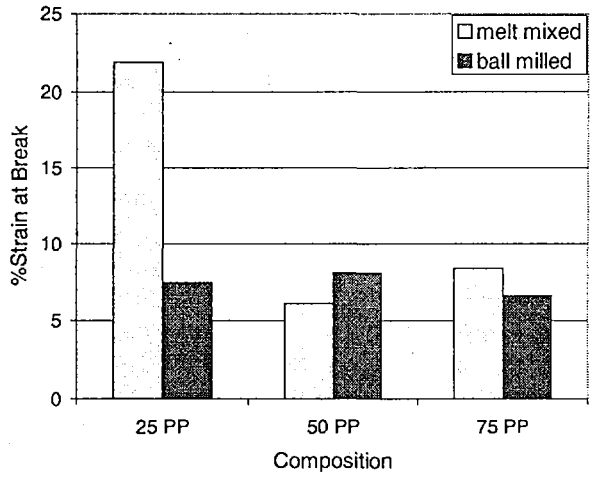

Figure 2b. Strain at Break Values of Melt Mixed and Ball Milled Systems

It was observed that pure polymers have approximately equal Young's modulus values. In common sense, melt mixing didn't change the stiffness except 75PP system. For this composition the value drops down to 650 MPA. On the other hand , for ball milled samples it can be said that Young's modulus is not affected from the composition the value of which lies between 550-450 MPa. However, it is clear that ball milling results less stiff material than melt mixed.

Pure PP and HDPE have strain at break values 366% ,636 % respectively. As seen in Figure 2b strain at break values indicates a sharp decrease for both melt mixed and ball milled systems. Generally, for melt mixed and ball milled systems this value does not exceed 10 %.

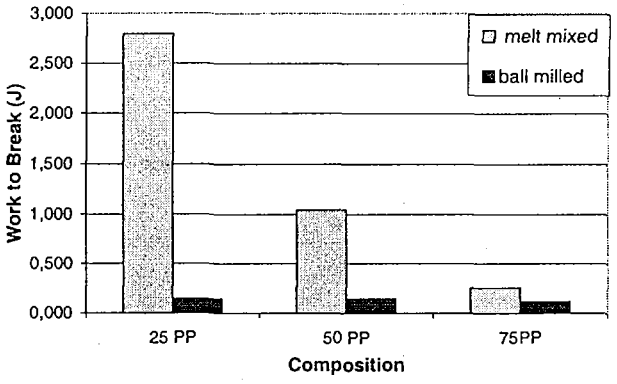

Figure 2c. Work to Break Values of Melt Mixed and Ball Milled Systems

Work to break values of pure PP and HDPE are 37 J and 113 J respectively. It can be seen from Fig 2c ,in melt mixed systems, as the amount of HDPE decreases , work required to break samples also decreases. This property can be attributed to the high energy absorption capability of HDPE. This linear relation , however, is not observed in the ball milled systems.

DSC studies gave valuable information about the thermal properties of polymers and effect of processing conditions. In all DSC thermograms, each polymer showed its own endothermic melting peak. It is observed that Tm is not effected from the processing condition, melt mixed or ball milled.

Another valuable data obtained from the DSC thermograms are the % crystallinity of the polymers. The crystallinity percentage of polymers was calculated according to Eq. (1) .The values for complete crystallinity are given in literature (198 J/g for PP [5] and 285.8 J/g for HDPE[10]). The percent crystallinity is calculated by:

$$\%Crystallinity = \left[\frac{\Delta H_{melt}}{\Delta H_{100\%crystalline}}\right] \times 100 \qquad (1)$$

DSC peaks show that crystalline amount is strongly process dependent Effect of process on % crystallinity of PP and HDPE is given in Figure 3.

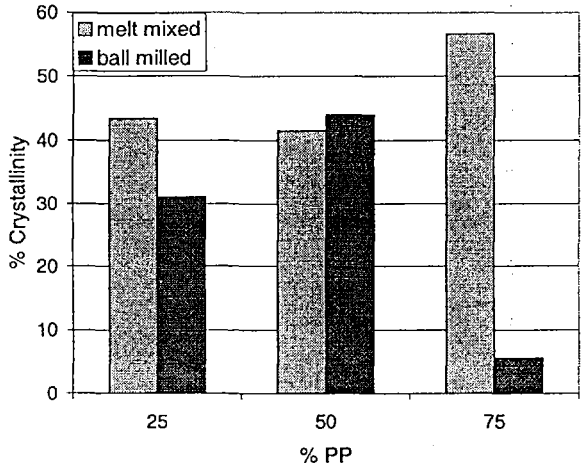

Figure 3a. Effect of Process Method on Crystallinity of HDPE

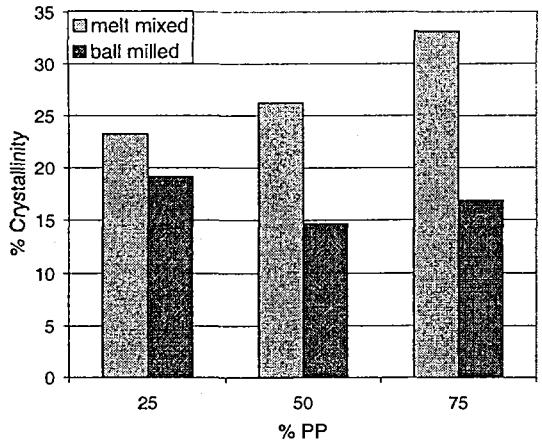

Figure 3b. Effect of Process Method on Crystallinity of PP

It is obvious in Figure 4 that ball milling decreases the crystallinity of the polymers. Compressive and shear deformation introduced during ball milling probably destroys the regular arrangements of polymer chains. The amorphization of polymers is material dependent. However, in our case the polymer was melt mixed or ball milled with another polymer which may also affect the amorphization. Figure 4 explores the situation.

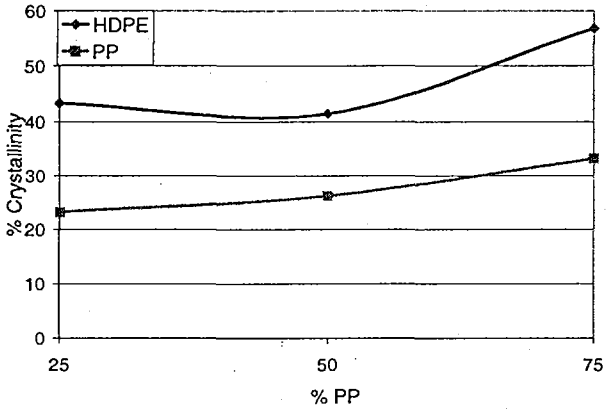

Figure 4a. Crystallinity of Melt Mixed Systems

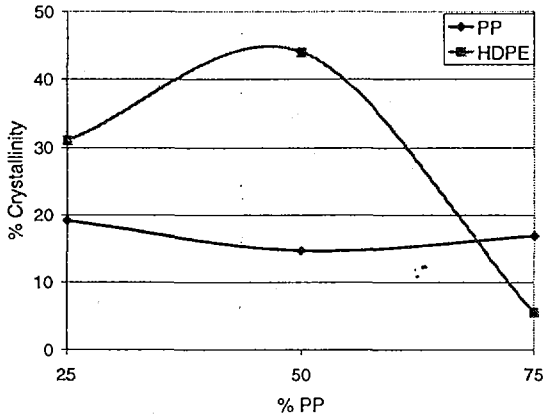

Figure 4b. Crystallinity of Ball Milled Systems

In Figure 4a , the general trend is increase in crystallinity with increasing PP amount. On the other hand , in ball milled systems , high amount of PP results very low crystallinity in HDPE. An inverse relation between crystallinity content of polymers , as PP amount increases , can be figured out. The change in HDPE crystallinity is more clear.

4.CONCLUSIONS :

In this study effect of ball milling on HDPE and PP mixtures were examined. Tensile tests and DSC studies were carried out to characterize the systems mechanically and thermally . Ball milled samples were compared with melt mixed systems to figure out the milling.

From the literature it is known that these two polymers are immiscible and without a compatibilizer blends of these polymers have low mechanical properties. Tensile tests showed that ball milling does not make a contribution to improvement of mechanical properties. In all mechanical tests it is observed that mechanical properties are composition dependent in melt mixed systems. However, for ball milled systems , composition does not affect the mechanical properties. Low percent strain and moderate Young's Modulus values are indication of high immiscibility of the phases.

It should be noted that at ball milling temperature PP is in glassy state whereas HDPE is above its Tg. Therefore, the processes caused PP to fracture in brittle manner. It would not be wrong to say that the deformation in PP is largely in macro scale. However, deformation of chains and crystals is more dominant for HDPE. From the DSC results, it can be observed that HDPE is more sensitive to ball milling conditions. An increase in PP content makes HDPE less crystalline which supports that in HDPE micro scale deformation is more dominant. It can be thought that glassy PP contributes the destroy of crystalline regions of HDPE especially at high PP compositions.

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