Title:
New Approaches to the Processing of Rutile-Filled Polyolefins

Intro:

Titanium dioxide is by far the most widely used white pigment for plastics (1). It is found in nature in three different crystal modifications: rutile, anatase, and brookite (2). Among the three, rutile is the crystal modification that is the most frequently used as a pigmentation agent. Indeed, aside from being the most common crystalline form, rutile has a higher refractive index (2.70) than anatase and brookite, which gives it superior hiding power (3). Naturally-occurring rutile is usually colored, sometimes even black. Therefore, pigment-grade material is generally obtained by synthetic means. The two main methods of preparation are the sulfate process and the chloride process. The first method involves the preparation of a titanium (IV) sulfate solution followed by the hydrolysis of the sulfate through the addition of a base (2,3). The hydrated oxide is subsequently calcinated at 1000 °c to produce rutile of a desired particle size. The second method involves the formation of titanium tetrachloride and its subsequent vapor-phase oxidation with oxygen (2,3). But, differences between commercially available rutiles are not limited solely to differences in manufacturing processes. Particle size and surface treatment are also important features that can be used to differentiate rutiles. The use of surface treatment on rutiles to modify the polymer/particle interaction is becoming increasingly common. Both inorganic and organic coatings are used; inorganic coatings usually are oxides such as alumina or silica and organic coatings generally consist of amines, polyols, fatty acids, or siloxanes (3). These coatings, by modifying the polymer/particle interaction can, for example, improve the weatherability of rutile-filled systems by preventing the pigment from acting asa catalyst for photodegradation (3). They can also provide an excellent means of improving the dispersibility of rutiles in organic polymer matrixes thereby lowering melt viscosities and increasing the opacity of rutile-filled compounds (3). Since surface treatments applied to rutiles can bring about dramatic changes in the nature of the interaction between the pigments and host polyolefin resins, they most probably could also influence the way in which a rutile can interact with other additives commonly present in commercial polyethylene resins. Earlier work in this laboratory has already pointed out the effect of a number of other additive interactions on the performance of fluorocarbon elastomer processing additives in particular. In these studies, fluorocarbon elastomers, which are considered to act as external lubricants (4-7), were found to be sensitive to factors that can either restrict, through physical or chemical interactions, their mobility in polyethylene melts or promote the abrasion of the surface layer they form on metal parts. Given the importance of both rutile and fluorocarbon elastomers in linear low density polyethylene film manufacturing and early reports that there may be negative interactions between the two (8),a series of experiments was designed to investigate the effect of various rutiles on the performance of this type of processing additive. The objective of the investigaton was not only to study the effects of these pigments on the flow properties of processing additive-containing polyethylenes but also to rationalize any observed differences in the interactive effect of the various rutiles.

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No. 7

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INTRODUCTION

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The use of surface treatment on rutiles to modify the polymer/particle interaction is becoming increasingly common. Both inorganic and organic coatings are used; inorganic coatings usually are oxides such as alumina or silica and organic coatings generally consist of amines, polyols, fatty acids, or siloxanes (3). These coatings, by modifying the polymer/particle interaction, can , for example, improve the weatherability of rutile-filled systems by preventing the pigment from acting as a catalyst for photodegradation (3). They can also provide an excellent means of improving the dispersibility of rutiles in organic polymer matrixes thereby lowering melt viscosities and increasing the opacity of rutile-filled compounds (3).

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EXPERIMENTAL

Materials

The fluorocarbon elastomer processing additive used in the course of this study was a commercially available copolymer of vinylidene fluoride and hexafluoropropylene known as Dynamar (TM) Brand Polymer Processing Additive FX-9613. This product is a free flowing powder containing ten weight percent inorganics (primarily microtalc) and will be referred to hereafter as PPA.

The linear low density polyethylene (LLDPE) used in this study was a 0.8 melt index resin with a density of of 0.918 g/cm^3 containing 2-3 weight percent hexene-1 as a comonomer. The resin contained no additives except for a minimal amount of a hindered phenolic antioxidant.

The titanium dioxides considered in this work were commercially available pigment-grade rutiles commonly used in blown flim extrusion operations. They are listed in Table 1 and will be referred to in the text by the indicated abbreviations.

Inverse Gas Chromatography Measurements

The method of inverse gas chromatography (IGC) has proven to be useful in the determination of interaction tendencies for non-volatile components of polymer systems. Various theoretical and experimental aspects of the IGC method have been considered in several recent publications (9). Specifically, recent developments have permitted the determination of acid/base interaction potentials for polymers and pigments alike (10). These developments were applied in the present work to evaluate the relative acidities or basicities of rutiles and fluorocarbon elastomer processing additives, so as to gauge the interaction tendencies among these materials.

A Perkin-Elmer dual-column gas chromatograph with thermal conductivity detector was used for retention time measurements at 30 °C. Two probes were involved in these experiments. The basic reference probe was n-butylamine, the acid reference probe was t-butyl alcohol. Retention volumes (V_g) for minute injections of vapors (< 1 microliter) were measured at least three times, and in some cases in more numerous repetitions. The reproducibility of the retention volumes was found to be better than 3%.

Inherent Agglomeration Index Measurements

An additional important factor affecting the performance of particulate additives in a polymer matrix is the dispersibility of the solids in the host polymer. Since rutiles may be variously surface-modified, as noted, it is important to consider their dispersibility in quantitative terms. In this regard it has been useful to evaluate the agglomeration tendency of particulates, or the strength of interparticle bonds in pigment clusters. The key parameter is an inherent agglomeration index, C, which may be measured by applying the principles of powder rheology. A detailed account of the procedure has been given elsewhere (11).

The inherent agglomeration index (C) of the various rutiles was determined by milling the dry powders in a Brabender mixing chamber under controlled variable loads. The specific procedure involved introducing 660 grams of dry rutile powder in the mixing chamber of a Brabender Plasticorder fitted with sigma blades, placing a free floating glass plate on the sample and loading it with a calibrated weight; the calibrated weight exerting a normal force on the powder. The samples were then sheared at a constant rotor speed (50 rpm) until a constant torque value was obtained. The same procedure was repeated for all samples when a series of calibrated weights was placed on the glass plate, and the torque generated as a function of the load measured. The torque generated was found to be a linear function of the applied load and followed the Coulomb equation:

$$Fe = CA - \mu A\ Fn \qquad (1)$$

where Fe is the equilibrium torque or resistance to shear, Fn is the applied load, μ is a frictional coefficient due to the presence of the sample and A is a torque component due to the operation of the mixer when empty. Once A was obtained by calibration, C was measured from an extrapolation to the intercept of a plot of Fe as a function of Fn. The results of this procedure for two typical rutiles (11) are illustrated in Figure 1. They show that linearity is well obeyed in these cases. Adherence to linearity was also obtained in the cases studied here. The variation in slopes for the two rutiles considered in Figure 1 is assumed to reflect a difference in the frictional coefficient for interparticle movement. The difference is most probably due to the type of surface coating on the pigment (11) It should also be noted, as expressed in equation 1, that the value of the equilibrium torque should be independent of shear rate or rotor speed. Experiments performed at constant applied load and variable motor speed confirmed the prediction.

Capillary and Blown Film Extrusion

Preparation of both control and PPA-containing samples for capillary extrusion was done with an HBI system 40 Torque Rheometer using a Rheomix 3000 mixer with roller blades. The blended materials were ground at ambient temperature prior to their evaluation by capillary extrusion.

Capillary extrusion to determine the shear rate at which the onset of melt fracture occurred for the various samples was done with an Instron Model 4202

System equipped with a 3210 Capillary Rheometer using a flat entry die, 0.51 mm in diameter and with a length/diameter ratio of 40:1. A temperature of 190 °C and a 10 minute dwell time were used. Viscosities are reported uncorrected for end effects. Melt fracture analyses were done by a combination of visual inspections of photomicrographs (30x) of air cooled samples as well as by analyses of rheometer plots of apparent viscosity vs apparent shear rate.

Blown film extrusion experiments were performed on a 4.41 cm lab-sized film line with a length/diameter ratio of 32:1. The die was 5.08 cm in diameter with a gap of 0.635 mm. The temperature profile ranged from 177 °C to a maximum of 215 °C producing melt temperatures of approximately 220 °C.

Samples for capillary extrusion were obtained by preparing combined masterbatches in LLDPE of 40 % rutile, and 2% PPA using a compounding sequence of 2 minutes at 15 rpm, 1 minute of ramping to 50 rpm, and 6 minutes at 50 rpm. The mixing bowl was heated at 230 °C for 1 minute and 180 °C for the remaining 7 minutes. The masterbatches were then let down with more LLDPE to final concentrations of 10% rutile and 500 ppm PPA and compounded again using the sequence described above. Separate masterbatches of 30% rutile and 2% PPA were also preprared in a similar fashion and were subsequently let down with LLDPE to final concentrations of 10% rutile and 500 ppm PPA and compounded using the procedure given above. A control containing only PPA was prepared in a similar fashion. Finally, samples containing only 5% rutile were prepared by tumble-blending and melt mixing, as described above, the appropriate amount of rutile and LLDPE.

Samples for blown film extrusion were obtained by first preparing separate masterbatches of 30% rutile, 2% PPA and 2% PEG in LLDPE using a tumble blender. The masterbatches were then let down with LLDPE and compounded with a twin screw extruder, and continuously feed to a single screw extruder fitted with a die face pelletizer. Final concentrations were 500 ppm PPA, 10% rutile, and, when present, 2000 ppm PEG.

RESULTS AND DISCUSSION

The effect of incorporating a 5% loading of rutile on the apparent viscosity and shear rate for onset of fracture in the LLDPE resin in the absence of any processing additive was first measured by capillary rheometry. The results, given in Figure 2, show that the five different rutiles from Table 1 increased the apparent viscosity of the resin and slightly lowered the shear rate for the onset of melt fracture. Note that rutile C caused the most noticeable increase in viscosity. As can be seen in Table 1, rutile C is the only one considered here that was described by its manufacturer as having neither an inorganic nor an organic coating. These results thus illustrate the kind of flow behaviour modification of pigmented systems that can be achieved by the use of surface coatings.

Similar measurements were then performed with the same resin, but this time both rutile and PPA were incorporated using either separate rutile and PPA masterbatches or a combined PPA/rutile masterbatch.

Capillary extrusion results for rutile/PPA combinations prepared using separate masterbatches are presented in Table 2. The results show that all rutiles interfered, to some extent, with the processing additive. Indeed, increases in apparent viscosity of 15% to 30% were observed in all cases when compared to a PPA-containing, but rutile-free, control at 600 1/s. It is noteworthy that the increases in apparent viscosity for compounds with rutile B and rutile C were accompanied by the appearance of melt fracture at much lower shear rates than that for the other compounds or the control resin containing PPA only. Therefore, the consequences of PPA/rutile interaction can range from a simple increase in melt viscosity to the complete failure of the processing additive to postpone the onset of melt fracture.

The results for the rutile/PPA combinations prepared using combined masterbatches are given in Table 3. Upon examination of the results, it is clear that the use of combined rutile/PPA masterbatches can further increase the degree to which rutiles can interfere with the performance of the processing additive. The same phenomenon has already been observed in this laboratory with silica-based antiblocking agents (12). Apparent viscosity values, as measured at 600 1/s, are reported only for compounds containing rutiles A, D, and E. The occurence of severe melt fracture, coinciding with wide fluctuations in extrusion pressures at shear rates higher than 400 1/s, prevented the computation of a meaningful viscosity value at 600 1/s for compositions containing rutile B and C. However, comparative values for all five samples were measurable at 400 1/s and are also reported in Table 3. The viscosity data confirms the increased interference for all samples.

In light of the results obtained by capillary rheometry techniques, it was decided to investigate the behaviour of compounds containing rutile A and rutile C under blown film extrusion conditions. Rutile A and rutile C were chosen because they represented, in the series of pigments considered here, extremes in behaviour in their effect on the processability of PPA-containing polymers.

The samples for blown film extrusion were prepared using separate masterbatches to reproduce the compounding sequence generally used in the field (Figure 3). Final concentrations were 10% rutile and 500 ppm PPA.

The results for the two PPA/rutile combinations, shown in Table 4, closely parallel the capillary extrusion data. Again, rutile C severely interfered with the processing additive while rutile A did not do so to any significant extent. But, a slight degree of melt fracture was noticed for the compound containing rutile A when the output rate was increased. This result suggests that while the use of certain coated rutiles can certainly help avoiding melt fracture problems, the success of this strategy depends on the intensity of the mixing during compounding operations as well as the extrusion output rates.

Another approach to lessening detrimental interactions that has been studied in this laboratory is the addition of a synergistic PPA blend (13-14). As can be seen in Table 4, the substitution of the neat PPA by a 1:4 PPA/synergist blend in the compound containing rutile C, allowed for the rapid and complete elimination of melt fracture. It is noteworthy that the synergistic blend in the presence of rutile C outperformed the neat fluorocarbon elastomer in the presence of the well behaved rutile A even at higher output rates. The use of a synergistic blend could therefore be another solution to melt fracture problems in addition to the use of optimized rutiles (*).

(*) An optimized PPA/Synergist combination, Dynamar (TM) Brand Polymer Processing Additive FX-5920, is now commercially available from the 3M Company.

All the capillary and blown film extrusion data discussed above clearly illustrate how a simple change in the type of rutile incorporated in a resin can lead to unanticipated melt fracture problems. Therefore, it is important to identify the reasons for these wide variations in behaviour and to develop strategies that will allow for a certain measure of control over rutile/PPA interactions. The rutiles considered here differ from each other in the nature and consequently the characteristics of their surfaces. As can be seen in Table 1, three of these rutiles had both organic and inorganic coatings, one had only an alumina-based inorganic coating, while another had no coating at all. Since surface coatings strongly influence dispersability and acid-base characteristics of rutiles (11), the influence of these parameters on the effectiveness of fluorocarbon elastomer processing additives were investigated.

The relative acidity or basicity of rutile surfaces was determined by inverse gas chromatography. This technique has already been used in the past to fulfill this purpose and is discussed at length in other recent publications (9). Briefly, a reference acid probe and a reference base probe as well as the proper experimental conditions were selected using and adapting the concepts of Drago (15). The specific retention volumes, Vg, were then used to define an acid/base interaction parameter using the following expression:

$$\theta = 1 - (Vg)b/(Vg)a < 0 \qquad (2)$$

$$\theta = (Vg)a/(Vg)b - 1 > 0 \qquad (3)$$

where the a and b subscripts refer to the reference acid and base vapors. A negative value of θ then indentifies the pigment with an acidic surface interaction potential while a positive value of θ identifies the pigment with a basic surface interaction potential. When θ is close to being null, the material is considered as amphipatic in nature.

The dispersibility of the various rutiles was assessed by measuring their inherent agglomeration indexes using the technique and principles described earlier. This technique has already been used in the past (11) to assess the dispersibility of a series of rutiles in a low density polyethylene matrix. In that study, the dispersibility of the rutiles was also studied by contact microradiography and a direct relationship was found to exist between the quality of the dispersion and the agglomeration index; the rutile displaying the lowest inherent agglomeration index, C, giving the best dispersion.

Acid-base interaction potential values for the PPA and the rutiles investigated here are given in Table 5. The results indicate that while rutile B displayed a strongly basic surface interaction potential, rutile A and E displayed intermediate basic interaction potentials. On the other hand, rutile C and D were found to be essentially amphipatic or neutral. Finally, the PPA was found to be slightly acidic.

Agglomeration index values for the same five rutiles are given in Table 6. The data show that uncoated rutile C, in contrast to the coated rutiles, has a very high agglomeration index (C). Rutiles D and E displayed intermediate values of C while rutiles A and B were found to have the lowest C values. These results suggest that the uncoated rutile is the least dispersible pigment while coated rutile A is the most dispersible one. These results clearly demonstrate how surface coatings can influence the dispersibility of various rutiles.

Agglomeration index and acid-base interaction potential data have been compiled in Table 7 along with a relative ranking of PPA/rutile interference levels based on equilibrium viscosities and the shear rates for the onset of melt fracture. As can be seen, both acid-base characteristics and pigment agglomerate cohesive strength can influence the performance of fluorocarbon elastomer processing additives.

The results (Table 7) indicate that the magnitude of the interaction between the processing additive and the various pigments increases as the basicity of the rutile surface coatings increases, as illustrated by the behavior of the compound containing rutile B. This may be due to the existence of acid-base interactions between the acidic fluorocarbon elastomer and highly basic rutile surface coatings. The net result of the interaction is a depletion of the processing additive from the melt as it attaches itself onto the basic rutile surfaces.

The results presented in Table 7 also indicate that the magnitude of the interference between the pigments and the processing additive increases as the pigment dispersibility decreases. This is illustrated by the behavior of the compound containing rutile C. It is believed that the melt becomes increasingly abrasive as the pigment agglomerate size increases. As a result, the rate of removal of the additive from the die wall can eventually exceed the rate at which the additive is replenished at this site. Consequently melt fracture is affected.

Finally, the result also indicate that, aside from acid-base interactions and abrasion, intimate contact between the processing additive and large surface area inorganic materials such as pigments can alter the performance of the additive. It is believed that extensive and prolonged contact between pigment and additves, as in the case of a combined masterbatch, promotes the adsorption of the additive onto the pigment thereby depleting the melt from the additive.

CONCLUSIONS

All rutiles considered in this study were found to interfere, to some extent, with the fluorocarbon elastomer processing additive. The results, however, also showed that interferences between rutile and the processing additive can be minimized by several means. Incorporation of the pigment and PPA using separate rutile and PPA masterbatches was found to reduce interferences caused by intensive mixing and therefore intimate contact between the two components. The use of a surface coating to improve dispersibility of the pigment was also found to reduce PPA/rutile interferences; provided that the surface coating was not too basic in nature. Finally, the use of a synergistic composition was found to be very effective at reducing PPA/rutile interferences even in the most difficult case.

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TABLE 1

TiO_2 PIGMENT DESCRIPTION

CODE	FORM	MFG. PROCESS	AVG. PART. SIZE (U)	INORGANIC COATING	ORGANIC COATING
TiO_2-A	RUTILE	CHLORIDE	0.18 - 0.20	1.0% Al_2O_3 CO-OXIDIZED 0.5% Al_2O_3 FROM MFG.	0.5% PHOSPHORYLATED FATTY ACID
TiO_2-B	RUTILE	CHLORIDE	0.18 - 0.20	1.0% Al_2O_3 CO-OXIDIZED 3.5% Al_2O_3 FROM MFG.	------------------
TiO_2-C	RUTILE	CHLORIDE	0.20 - 0.30	-------------------	------------------
TiO_2-D	RUTILE	CHLORIDE	0.20 - 0.30	0.5% Al_2O_3	0.25% TRIETHANOL ETHANE
TiO_2-E	RUTILE	CHLORIDE	0.19	2.0% Al_2O_3 TRACE SiO_2 (MFG.)	0.33% PROPRIETARY

TABLE 2

CAPILLARY RHEOMETRY RESULTS FOR TiO_2/PPA COMBINATIONS

SEPARATE MASTERBATCHES

TiO_2	Apparent Viscosity at 600 S^{-1} (Poise)	Shear Rate for Onset of Melt Fracture (S^{-1})
A	3950	1600
B	4600	1000
C	4250	600
D	4050	1400
E	4600	1400
None	3400	1400

TABLE 3

CAPILLARY RHEOMETRY RESULTS FOR TiO_2/PPA COMBINATIONS

COMBINED MASTERBATCH

TiO_2	Apparent Viscosity at 400 S^{-1} (Poise)	Apparent Viscosity at 600 s^{-1} (Poise)	Shear Rate for Onset of Melt Fracture (s^{-1})
A	5700	4400	1600 (ripple)
B	8050	--	200 (sharkskin) 600 (cyclic)
C	9000	--	200 (sharkskin) 600 (cyclic)
D	7450	5350	400 (sharkskin) 800 (cyclic)
E	7240	5200	900 (cyclic)

TABLE 4

BLOWN FILM TRIAL RESULTS

TiO_2	PPA (PPM)	Synergist (PPM)	Average Output (Kg / Hr.)	Melt Fracture Status
A	500	---	8.5	Melt Fracture Eliminated Within 30 Minutes
A	500	---	11.4	Some Fracture
C	500	---	8.3	100% Melt Fracture
C	500	2000	8.6	Melt Fracture Eliminated Within 20 Minutes
C	500	2000	11.6	Melt Fracture Eliminated Within 20 Minutes

TABLE 5

ACID/BASE INTERACTION POTENTIALS (θ)
OF TITANIUM DIOXIDE SAMPLES AND PPA

TiO_2	θ @ 30°C
A	0.67
B	1.26 (most basic)
C	0.18
D	- 0.06
E	0.90
PPA	- 0.32

TABLE 6

INHERENT AGGLOMERATION INDEXES (C)
OF TITANIUM DIOXIDE SAMPLES

TiO_2	(C)
A	110
B	160
C	440
D	240
E	210

TABLE 7

INHERENT AGGLOMERATION INDEXES (C)
AND ACID/BASE INTERACTION POTENTIALS (θ) OF TITANIUM DIOXIDE SAMPLES
AND RELATIVE RANKING OF PPA/TiO_2 INTERFERENCE LEVELS

			Relative PPA/TiO_2 Interference Ranking *	
TiO_2	θ @ 30°C	(C)	Separate Masterbatches	Combined Masterbatch
A	0.67	110	1	1
B	1.26	160	4	4
C	0.18	440	5	5
D	- 0.06	240	3	2
E	0.90	210	2	3

* Interference increases from 1 to 5.

Figure 1

STEADY-STATE TORQUE AS A FUNCTION OF APPLIED LOAD

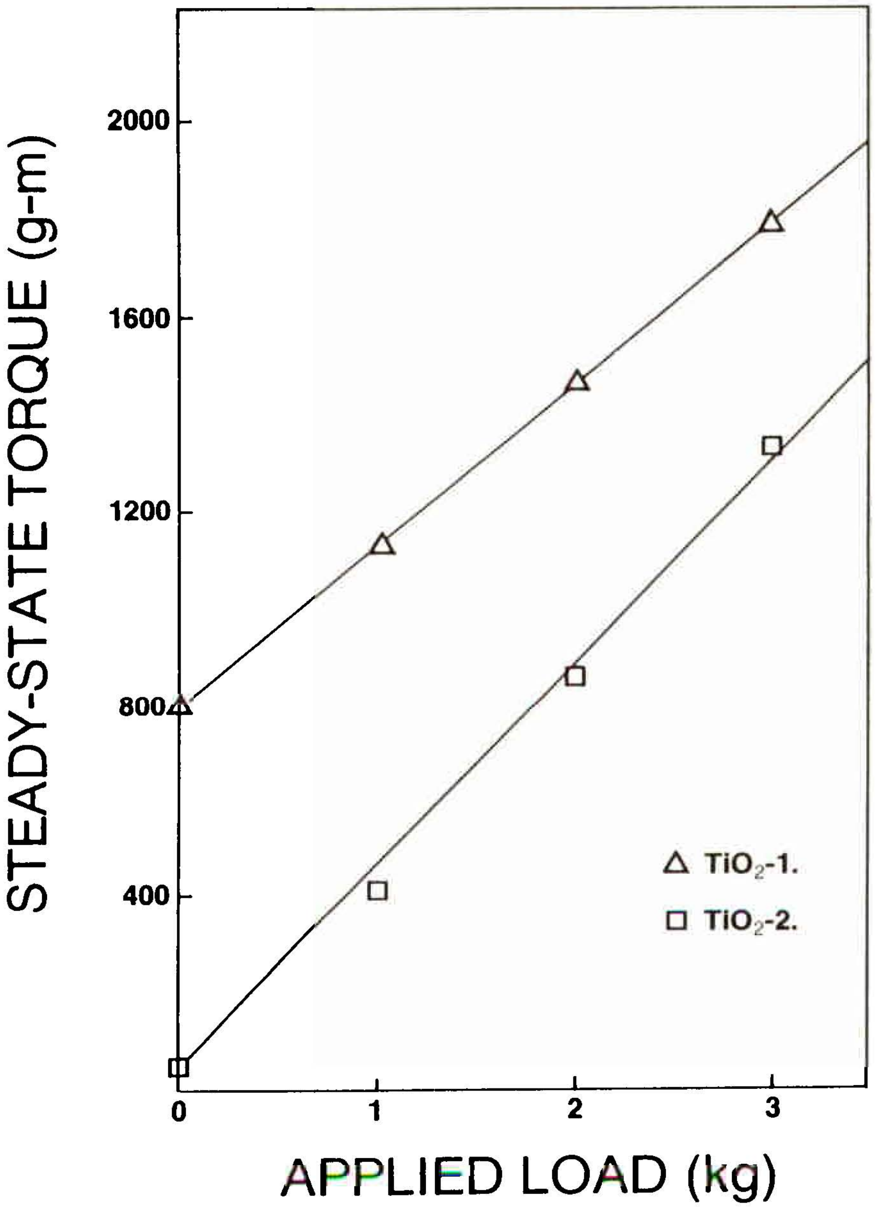


Figure 2

EFFECTS OF TiO_2's ON VISCOSITIES

5% TiO_2 in LLDPE, NO PPA

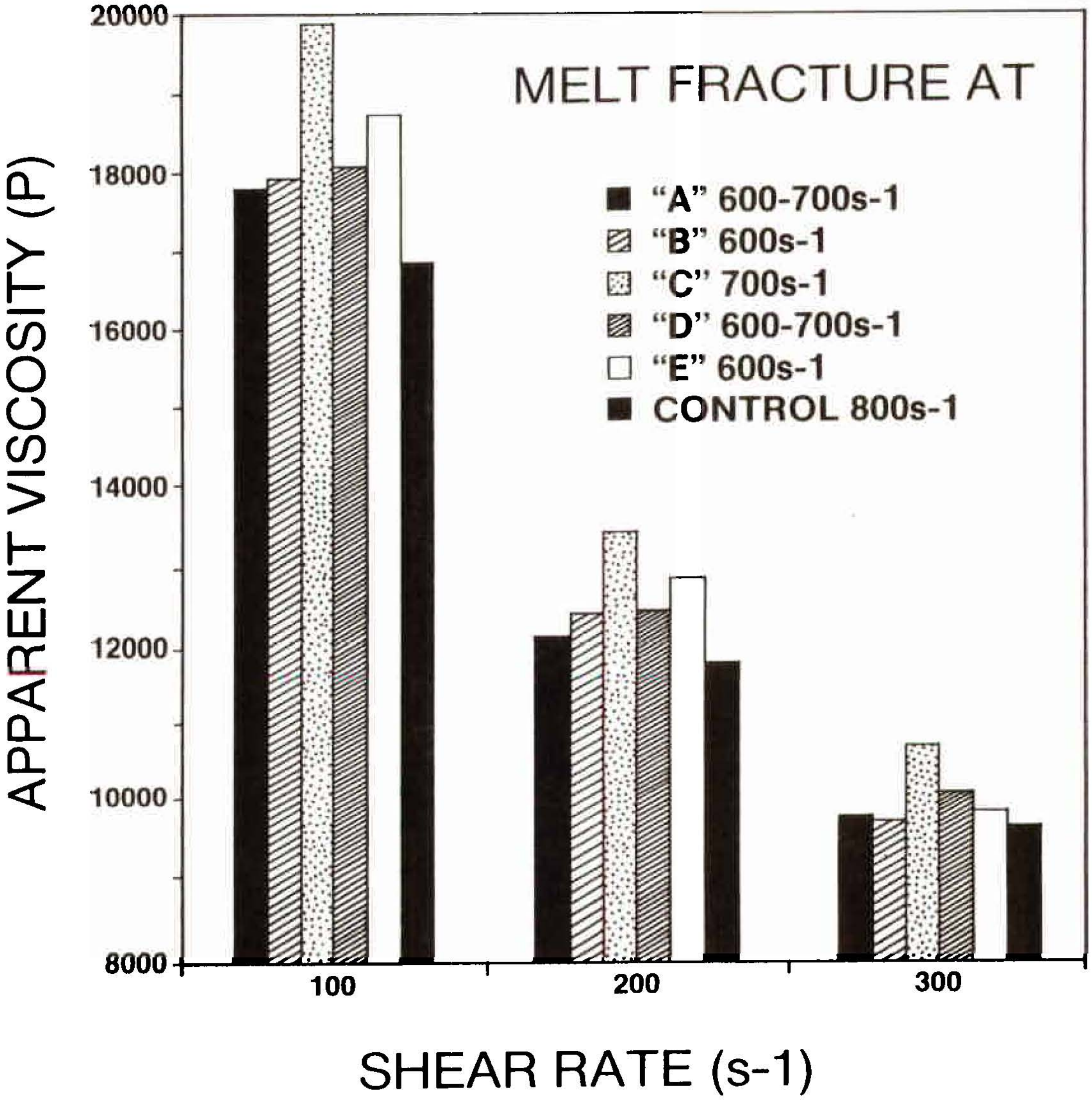
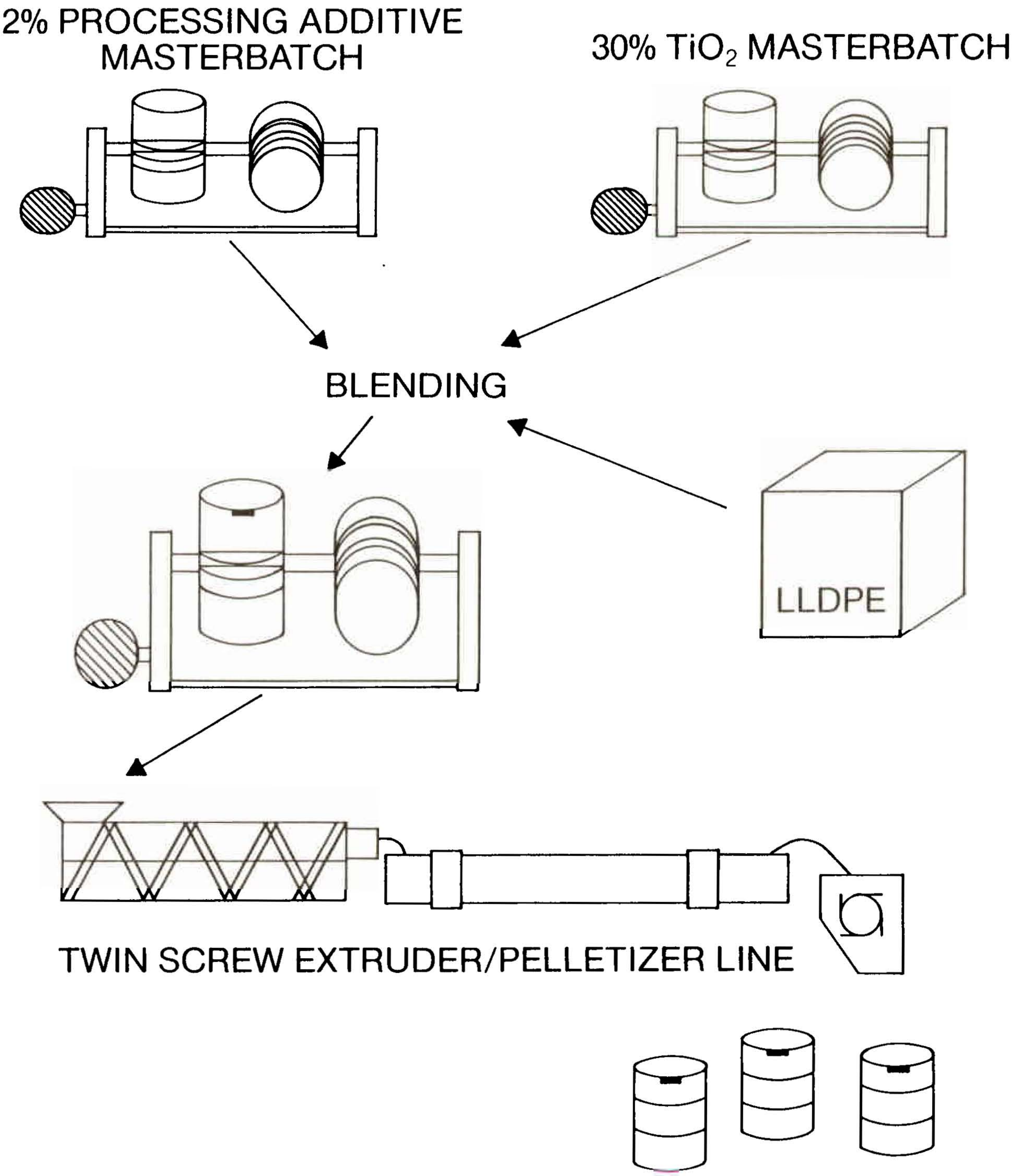


Figure 3

PREPARATION OF SAMPLES FOR FILM TRIAL



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