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CHARACTERIZATION OF FLUOROPOLYMER POWDERS MADE BY
SUPERCRITICAL ASSISTED MIXING WITH CRYSTALLINE ADDITIVES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of
Science in Engineering at Virginia Commonwealth University.

by

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Acknowledgment

I would like to express my sincere gratitude to my advisors, Dr. Mark McHugh and Dr. Gary Huvard for their guidance and financial support of this work, for I have exceedingly benefited from their vast knowledge and experience. I would also like to thank Dr. Esther Hughes who was a member of my advisory committee, for all her assistance, encouragement and suggestions that were extremely helpful. Special thanks to the members of Dr. McHugh's research group – Yongchul Kim, Jun Liu and Andrei Kostko for their participation in this project every step of the way, especially Yongchul who was responsible for making the powders used in this study. I would also like to thank the employees of ChemEngine for their assistance especially Tayloria Adams who was a big part of the viscosity studies; Julia Allen, Michael Burt and Dana Richards who were responsible for the Thermogravimetric analysis. Finally, I would not forget to thank my friends and family for all the encouragement and moral support they never failed to give throughout my graduate education.

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Abstract

CHARACTERIZATION OF FLUOROPOLYMER POWDERS MADE BY SUPERCRITICAL ASSISTED MIXING WITH CRYSTALLINE ADDITIVES

By Ntoh Atem-Tambe, Master of Science.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering at Virginia Commonwealth University.

Virginia Commonwealth University, 2005

Director: Dr. MARK A. M^CHUGH
Ph.D., Chemical Engineering

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This research project investigates a new technique to efficiently mix crystalline solid additives with polymers by gentle ball milling with steel balls in the presence of carbon dioxide (CO₂) at 17 to 30 °C and 1300 to 2500 psig. As the ball milling system is agitated, the steel balls transfer mechanical energy to the fluoropolymer and additive thereby converting them to powders. CO₂ is added into the chamber to expand the

polymer and make it amenable to impregnation by the additive. At the end of the mixing process, a free flowing powder is produced consisting of the additive coated with fluoropolymer.

The additives were extracted from the powders and intrinsic viscosity measurements were done on the remnant fluoropolymer. Viscosity studies showed that the virgin and post-ball milled fluoropolymers had similar intrinsic viscosities, hence similar molecular weights within experimental error limits. This implies that most of the polymer chains were simply disentangled during the mixing process and not broken. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) were done on the virgin polymer, the additives and the fabricated powders to determine the loading levels and to ascertain if there were any changes to the physical properties of the polymer. Scanning electron micrographs showed that some of the powder particles had additive particles stuck on the surface, but when these additives were washed off the surface of the powders with a suitable solvent that did not dissolve the polymer, DSC analysis showed the presence of additive incorporated into the polymer matrix.

CHAPTER 1 Introduction

This research project investigates a new method of making powders from fluoropolymers by ball milling with a crystalline solid additive in the presence of supercritical carbon dioxide (CO₂). The crystalline additive has to be soluble in CO₂ but if it does not exhibit a high enough solubility, it is then dissolved in a liquid solvent that can also dissolve in CO₂. However, the liquid solvent should not dissolve the polymer to any significant extent. Acetone or methanol is used to dissolve the crystalline solid, and the solution together with solid polymer is gently ball milled using stainless steel balls in the presence of CO₂ at temperatures between 17 to 30 °C and pressures between 1300 to 2500 psig. At these modest operating conditions, in the presence of CO₂, the additive associates with the polymer, drops out of solution and, with agitation or mastication, produces a free flowing powder of polymer/additive particles. The system is then flushed with a stream of nitrogen or CO₂ at the end of the mixing process to remove the remaining CO₂ and the liquid solvent in solution so that the free flowing powder of polymer/additive particles can be recovered.

The polymers used for this application should be those that contain substituent groups that can form a chemical complex, such as a proton-donor/proton-acceptor complex with the additive. Examples of such substituent groups are cyanide groups, aromatic groups, carbonyls, amines etc. Fluoropolymers (containing vinylidene fluoride (VDF) as

the polar substituent group) were used for this study since the fluorine atoms in the VDF component can chemically complex to the polar sites of the crystalline additive.

This process is used to form free flowing powders, which can be molded, extruded or subjected to other processing operations that result in the uniform distribution of a chemical agent within a polymer matrix (i.e. chemical agent coated with polymer) or that forms part of the polymer matrix due to interactions with the polymer. The ball milling process is gentle and so the kinds of interactions that result between the fluoropolymers and additives are most probably not due to stronger bonding interactions like ionic or covalent bonding but are most likely due to simpler interactions like dipole-dipole interactions and/or hydrogen bonds. This technique may also be useful to industries that fabricate powders such that flavors and/or other additives are encapsulated into polymers or other coating materials.

Carbon dioxide is a non-harmful fluid medium and is suitable for this application because of its solvent characteristics as a function of temperature and pressure. It has been used as a fluid medium for applications like the synthesis of polymers in which monomers are first dissolved in CO₂ and then polymerized to form the polymers of interest^{1, 2}. Other applications of CO₂ include the extraction of low molecular weight components from polymer matrices³, as a blowing agent in the production of polymer foams⁴, and in polymer processing^{5, 6}.

Eight fluoropolymers with different molecular weights were used for this study; four were copolymers of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) in the ratio 78:22; and the other four were terpolymers consisting of vinylidene fluoride (VDF),

tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) in the ratio 64:18:18. The molecular weights of the copolymers labeled C-1, C-2, C-3 and C-4 were 40,000, 60,000, 80,000 and 200,000 g/mol respectively. The terpolymers labeled T-1, T-2, T-3 and T-4 had molecular weights of 30,000, 40,000, 70,000 and 200,000 g/mol respectively. Only the C-4 and T-4 polymers with the highest molecular weights resulted in powder formation.

Fluorine is a highly electronegative atom which means that it has a strong electron attracting effect. This effect influences the physiological properties of the fluoropolymer by enhancing acidity, results in a high dielectric constant causing piezoelectricity effect, and influences the fluoropolymer's optical activity, e.g. in the formation of liquid crystal materials⁷. For example, in poly(vinylidene fluoride), PVDF, the hydrogen atoms in the vinylidene fluoride monomer are acidic due to the electron attracting effect of the fluorine atoms in the monomer and this polymer is piezoelectric as a result of its high dielectric constant. The same electron attracting effect of fluorine is responsible for the creation of a small dipole moment in the polymers resulting in⁸

1. Non-stick properties which make it applicable as a mold release agent
2. Low surface tension making it applicable as a surfactant
3. A low coefficient of friction thereby enhancing its slip (lubrication) properties
4. Oil and water repellency, hence is used as a repellent
5. Low refractive index which makes it a suitable material for a number of optical applications.

The C-F bond has a strong bonding energy which results in thermal stability, chemical resistance and weatherproof properties for these polymers e.g. poly (tetrafluoroethylene), PTFE⁷. There are so many applications for fluoropolymers already in use due to their very interesting properties and many more that remain hidden or undiscovered; this gives even more reason why this new ball milling technique is very important and should be further developed.

CHAPTER 2 The Ball Milling Process

The Mixing and Flushing Process

The ball milling process was developed by McHugh and Li as a new method to efficiently mix crystalline solid additives with polymeric material⁹. For this process to be successful, it is important to find a way of opening up the polymer matrix to increase its surface area for interaction with the additive. This is the role of the CO₂ which expands the polymer making it more amenable to impregnation by the additive. The additive has to be soluble in CO₂ so that it can be carried along with the CO₂ as it penetrates the polymer. If the additive does not exhibit a high enough solubility in CO₂, it is then dissolved in a liquid solvent that also dissolves in CO₂. However, the liquid solvent should not dissolve the polymer to any significant extent.

The ball milling process can be divided into two major parts: a mixing and a flushing process. The first part is the mixing process which is a simple batch process. The second part is a flushing process, which is a continuous stir flow process where the system is flushed with nitrogen or carbon dioxide in preparation for removal of the powder.

The ball miller used in this study was a mini bench top mixer shown in Figure 1, with a volume of 100 ml, obtained from the Parr Instrument Company (model 4565 with a model 4842 controller). Stainless steel balls, of weight between 0.7 g to 2.0 g each and diameter ranging from 6 to 9 mm were used to process the polymer into powder. Carbon

dioxide, the fluoropolymer and the additive (or an additive/solvent mixture) were loaded into the mixing vessel which had been pre-flushed with CO₂ to remove any air that may induce oxidization of the additive. For each ball milling experiment the weight ratio of fluoropolymer to additive loaded into the chamber was noted for future reference. An ethylene propylene rubber O-ring was used to seal the vessel and the mixing process was initiated by a four-blade impeller which rotated at approximately 125 revolutions/min. The total weight of steel balls in the vessel was 150 g and as the system was agitated, the steel balls moved with varying velocities, thereby transferring energy of $\sim 13 \mu\text{J}/\text{hit}$ due to 6 mm steel balls and $\sim 39 \mu\text{J}/\text{hit}$ due to 9 mm steel balls to the polymer and additive and converting them to powders¹⁰.

The mixing process operates for 30 minutes once the temperature of the system reaches the desired temperature, and the pressure increased to approximately 1800 psig. An advantage of this method is that it is successful at fairly low temperatures and pressures. The temperature and pressure varied slightly during the entire mixing process to values approximately $\pm 3 \text{ }^\circ\text{C}$ and $\pm 200 \text{ psig}$ respectively.

At the end of the mixing process an inlet valve in the system is opened to supply either CO₂ or N₂ to flush any remaining CO₂/solvent/additive mixture after the additive had dropped out of solution. The flushing pressure was usually between 1400 to 1700 psig. After the flushing process was done, the inlet valve was closed and the system was slowly degassed at a rate approximately 200 psig/min. The powder was removed from the vessel and passed through a sieve to obtain fine particles.

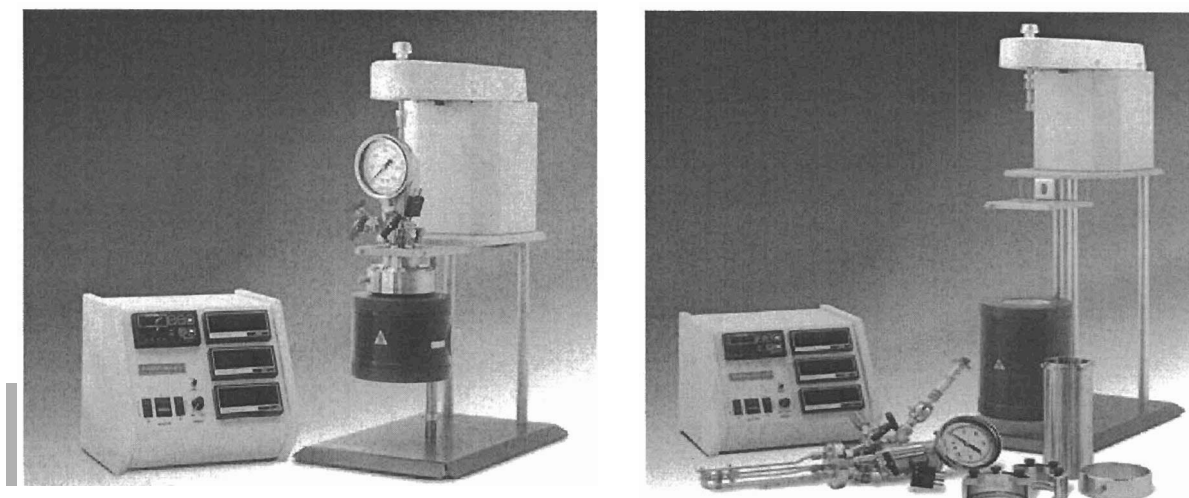
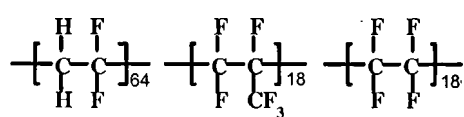


Figure 1. Parr mini bench top mixer, model 4565, with a model 4842 controller.

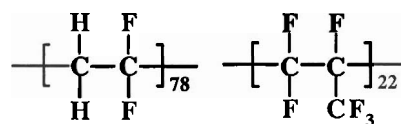
The Ball Milling Data

The fluoropolymers used for the ball milling experiments were the copolymers C-1, C-2, C-3 and C-4 (FluorelTM, 3M corporation) as well as the terpolymers T-1, T-2, T-3 and T-4 (DyneonTM THV, 3M corporation). Benzyl triphenyl phosphonium chloride (BTPPC, DuPont corporation) and bisphenol AF (BAF, Sigma Aldrich company) were the additives used for the blending process. The structures of these compounds are given in Figure 2.

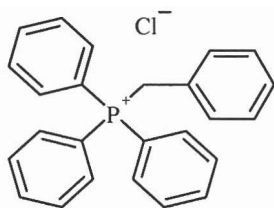
Vinylidene fluoride is the polar component in these fluoropolymers due to the high electronegativity of fluorine pulling the electron cloud towards itself leaving a slightly positive carbon atom. This makes it possible for the electropositive phosphorous in BTPPC to interact with the electronegative fluorine atoms in VDF. The case of BAF is slightly different; the hydrogen atom in the phenol group will tend to hydrogen-bond to fluorine in VDF.



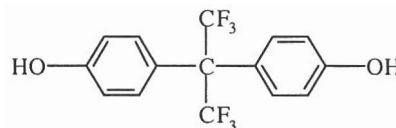
(A)



(B)



(C)



(D)

Figure 2. (A) Structure of terpolymers T-1, T-2, T-3 and T-4 (VDF/HFP/TFE = 64/18/18), (B) structure of copolymers C-1, C-2, C-3 and C-4 (VDF/HFP = 78/22), (C) the additive, BTTPC and, (D) the additive, BAF.

Li performed a series of preliminary experiments to determine the impact of the process variables for this process¹¹. Her results are described here. In one instance the fluoropolymers and additives were masticated with steel balls at atmospheric pressure and temperature 60 °C in the absence of CO₂. The physical appearance of the polymer changed from a clumpy white elastomeric mass to a more open structure but very poor blending was observed between the fluoropolymer and additive. When the fluoropolymers were exposed to CO₂ in the mixing chamber at 60 °C and 2500 psig, in the absence or presence of a small amount of acetone, the morphology of the polymer changed once again from a clumpy white elastomeric mass to a more open porous structure. This is due to CO₂

dissolving into the fluoropolymer thus expanding and swelling it. The presence of acetone had very little effect on the morphology of the fluoropolymer. In another preliminary experiment, the fluoropolymer, and additive with a small amount of acetone and N₂ (to replace CO₂) were combined in the vessel at 60 °C and 2000 psig. There was very little change in the fluoropolymer morphology. This is due to N₂ dissolving to a very low extent in the fluoropolymer. Hence the effect of nitrogen is similar to that of hydrostatic pressure alone. Although effective mixing did not occur in any of the above preliminary experiments, we can deduce that if the SCF solvent exhibits reasonable solubility in the polymer, the final polymer morphology will be more open and the resulting increased surface area of the polymer will create a suitable scenario for effective mixing with the additive.

Table 1 shows that there was powder formation when the fluoropolymers and additives were ball milled in the presence of CO₂. These powders were made by Y. Kim¹² using the technique described by McHugh and Li¹¹ and working in the McHugh laboratories. Each ball milling experiment was loaded with approximately 80 g of CO₂ and flushed with N₂ at the end of the mixing process. The solvents used to pre-dissolve the additives were aprotic solvents, such as acetone, that could dissolve the additive at room temperature. A number of ball milling experiments were done for the copolymers and terpolymers but only C-4 and T-4 resulted in some amount of powder formation as can be seen below from experiment # 42, 45, 49, 51, 52 and 58. The terpolymer T-4 resulted in powder formation when ball milled with an additive in the presence of CO₂ but did not

form powder when ball milled in CO₂ only. Figures 3 and 4 show pictures of the additives, polymers, and some of the results Kim obtained for C-3, C-4, T-3, and T-4.

Table 1. Ball milling data for copolymers and terpolymers obtained by Kim¹².

Exp. Name	Polymer	Additive/ Solvent	Polymer in vessel (g)	Additive in vessel (g)	Solvent in vessel (g)	Mixing press. (psig)	Mixing temp. (°C)	Mixing time (mins.)	Fine powder yield (wt %)
# 46	C-3	BTPPC/ Methanol	2.05	0.11	0.10	2000	24	60	0
# 71	C-3	None	2.02	0	0	1570	20	30	0
# 45	C-4	BTPPC/ Methanol	2.06	0.11	0.10	1470	24	30	90
# 28	T-1	BAF/ Acetone	2.07	0.14	0.07	2060	18	30	0
# 70	T-2	None	2.07	0	0	1500	23	30	0
# 35	T-3	BAF/ Acetone	2.02	0.15	0.07	1630	41	30	0
# 68	T-3	None	2.02	0	0	1620	23	30	0
# 42	T-4	BAF/ Acetone	2.03	0.13	0.09	1530	20	30	83
# 52	T-4	BAF	2.01	0.13	0	1530	25	30	33
# 49	T-4	BTPPC/ Methanol	2.01	0.12	0.11	1480	23	30	90
# 51	T-4	BTPPC	2.02	0.12	0	1510	32	30	88
# 58	T-4	BTPPC	2.01	0.12	0	1930	19	15	67
# 66	T-4	None	2.03	0	0	1800	22	30	0



(A)



(B)

Figure 3. Picture of (A) BTPPC crystals, (B) BAF crystals before ball milling.

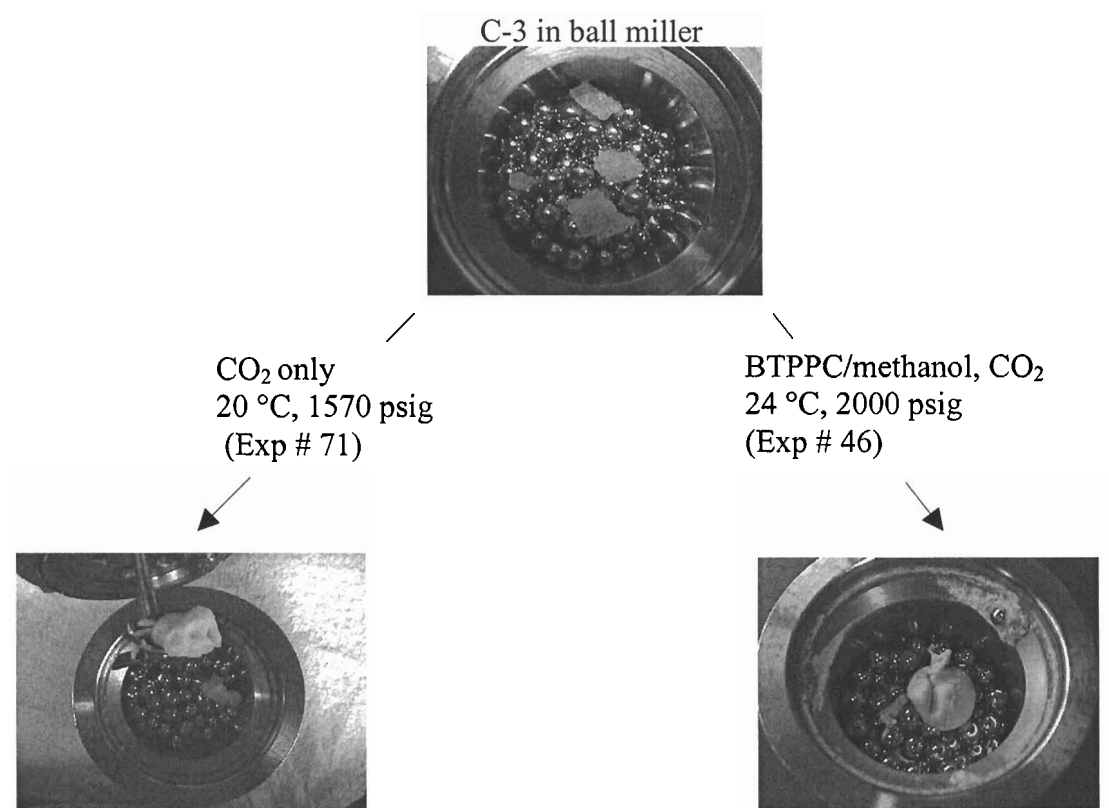


Figure 4. (A) Results for the ball milling of C-3 in CO₂ with (# 46) and without (# 71) BTPPC.

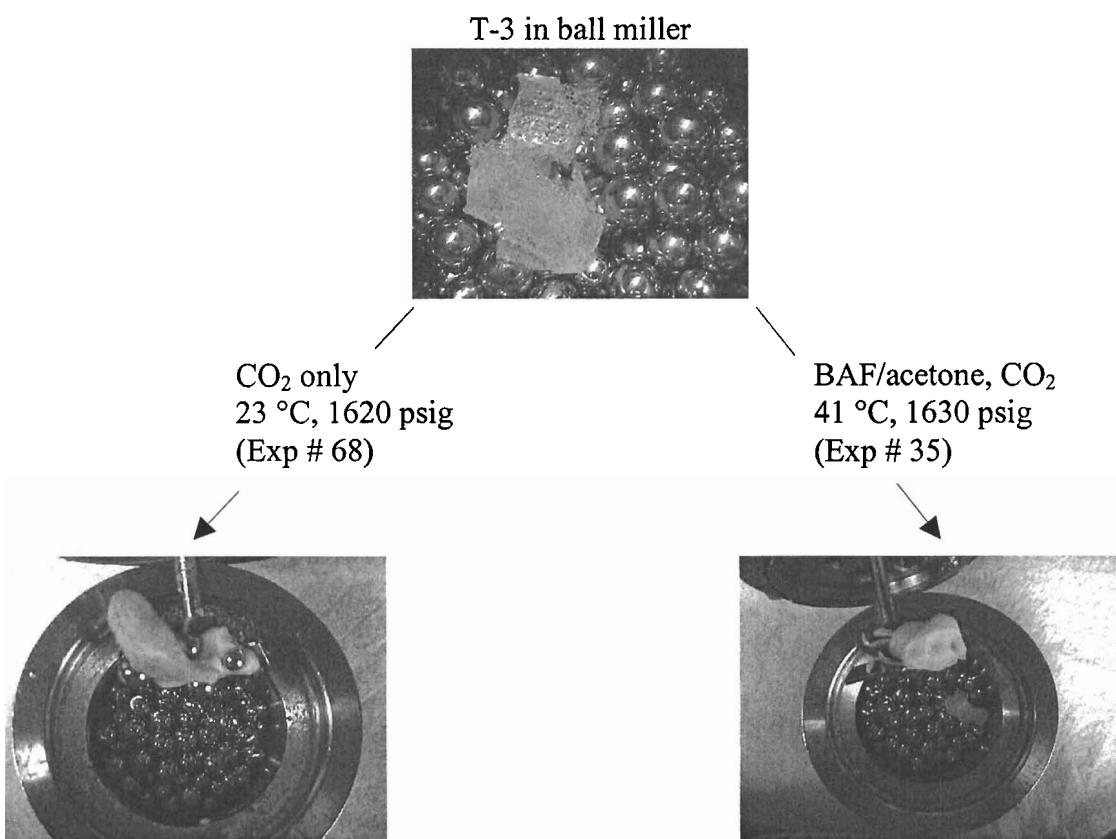


Figure 4. (B) Results for the ball milling of T-3 in CO₂ with (# 35) and without (# 68) BAF.

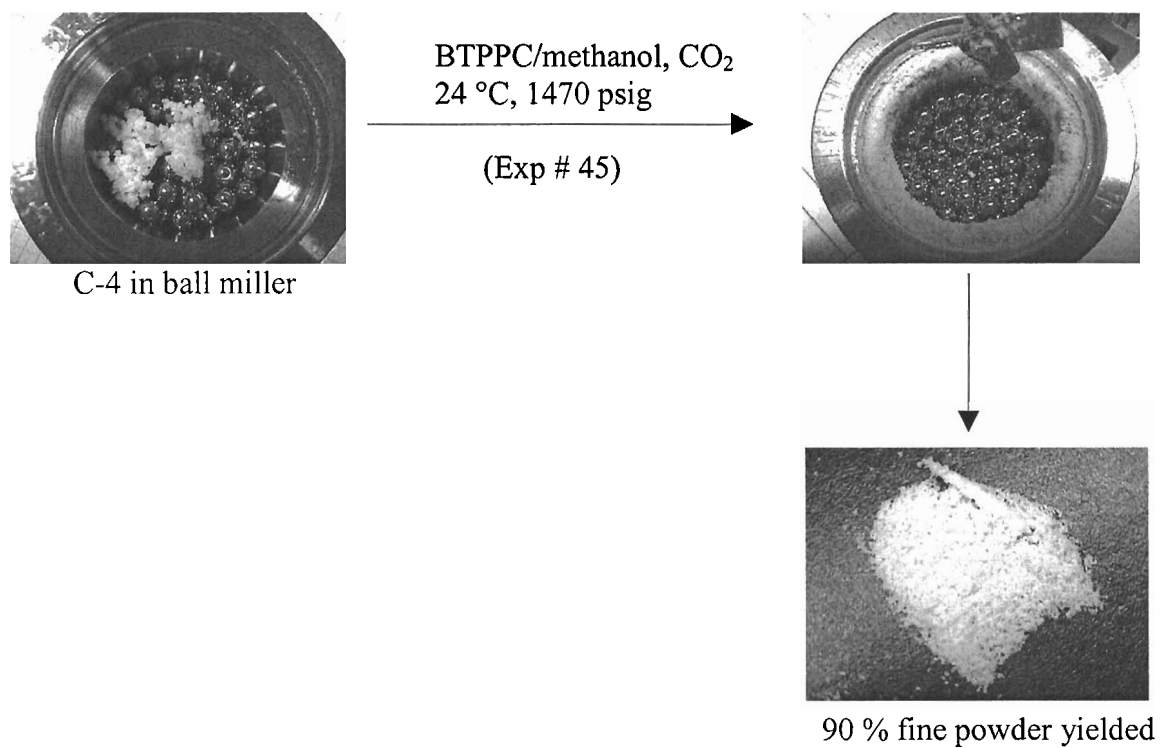


Figure 4. (C) Results for the ball milling of C-4 in CO₂ with BTPPC (# 45), 90 % fine powder produced.

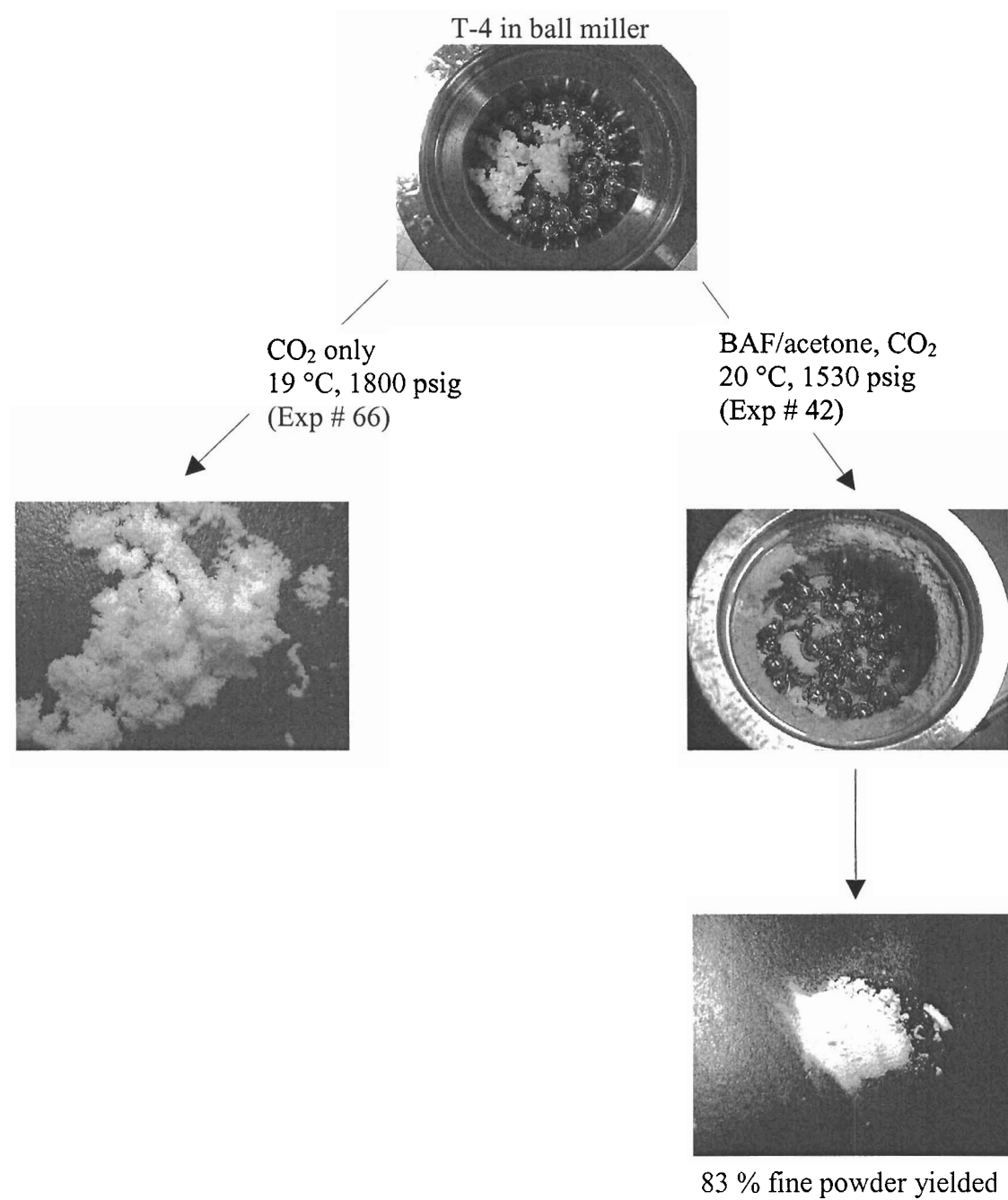


Figure 4. (D) Results for the ball milling of T-4 in CO₂ with BAF (# 42, 83 % fine powder produced) and without BAF (# 66).

The Chemistry of the Ball Milling Process

The efficacy of this process is directly related to the phase behavior of the (solid additive + liquid solvent + CO₂ solvent) mixture. The mechanical properties and fracture mechanics of the fluoropolymers are also very important and must be taken into consideration. One of the first steps in these ball milling experiments is the preparation of the (crystalline additive + liquid solvent) solution. The solvents used were acetone and methanol, which are both polar solvents. The main interactions in acetone are dipole-dipole interactions and London dispersion forces (induced dipole-induced dipole interactions). Acetone does not hydrogen-bond to itself though it can hydrogen-bond to other species, hence the reason why crystalline solids will dissolve in it. For methanol, in addition to dipole-dipole interactions and London dispersion forces, it exhibits hydrogen-bonding to other molecules as well as to itself. The effect of hydrogen-bonding in methanol is the largest of all the possible intermolecular interactions present; hence the reason for methanol's high boiling point (67 °C as compared to 56 °C in acetone) despite its small size.

Carbon dioxide has a critical temperature and pressure of 31 °C and 73 bar (1070 psi) respectively. Acetone has a critical temperature and pressure of 235 °C and 48 bar (696 psi) respectively. The critical conditions for methanol are slightly higher than for acetone with a critical temperature 240 °C and critical pressure 78.5 bar (1139 psi).

The vapor pressure of both acetone and methanol are smaller than that of CO₂ at room temperature. For the ball milling experiments in which acetone was the solvent used

to dissolve the additives, at 20 °C, the schematic phase diagram for the acetone/CO₂ system will be expected to be as shown in Figure 5.

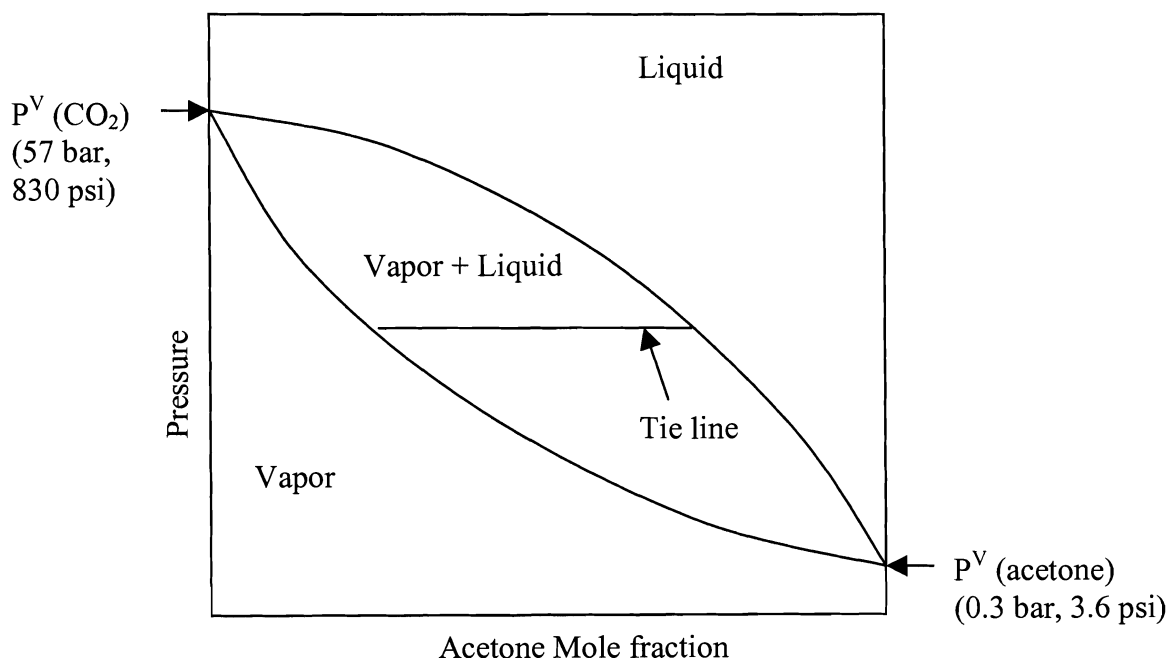


Figure 5. Schematic phase diagram expected for the acetone/CO₂ system at 20 °C.

As can be seen from the diagram above, there are regions in this system where two phases exist and others with one phase only. It is important that during the mixing process, the system should be in the one-phase region to create uniformity in the density and diffusivity of the system. For the experiments done at temperatures around 20 °C, the operating pressures were between 1300 to 2000 psi and from the diagram in figure 5, it is expected that at those pressures, the system exists in one phase.

However, there were other experiments done at temperatures as high as 60 °C and the phase diagram for these systems is slightly different. The critical temperature of CO₂ is 31 °C, so at 60 °C, no vapor pressure exists for CO₂. Figure 6 shows the difference in the phase equilibrium compared to figure 5.

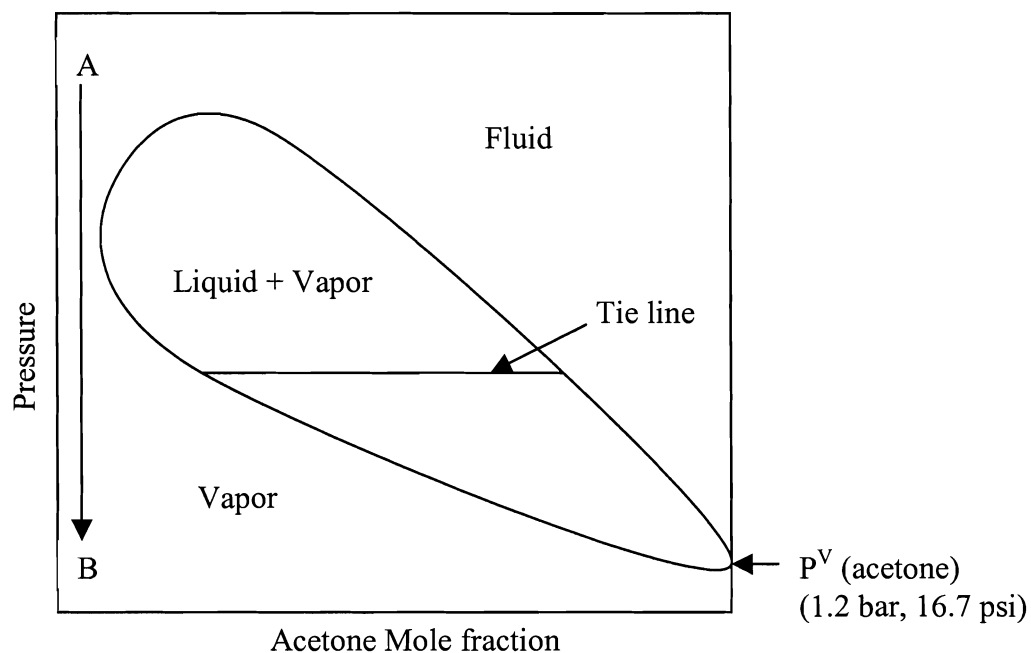


Figure 6. Schematic phase diagram for the acetone/CO₂ system at 60 °C. Decreasing the pressure in the system from point A to B will not produce moist sticky powder because the two-phase region is not entered.

McHugh and Li¹¹ recommend that at the end of the ball milling process, the system is flushed with a gas for 10 minutes to remove the remnant acetone/CO₂ solution and the vessel is depressurized at a rate of 200 psig/min in order to retrieve the powder formed. From the phase diagram in figure 5, notice that at 20 °C, as the pressure drops from the

single phase region, it enters the two phase region containing both liquid and vapor. If any powder was made during the ball milling process, it will be wet by the liquid present in this two-phase region. For ball milling carried out at 60 °C, when flushed with CO₂, decreasing the pressure in the system from point A to B will not produce moist sticky powder because it does not cross the two-phase region as can be seen in figure 6. In order to avoid the probability of obtaining moist sticky powder, the system can be flushed with nitrogen which has a critical temperature of -150 °C and so at temperatures between 17 to 60 °C it does not have a vapor pressure. As a result of flushing away the acetone/CO₂ solution, the system does not cross into the two-phase region while depressurizing the vessel. The end product will be a free flowing powder.

It is also very important to look at the phase behavior of the fluoropolymer-solvent (CO₂ + additive + acetone) mixture. CO₂ has the potential to swell these fluoropolymers. An open, porous mass of polymer was observed in the experiments in which the fluoropolymers were ball milled with CO₂ only due to CO₂ gas being trapped in the polymer during the milling process. It is for this reason that the crystalline solid is dissolved in CO₂ which serves as a carrier medium for the crystalline solid into the fluoropolymers. The amount of swelling in the fluoropolymers increases with an increase in the amount of vinylidene fluoride content present.

The intermolecular forces in operation between the solvent-solvent, solvent-polymer segment and polymer segment-segment pairs in solution are also responsible for the amount of swelling observed. The free volume difference between the polymer and solvent is another important factor that influences swelling. At lower temperatures and

pressures, the free volume difference between the polymer and the solvent is large and so the polymer does not go into solution. For the fluoropolymers with lower vinylidene fluoride contents, the polymer segment-segment interactions are stronger than the solvent-polymer segment interactions. As the vinylidene fluoride content in the fluoropolymers increases, the solvent-polymer segment interactions become larger leading to more swelling in the fluoropolymers. Considering the impact these intermolecular forces have on solubility, the following expression¹³ shows how the intermolecular potential energy, Γ_{ij} , of an i - j pair of segments or molecules depends on the physical properties of the polymer and the solvent.

$$\Gamma_{ij}(r, T) \approx -C_1 \frac{\alpha_i \alpha_j}{r^6} - C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} - C_3 \frac{Q_i^2 Q_j^2}{r^{10} kT} - C_4 \frac{\mu_i^2 Q_j^2}{r^8 kT} - C_5 \frac{\mu_j^2 Q_i^2}{r^8 kT} + \text{complex formation} \quad (1)$$

Where,

$i, j = \text{CO}_2$, polymer segment pair α = dispersion interactions

μ = dipole moments Q = quadrupole moments

C_{1-5} = constants T = absolute temperature

k = Boltzmann's constant r = distance between molecules

The C-F bond in the vinylidene fluoride group of the fluoropolymer is polar and possesses a dipole moment. Carbon dioxide however does not possess a dipole moment due to structural symmetry but does possess a quadrupole moment. There exist a high affinity of amorphous fluoropolymers for CO_2 due to interactions between the partial

positive carbon in CO₂ and the fluorine in the C-F bonds in the fluoropolymer.^{14, 15, 16} This is why CO₂ has the potential to cause swelling of the fluoropolymers.

From an energetic point of view, the criterion for whether a polymer will dissolve in CO₂ is determined by the interchange energy, ω , of mixing i - j pairs and is given by

$$\omega = z \left[\Gamma_{ij}(r, T) - \frac{1}{2}(\Gamma_{ii}(r, T) + \Gamma_{jj}(r, T)) \right] \quad (2)$$

where z = number of dissimilar solvent-segment pairs. For the fluoropolymer to exhibit some solubility in CO₂, the first term, $\Gamma_{ij}(r, T)$ has to be more significant than the second term, $\frac{1}{2}(\Gamma_{ii}(r, T) + \Gamma_{jj}(r, T))$. Carbon dioxide has a low value for polarizability and this causes the effect of the quadrupole moment to be magnified. There exists an inverse proportionality between quadrupolar interactions and temperature, so at low temperatures, the interchange energy for CO₂ quadrupolar interactions dominate. However, the C-F bond in vinylidene fluoride has a large dipole moment (inversely proportional to temperature) which means at lower temperatures, the interchange energy for the fluoropolymers might be dominated by polymer-polymer interactions rather than polymer-CO₂ interactions.

Acetone was used to pre-dissolve BAF while methanol was used for BTPPC. Both BAF/acetone and BTPPC/methanol solutions exhibit hydrogen-bonding between the additive and solvent in solution. Hydrogen-bonding is inversely proportional to temperature and so as the temperature of the system increases, the distance between molecules in the solution is increased and the hydrogen-bonding of the additive to acetone or methanol is not favored. As the CO₂ serving as a carrier medium for the additive

diffuses into the polymer, the polar site on the additive associates with the polar site on the fluoropolymer, and as a result, the crystalline solid drops out of solution and crystallizes onto the polymer.

The solubility of the fluoropolymer in CO₂ is also dependent on the CO₂ density. This can be seen in the equation¹⁷ given below.

$$\frac{U_{mixture}}{kT} \approx A_0 + A_1 \frac{\rho(P,T)}{kT} \sum_{ij} x_i x_j \int \Gamma_{ij}(r,T) g_{ij}(r,T,\rho) r^2 dr \quad (3)$$

$U_{mixture}$ = internal energy of mixture

A_0, A_1 = constants

g_{ij} = radial distribution function

x = mole fraction

ρ = density of solvent

Equation (3) shows that internal energy of the mixture is a function of density and the higher the CO₂ density, the more soluble the fluoropolymer will be. Increasing the pressure of the system increases the density of the solvent; hence swelling of the fluoropolymer is favored by increase in pressure of the system.

Mechanism for Powder Formation

The cartoon in figure 7 illustrates the mechanism proposed by McHugh and Li for the mixing process¹¹. Carbon dioxide has the potential to swell the polymer and increase its surface area. Since the solvent (S) and additive (A) are dissolved in CO₂, this allows for the additive's polar sites to interact with the polar sites on VDF as it is carried into the polymer matrix. As a result, the additive drops out of solution, crystallizes with the fluoropolymer and on impact with the steel balls, converts to powder.

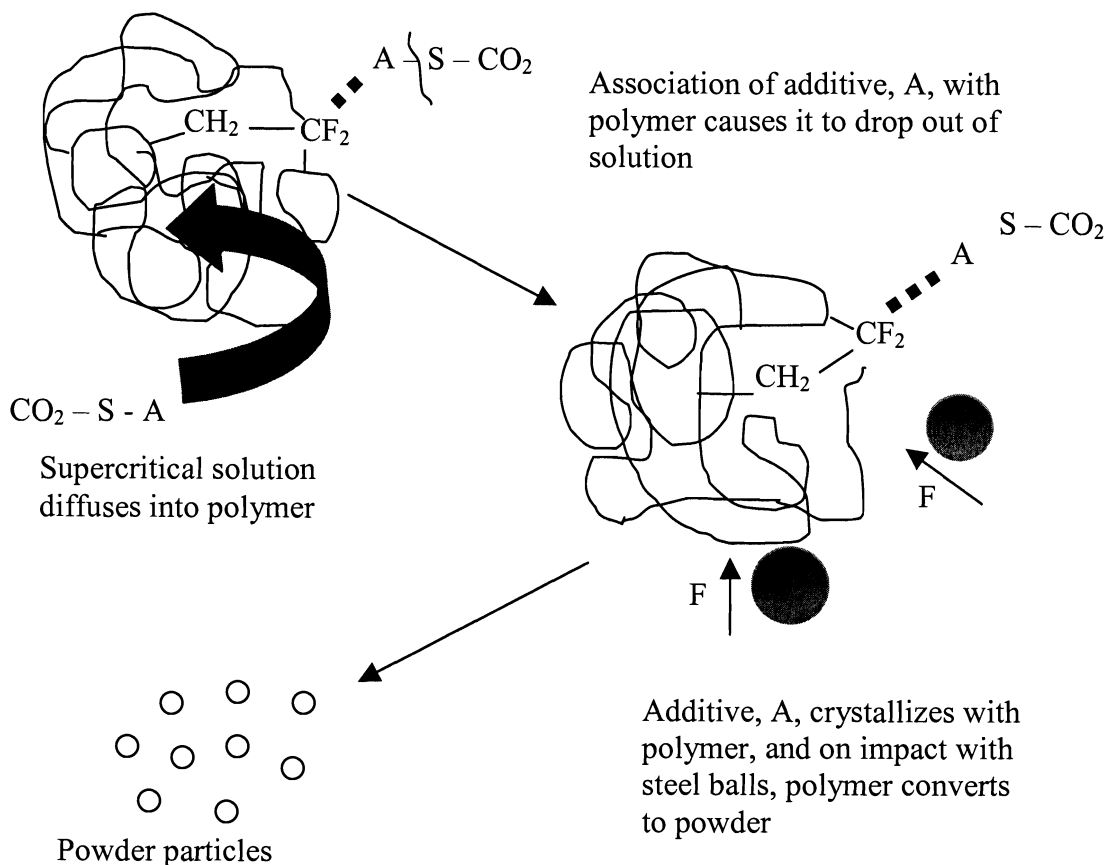


Figure 7. Cartoon illustrating the mechanism for powder formation.

Titration calculations

The fluorocopolymer, VDF/HFP containing 78 mole % of VDF is used for this calculation. The purpose of this calculation is to find the amount of BTPPC needed to titrate the vinylidene fluoride group in 1 g of C-4. Assuming the only interactions present between the additive and the polymer to be associations from the electropositive phosphorous in the additive and the electronegative fluorine atoms in VDF, the amount of

BTPPC needed to titrate VDF in C-4 can be calculated below. Figure 8 shows the structures of C-4 and BTPPC. For every mole of VDF, two moles of BTPPC are needed for the titration since BTPPC contains one phosphorous atom as opposed to two fluorine atoms in VDF.

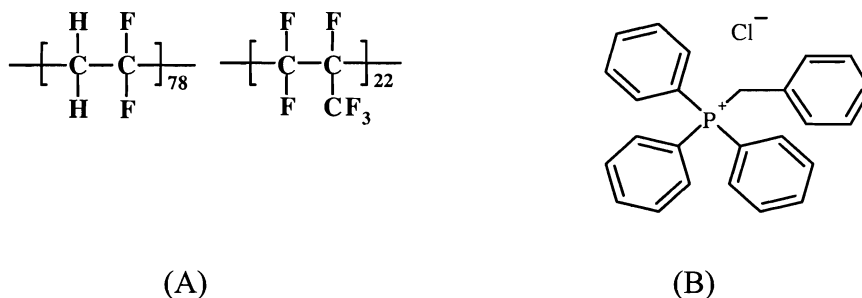


Figure 8. Structure of (A) C-4 (VDF/HFP) and (B) BTPPC. The molecular weight of vinylidene fluoride group, M_{VDF} , is 64 g/mol; molecular weight of hexafluoropropylene group, M_{HFP} , is 150 g/mol; and the molecular weight of the fluorocopolymer, $M_{\text{VDF/HFP}}$, is 200,000 g/mol.

The molecular weight was reported by the supplier, and it was not specified whether this was a number average, weight average or z-average molecular weight. In order to do these calculations, the assumption is made that this polymer is monodisperse.

The average molecular weight of one polymer chain is given as 200,000 g/mol. In 1 g of the fluoropolymer, there is more than one polymer chain present. Assuming that the ratio VDF to HFP in each polymer chain is the same irrespective of how many chains are present,

$$\frac{m}{n} = \frac{78}{22} = \frac{3.5}{1}$$

$$\Rightarrow m = 3.5 n \quad (4)$$

$$\Rightarrow n M_{\text{HFP}} + m M_{\text{VDF}} = 1 \text{ g}$$

Since $m = 3.5 n$

$$(n)(150 \text{ g}) + (3.5 n) (64 \text{ g}) = 1 \text{ g}$$

So, $n = 0.0027$ HFP repeat groups and $m = (3.5) (0.0027) = 0.0095$ VDF repeat groups

For every mole of BTPPC, there is 1 mole of phosphorous; and for every mole of VDF, there are 2 moles of fluorine. Hence 2 moles of BTPPC are needed to titrate 1 mole of VDF.

$\Rightarrow 0.0190$ moles of BTPPC are needed to titrate 0.0095 moles of VDF

Molecular weight of BTPPC, $M_{\text{BTPPC}} = 388.8 \text{ g/mol}$

Mass = number of moles \times Molecular weight

$$\text{Mass}_{\text{BAF}} = 0.0190 \text{ moles} \times 388.8 \text{ g/mol} = 7.39 \text{ g}$$

So 7.39 g of BTPPC are needed to titrate the VDF groups in 1 g of C-4 (VDF/HFP).

Powder Analysis

It is very important to know what kind of powder was formed at the end of the ball milling process which leads to fundamental questions such as: - did the polymer successfully coat the additives? Were fluoropolymer chains broken into smaller chains in the course of ball milling, or were these chains simply disentangled? If the fluoropolymer

chains were broken such that the resulting powder consists of shorter fluoropolymer chains, then the properties of the fluoropolymer in the powder may be different from that of the original. Hence it is very important to analyze any differences in the properties of the fluoropolymer that may have been caused due to the mixing process. A couple of analytical techniques listed below were carried out to answer these questions.

1. Viscosity studies were used to determine the molecular weight of the polymer chains present in the fluoropolymer powders and the original fluoropolymer. A decrease in the molecular weight for the fluoropolymer in the powder will mean polymer chains have been broken. If the average molecular weight of the fluoropolymer chains in the powder and original fluoropolymer remain similar, then the polymer chains in the powder were simply disentangled due to the effect of CO₂ swelling the polymer.

2. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) were conducted to study the thermal properties of the additives, the original fluoropolymer and powders fabricated from these fluoropolymers. These studies were used to verify the presence of the additives in the ball milled powders.

3. Scanning Electron Microscopy (SEM) was used to verify whether the additives were coated by the fluoropolymers.

CHAPTER 3 Results and Discussion

Viscosity Studies

Intrinsic viscosities for the copolymers (C-1, C-2, C-3 and C-4) and terpolymers (T-1, T-2, T-3 and T-4) were done at 30 and 40 °C. This quantity is important for the purposes of polymer characterization since it relates to the intrinsic ability of a polymer to increase the viscosity of a particular solvent in a given temperature. The intrinsic viscosity, $[\eta]$, of a polymer is related to its viscosity-average molar mass, M , by the Mark-Houwink equation given by

$$[\eta] = kM^a \quad (5)$$

where k and a are characteristic constants for a given polymer/solvent/temperature system.

Huggins and Kraemer were able to establish linear relationships¹⁸ between the reduced viscosity η_{red} , the inherent viscosity η_{inh} , and the intrinsic viscosity $[\eta]$. In these relations, η_{red} and η_{inh} are plotted against concentration, c , and the line plots are extrapolated to the point where $c = 0$ to obtain $[\eta]$, where

$$\eta_{red} = \frac{\text{Specific viscosity}}{\text{concentration of polymer solution}} = \frac{\eta_{sp}}{c} \quad (6)$$

$$\eta_{inh} = \frac{\ln(\text{relative viscosity})}{\text{concentration of polymer solution}} = \frac{\ln(\eta_r)}{c} \quad (7)$$

Huvarad has proposed an even simpler method of calculating accurate estimates for intrinsic viscosity values¹⁹ with a single η_r measurement, as opposed to methods used by Huggins and Kraemer in which multiple measurements for η_r must be obtained.

$$\eta_r = \frac{\text{viscosity of polymer solution}}{\text{viscosity of solvent}} \cong \frac{\text{Polymer solution flow time}}{\text{solvent flow time}} \quad (8)$$

Recently, Pappas²⁰ developed a linear correlation between the difference of $\left(\frac{\eta_{red} - \eta_{inh}}{c}\right)^{\frac{1}{2}}$,

which he termed $\left(\frac{\Delta V}{c}\right)^{\frac{1}{2}}$, and the concentration of a dilute polymer solution. Huvarad was able to develop the mathematical basis of the Pappas correlation starting from the Huggins and Kraemer equations to obtain a relation between $[\eta]$ and ΔV . Huvarad's 'single measurement' equation is given below as

$$[\eta] = \frac{1}{2} \left[\left(\frac{\Delta V^2}{16} + \frac{8\Delta V}{c} \right)^{1/2} - \frac{\Delta V}{4} \right] \quad (9)$$

where $\Delta V = \eta_{red} - \eta_{inh}$. This equation is quite accurate for dilute concentrations below 0.5 g/dL. Figure 9 shows the presentation of ΔV as a function of c on a Huggins/Kraemer plot for obtaining $[\eta]$.

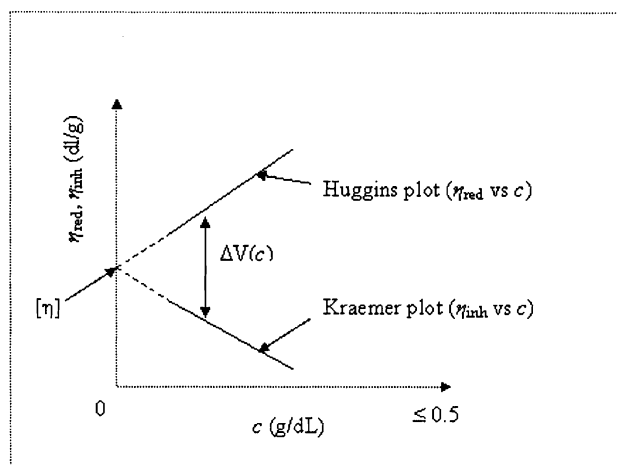


Figure 9. Representation of ΔV as a function of concentration on a Huggins/Kraemer plot for obtaining $[\eta]$.

The solvent used for these viscosity studies was N, N-Dimethylformamide (DMF, Sigma Aldrich company), which has a density 94.8 g/dL and boiling point of 153 °C. Dilute polymer solutions (0.05 g/dL to 0.15 g/dL) for the copolymers and terpolymers in DMF were made and relative viscosities for these solutions were obtained. Borosilicate glass ubbelohde viscometers obtained from Fisher Scientific were used for this study. Two sizes were used – the size oc, suitable for applications in which the viscosity range is 0.6 to 3 cSt (centistokes), and the size 1, suitable for viscosity applications ranging between 2 to 10 cSt.

The flow times for the solvent and polymer solutions at different concentrations were taken at 30 and 40 °C. Temperature stability was obtained from the use of a water bath which was kept constant to within ± 1 °C. After each experiment the viscometers

were washed thoroughly with acetone then dried for 10 minutes in a vacuum oven at 40 °C.

In order to conduct the viscosity studies of the fluoropolymers in the powders to obtain their molecular weights, the additives had to be extracted. A Micro Soxhlet extractor (Ace Glass Inc.) was used with 0.5 g of powder sample placed in a 10 × 50 mm cellulose thimble. The additives were extracted from the powder samples for 12 hours using a 5% methanol + 95 % water solution. The choice of solvent for extraction was very important because the goal of the extraction process was to dissolve the additive out of the powder and not dissolve the polymer. The solvent should not melt or soften the polymer but must be able to diffuse into the polymer to dissolve the additive. Fluoropolymers are insoluble in water so water was added to reduce the solvent power of methanol so that the polymer did not dissolve.

The fluoropolymer that remained in the thimble was dried at 60 °C in a vacuum oven and TGA was done on the dried samples to verify that the samples were completely dried (see appendix 2A). DSC showed that all the additives were extracted from the powders (see appendix 2B). Polymer solutions were made for these thoroughly dried samples and viscosity studies were done in order to compare the $[\eta]$ values with those of the original polymers. The results of relative and intrinsic viscosities obtained for the copolymers (C-1, C-2, C-3, and C-4), the terpolymers (T-1, T-2, T-3, and T-4) and the polymer that was left after extraction (C4-45, T4-51, T4-52, and T4-58) are given in tables 2 and 3.

Table 2. Intrinsic viscosities at 30 °C and 40 °C for copolymers C-1, C-2, C-3, C-4 and C4-45 (C4-45 is the C-4 polymer left after BTPPC had been extracted from powder # 45).

Sample	Temperature, °C	Concentration/(g/dL) $((m_C \times \rho_{DMF})/m_{soln})$	η_{rel} (t_{soln}/t_{DMF})	$[\eta]/(\text{dL/g})$	$[\eta]_{average}/(\text{dL/g})$
<i>C-1</i>	30	0.053	1.0164	0.3071	0.3117
	30	0.093	1.0331	0.3526	
	30	0.151	1.0422	0.2753	
	40	0.053	1.0124	0.2322	0.2431
	40	0.085	1.0223	0.2583	
	40	0.093	1.0223	0.2386	
<i>C-2</i>	30	0.057	1.0258	0.4445	0.4194
	30	0.088	1.0331	0.3701	
	30	0.093	1.0422	0.4437	
	40	0.057	1.0198	0.3424	0.3299
	40	0.088	1.0297	0.3330	
	40	0.093	1.0297	0.3141	
<i>C-3</i>	30	0.049	1.0258	0.5216	0.5117
	30	0.054	1.0285	0.4762	
	30	0.072	1.0420	0.5712	
	30	0.152	1.0749	0.4776	
	40	0.049	1.0198	0.4019	0.4065
	40	0.072	1.0297	0.4057	
	40	0.152	1.0644	0.4118	
<i>C-4</i>	30	0.052	1.0468	0.8825	0.8709
	30	0.066	1.0579	0.8599	
	30	0.077	1.0672	0.8520	
	30	0.129	1.1157	0.8610	
	30	0.151	1.1429	0.8989	
	40	0.052	1.0396	0.7483	0.7244
	40	0.077	1.0569	0.7243	
	40	0.159	1.1163	0.7007	
<i>C4-45</i> (BTPPC extracted)	30	0.037	1.0328	0.8836	0.8558
	30	0.057	1.0500	0.8549	
	30	0.069	1.0583	0.8287	
	40	0.037	1.0288	0.7786	0.7448
	40	0.057	1.0423	0.7305	
	40	0.069	1.0513	0.7252	

Table 3. Intrinsic viscosities at 30 °C and 40 °C for terpolymers T-1, T-2, T-3, T-4, T4-51 (which is the T-4 polymer left after BTPPC had been extracted from powder # 51), T4-52 (which is the T-4 polymer left after BAF had been extracted from powder # 52) and T4-58 (which is the T-4 polymer left after BTPPC had been extracted from powder # 58).

Sample	Temperature, °C	Concentration/(g/dL) $((m_T \times \rho_{DMF})/m_{soln})$	η_{rel} (t_{soln}/t_{DMF})	$[\eta]/(dL/g)$	$[\eta]_{average}/(dL/g)$
T-1	30	0.066	1.0164	0.2486	0.2476
	30	0.870	1.0233	0.2654	
	30	0.107	1.0248	0.2287	
	40	0.047	1.0100	0.2114	0.2160
	40	0.066	1.0149	0.2265	
	40	0.068	1.0149	0.2195	
	40	0.107	1.0224	0.2067	
T-2	30	0.048	1.0164	0.3411	0.3296
	30	0.074	1.0233	0.3128	
	30	0.112	1.0382	0.3349	
	40	0.044	1.0124	0.2844	0.2819
	40	0.048	1.0124	0.2592	
	40	0.058	1.0174	0.2998	
	40	0.112	1.0323	0.2844	
T-3	30	0.046	1.0258	0.5540	0.4963
	30	0.048	1.0230	0.4736	
	30	0.071	1.0350	0.4882	
	30	0.136	1.0656	0.4692	
	40	0.046	1.0199	0.4289	0.4207
	40	0.067	1.0299	0.4419	
	40	0.098	1.0398	0.4014	
	40	0.136	1.0572	0.4107	

Table 3. (Continued)

Sample	Temperature, °C	Concentration/(g/dL) $((m_T \times \rho_{DMF})/m_{soln})$	η_{rel} (t_{soln}/t_{DMF})	$[\eta]/(\text{dL/g})$	$[\eta]_{average}/(\text{dL/g})$
<i>T-4</i>	30	0.035	1.0500	1.3818	1.3431
	30	0.046	1.0640	1.3685	
	30	0.049	1.0679	1.3373	
	30	0.055	1.0749	1.3152	
	30	0.057	1.0794	1.3466	
	30	0.067	1.0880	1.2684	
	30	0.110	1.1527	1.3146	
	30	0.144	1.2207	1.4127	
	40	0.035	1.0423	1.1721	1.1737
	40	0.035	1.0446	1.2363	
	40	0.046	1.0513	1.1019	
	40	0.066	1.0821	1.2075	
	40	0.067	1.0769	1.1133	
	40	0.067	1.0846	1.2206	
	40	0.110	1.1343	1.1642	
<i>T4-51</i> (<i>BTPPC</i> <i>extracted</i>)	30	0.037	1.0515	1.3683	1.3254
	30	0.050	1.0640	1.2566	
	30	0.066	1.0880	1.2820	
	30	0.110	1.1625	1.3947	
	40	0.037	1.0457	1.2157	1.1922
	40	0.050	1.0597	1.1741	
	40	0.066	1.0804	1.1740	
	40	0.110	1.1393	1.2052	
<i>T4-52</i> (<i>BAF</i> <i>extracted</i>)	30	0.033	1.0468	1.3788	1.3448
	30	0.054	1.0750	1.3481	
	30	0.069	1.0960	1.3336	
	30	0.098	1.1354	1.3186	
	40	0.033	1.0398	1.1748	1.1475
	40	0.054	1.0622	1.1232	
	40	0.069	1.0769	1.0762	
	40	0.098	1.1244	1.2157	
<i>T4-58</i> (<i>BTPPC</i> <i>extracted</i>)	30	0.036	1.0492	1.3424	1.3464
	30	0.046	1.0640	1.3537	
	30	0.070	1.1000	1.3818	
	30	0.127	1.1780	1.3077	
	40	0.036	1.0423	1.1574	1.1661
	40	0.046	1.0572	1.2133	
	40	0.070	1.0893	1.2386	
	40	0.127	1.1418	1.0551	

Equation (9) was used to calculate $[\eta]$ from a set of relative viscosity measurements from various concentrations of polymer solutions and the average $[\eta]$ value was obtained. The results obtained showed that the intrinsic viscosity for these polymers increased with increase in molecular weight and decreased with increase in temperature. The intrinsic viscosity values obtained for the powder samples in which the additives had been extracted were very close and similar to the values for the original polymers. The molecular weights of the copolymers (C-1, C-2, C-3 and C-4) and the terpolymers (T-1, T-2, T-3, and T-4) were known. By obtaining the intrinsic viscosities of these polymers of known molecular weight, a relation between these two quantities was established. The purpose of these viscosity studies was to obtain a calibration curve relating the molecular weights of these fluoropolymers to their intrinsic viscosities so that the molecular weight of the fluoropolymers in the powder samples can be calculated. The tables and figures that follow show the calibration curves obtained for the copolymers and terpolymers at 30 °C and 40 °C relating molecular weight, M , to intrinsic viscosity, $[\eta]$. The graphs below were plotted using Mark-Houwink's equation given as

$$[\eta] = kM^a$$

$$\log[\eta] = a \log M + \log k \quad (10)$$

The slope of the graph gives the value of a , while k can be obtained from the intercept on the $\log [\eta]$ axis.

Table 4. Intrinsic viscosities for fluorocopolymers with varying molecular weights at 30 °C and 40 °C.

Polymer	$M/(g/mol)$	$\log (M/(g/mol))$	At T = 30 °C		At T = 40 °C	
			$[\eta]/(dL/g)$	$\log ([\eta]/(dL/g))$	$[\eta]/(dL/g)$	$\log ([\eta]/(dL/g))$
C-1	40,000	4.6021	0.3117	-0.5063	0.2431	-0.6142
C-2	60,000	4.7782	0.4194	-0.3774	0.3299	-0.4816
C-3	80,000	4.9031	0.5117	-0.2910	0.4065	-0.3909
C-4	200,000	5.3010	0.8709	-0.0600	0.7244	-0.1400

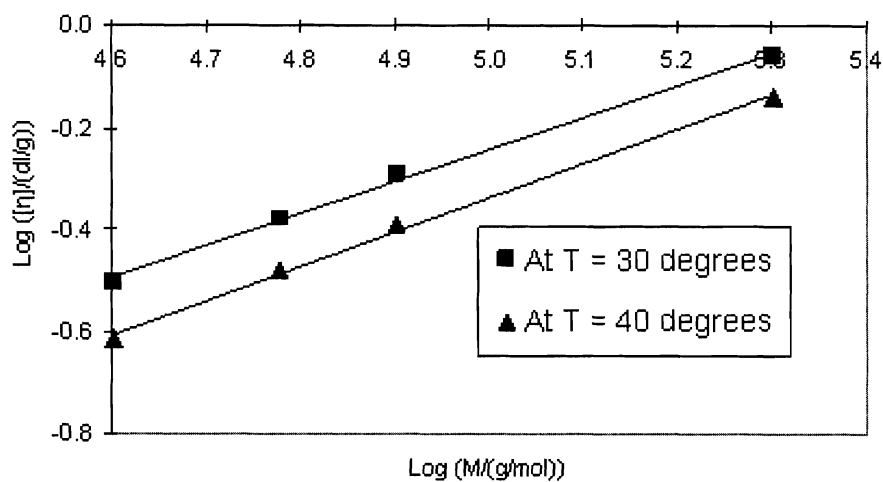


Figure 10. Intrinsic viscosity curves for copolymers at 30 °C and 40 °C.

Table 5. Intrinsic viscosities for fluoroterpolymers with varying molecular weights at 30 °C and 40 °C.

Polymer	$M/(g/mol)$	$\log (M/(g/mol))$	At $T = 30^{\circ} C$		At $T = 40^{\circ} C$	
			$[\eta]/(dL/g)$	$\log ([\eta]/(dL/g))$	$[\eta]/(dL/g)$	$\log ([\eta]/(dL/g))$
T-1	30,000	4.4771	0.2476	-0.6062	0.2160	-0.6655
T-2	40,000	4.6021	0.3296	-0.4820	0.2819	-0.5499
T-3	70,000	4.8451	0.4963	-0.3043	0.4207	-0.3760
T-4	200,000	5.3010	1.3431	0.1281	1.1737	0.0696

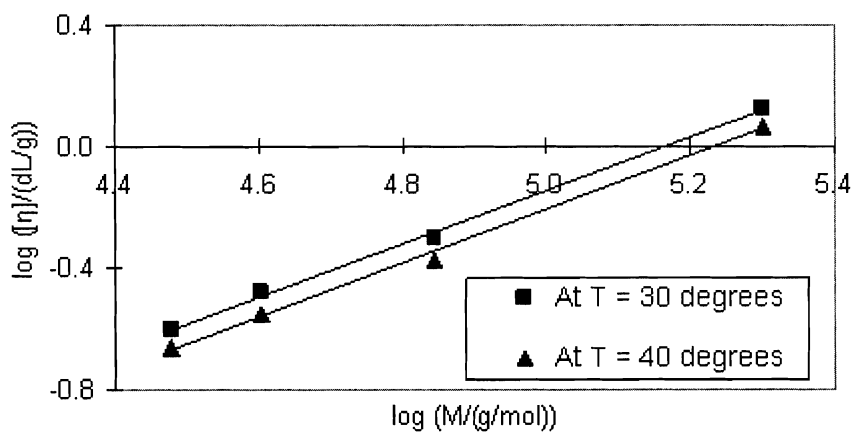


Figure 11. Intrinsic viscosity curves for terpolymers at 30 °C and 40 °C.

Error Analysis for Intrinsic Viscosity Measurements²¹

The intrinsic viscosity, $[\eta]$, was calculated from the solution concentration, c , and efflux time, t , such that

$$[\eta] = f(t, c)$$

The variances for concentration (δ_c) and time (δ_t), both measured N times are given by

$$\delta_c^2 = \frac{1}{N} \sum_{i=1}^N (\Delta c_i)^2 \quad (11)$$

$$\delta_t^2 = \frac{1}{N} \sum_{i=1}^N (\Delta t_i)^2 \quad (12)$$

where $\Delta c_i = c_i - \bar{c}$ and $\Delta t_i = t_i - \bar{t}$

In the same way, the variance of $[\eta]$ for N measurements will be

$$\delta_{[\eta]}^2 = \frac{1}{N} \sum_{i=1}^N (\Delta[\eta]_i)^2 \quad (13)$$

where $\Delta[\eta]_i = [\eta]_i - [\eta]$, $[\eta] = f(\bar{c}, \bar{t})$ and $[\eta]_i = f(c_i, t_i)$

$$\text{But } \Delta[\eta]_i \cong \frac{\partial[\eta]}{\partial c} \Delta c_i + \frac{\partial[\eta]}{\partial t} \Delta t_i \quad (14)$$

Inserting equation (14) into equation (13) gives,

$$\begin{aligned} \delta_{[\eta]}^2 &= \frac{1}{N} \sum_{i=1}^N \left[\frac{\partial[\eta]}{\partial c} \Delta c_i + \frac{\partial[\eta]}{\partial t} \Delta t_i \right]^2 \\ \delta_{[\eta]}^2 &= \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{\partial[\eta]}{\partial c} \right)^2 (\Delta c_i)^2 + \left(\frac{\partial[\eta]}{\partial t} \right)^2 (\Delta t_i)^2 + \left(\frac{\partial[\eta]}{\partial c} \right) \left(\frac{\partial[\eta]}{\partial t} \right) (\Delta c_i) (\Delta t_i) \right] \end{aligned} \quad (15)$$

The last term in equation (15), $\left(\frac{\partial[\eta]}{\partial c} \right) \left(\frac{\partial[\eta]}{\partial t} \right) (\Delta c_i) (\Delta t_i)$, consists of cross terms

which are equally likely to be positive or negative. For a large set of observations, the summation of the product of these terms will cancel each other or will be very near zero.

Hence this term will be dropped from equation 15.

$$\begin{aligned}
\delta_{[\eta]}^2 &= \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{\partial[\eta]}{\partial c} \right)^2 (\Delta c_i)^2 + \left(\frac{\partial[\eta]}{\partial t} \right)^2 (\Delta t_i)^2 \right] \\
\delta_{[\eta]}^2 &= \left(\frac{\partial[\eta]}{\partial c} \right)^2 \frac{1}{N} \sum_{i=1}^N (\Delta c_i)^2 + \left(\frac{\partial[\eta]}{\partial t} \right)^2 \frac{1}{N} \sum_{i=1}^N (\Delta t_i)^2 \\
\delta_{[\eta]}^2 &= \left(\frac{\partial[\eta]}{\partial c} \right)^2 \delta_c^2 + \left(\frac{\partial[\eta]}{\partial t} \right)^2 \delta_t^2
\end{aligned} \tag{16}$$

A. Error Analysis for Intrinsic Viscosity of Terpolymer, T-4

1. *Error contribution from concentration measurements of T-4 solutions*

The intrinsic viscosity, $[\eta]$, at 30 °C was measured for five different solutions of T-4 polymer at different concentrations. Table 6 shows the intrinsic viscosities calculated at different concentrations of T-4 in N, N – Dimethylformamide (DMF).

Table 6. Intrinsic viscosities for T-4/DMF solutions at different concentrations

Concentration/(g/dL)	d_i	d_i^2	$[\eta]/(\text{dL/g})$
0.035	-0.017	0.000282	1.3818
0.046	-0.006	0.000034	1.3685
0.054	0.002	0.000005	1.3481
0.057	0.005	0.000027	1.3466
0.067	0.015	0.000231	1.2684

$$N = 5$$

$$\bar{c} = \frac{1}{5} \sum_{i=1}^5 c_i = \frac{(0.035 + 0.046 + 0.054 + 0.057 + 0.067)}{5} \text{ g/dL} = 0.052 \text{ g/dL}$$

$$d_i = \text{deviation} = \Delta c_i = c_i - \bar{c}$$

$$\sum_{i=1}^5 d_i^2 = 0.000579 (\text{g/dL})^2$$

Hence the variance and standard deviation of concentration for the T-4 solutions can be calculated below.

$$\delta_c^2 = \frac{1}{N} \sum_{i=1}^N (\Delta c_i)^2 = \frac{0.000579}{5} (\text{g/dL})^2 = 0.000116 (\text{g/dL})^2$$

$$\delta_c = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta c_i)^2} = \sqrt{0.000116} = 0.011 \text{ g/dL}$$

The intrinsic viscosities at the different concentrations were calculated from the equation below,

$$[\eta] = \frac{1}{2} \left[\left(\frac{\Delta V^2}{16} + \frac{8\Delta V}{c} \right)^{1/2} - \frac{\Delta V}{4} \right] \quad (17)$$

where $\Delta V = \eta_{\text{reduced}} - \eta_{\text{inherent}}$. It is difficult to obtain a relationship between c and $[\eta]$ from equation (17) because concentration values are buried in the quantity ΔV . An easier way to obtain a relationship between c and $[\eta]$ is by plotting a graph using the values from table 6.

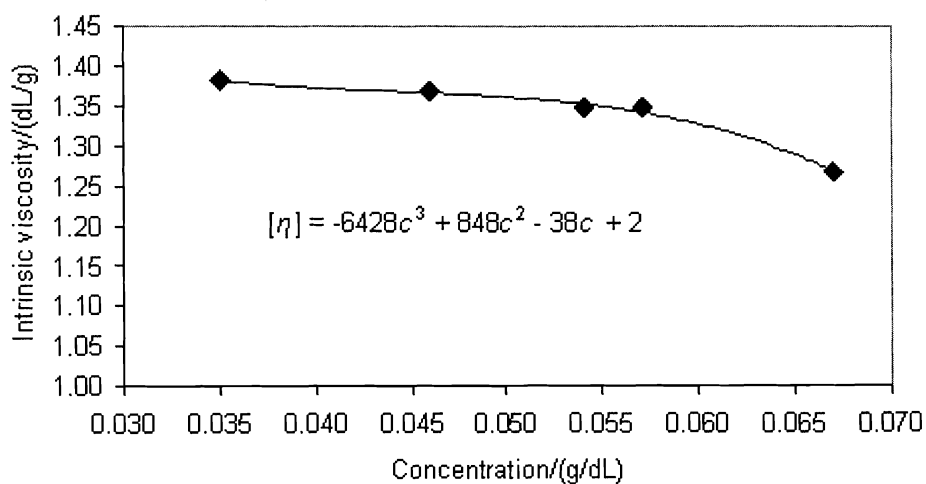


Figure 12. Relationship between intrinsic viscosity and concentration of T-4 at 30 °C.

From the graphical representation above,

$$[\eta] = -6428c^3 + 848c^2 - 38c + 2$$

$$\frac{\partial[\eta]}{\partial c} = (3)(-6428)c^2 + (2)(848)c - 38, \text{ but } \bar{c} = 0.052$$

$$\text{So, } \frac{\partial[\eta]}{\partial c} = (3)(-6428)(0.052)^2 + (2)(848)(0.052) - 38 = -1.9519$$

2. Error contribution from time measurements of T-4 solutions

Five consecutive measurements of time were taken for a 0.049 g/dL T-4/DMF solution and the intrinsic viscosities at 30 °C for each time were calculated.

Table 7. Intrinsic viscosities from five consecutive time measurements of a 0.049 g/dL

T-4/DMF solution.

Efflux time, t /mins.	d_i	d_i^2	$[\eta]/(\text{dL/g})$
4.5509	-0.00474	2.2468×10^{-5}	1.2964
4.5529	-0.00274	7.5076×10^{-6}	1.3054
4.5539	-0.00174	3.0276×10^{-6}	1.3099
4.5592	0.00356	1.2674×10^{-5}	1.3337
4.5613	0.00566	3.2036×10^{-5}	1.3431

$$N = 5$$

$$\bar{t} = \frac{1}{5} \sum_{i=1}^5 t_i = \frac{(4.5509 + 4.5529 + 4.5539 + 4.5592 + 4.5613)}{5} \text{ mins} = 4.5556 \text{ mins}$$

$$d_i = \text{deviation} = \Delta t_i = t_i - \bar{t}$$

$$\sum_{i=1}^5 d_i^2 = 7.7713 \times 10^{-5} (\text{mins})^2$$

Hence the variance and standard deviation of time for the T-4 solutions can be calculated below.

$$\delta_t^2 = \frac{1}{N} \sum_{i=1}^N (\Delta t_i)^2 = \frac{7.7713 \times 10^{-5}}{5} = 1.5543 \times 10^{-5} (\text{mins})^2$$

$$\delta_t = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta t_i)^2} = \sqrt{1.5543 \times 10^{-5}} = 0.0039 \text{ mins}$$

The relationship between t and $[\eta]$ is linear and can be obtained by plotting a graph.

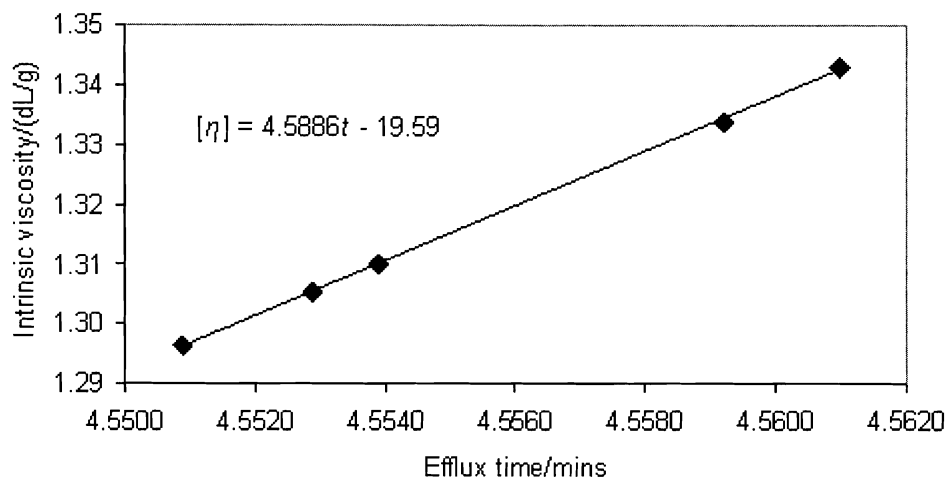


Figure 13. A graph of intrinsic viscosity versus time for a 0.049 g/dL T-4/DMF solution at 30°C.

The equation of the line can be obtained from the graph above.

$$[\eta] = 4.5886t - 19.59$$

$$\text{So, } \frac{\partial[\eta]}{\partial t} = 4.5886$$

3. Calculating the standard deviation for intrinsic viscosity measurements of T-4

From equation (16),

$$\delta_{[\eta]}^2 = \left(\frac{\partial[\eta]}{\partial c} \right)^2 \delta_c^2 + \left(\frac{\partial[\eta]}{\partial t} \right)^2 \delta_t^2 = (-1.9519)^2 (0.000116) + (4.5886)^2 (1.5543 \times 10^{-5})$$

$$\delta_{[\eta]}^2 = 4.4194 \times 10^{-4} + 3.2726 \times 10^{-4} = 7.6920 \times 10^{-4} \text{ (dL/g)}^2$$

$$\delta_{[\eta]} = \sqrt{\left(\frac{\partial[\eta]}{\partial c}\right)^2 \delta_c^2 + \left(\frac{\partial[\eta]}{\partial t}\right)^2 \delta_t^2} = 0.0277 \text{ dl/g} \quad (18)$$

But $[\eta]_{T-4} = 1.3431 \text{ dl/g}$, so the fractional standard deviation for T-4 can be calculated.

$$\frac{\delta_{[\eta]}}{[\eta]} = \frac{0.0277}{1.3431} = 0.021$$

4. Calculating the standard deviation in the molecular weight of T-4 due to error from $[\eta]$ measurements

Although intrinsic viscosity measurements are very efficient in calculating the molecular weight of polymers, caution must be taken when analyzing and comparing the results. Normally as $[\eta]$ changes, M should change too, but the calculated $[\eta]$ values carry some amount of error originating from the observed quantities – concentration and time (as shown earlier). From equation (13)

$$\delta_{[\eta]}^2 = \frac{1}{N} \sum_{i=1}^N (\Delta[\eta]_i)^2$$

where $\Delta[\eta]_i = [\eta]_i - [\bar{\eta}]$, $[\bar{\eta}] = f(\bar{c}, \bar{t})$ and $[\eta]_i = f(c_i, t_i)$

Hence it is very important to calculate how the error in $[\eta]$ affects the molecular weight by calculating the variance of M (δ_M^2) due to the variance in intrinsic viscosity ($\delta_{[\eta]}^2$).

Equation (19) gives a relationship between these two quantities.

$$\delta_M^2 = \left(\frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2 \quad (19)$$

The value of $\delta_{[\eta]}^2$ can be obtained from equation (18) and the quantity $\left(\frac{\partial M}{\partial [\eta]}\right)$ can be obtained by plotting a relationship between M and $[\eta]$ as given by Mark-Houwink's equation,

$$[\eta] = kM^a$$

where k and a are characteristic constants for a given polymer/solvent/temperature system.

The intrinsic viscosities obtained at 30 °C for the terpolymers T-1, T-2, T-3 and T-4 are given in table 8 below. These terpolymers all consist of vinylidene fluoride (VDF), tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) in the ratio 64:18:18 but each have different molecular weights.

Table 8. Intrinsic viscosities of VDF/TFE/HFP terpolymers with different molecular weights at 30 °C.

Polymer	Molecular weight, $M/(g/mol)$	Intrinsic viscosity $[\eta]/(dL/g)$	Log $(M/(g/mol))$	Log $([\eta]/(dl/g))$
T-1	30,000	0.2476	4.4771	-0.6062
T-2	40,000	0.3296	4.6021	-0.4820
T-3	70,000	0.4963	4.8451	-0.3043
T-4	200,000	1.3431	5.3010	0.1281

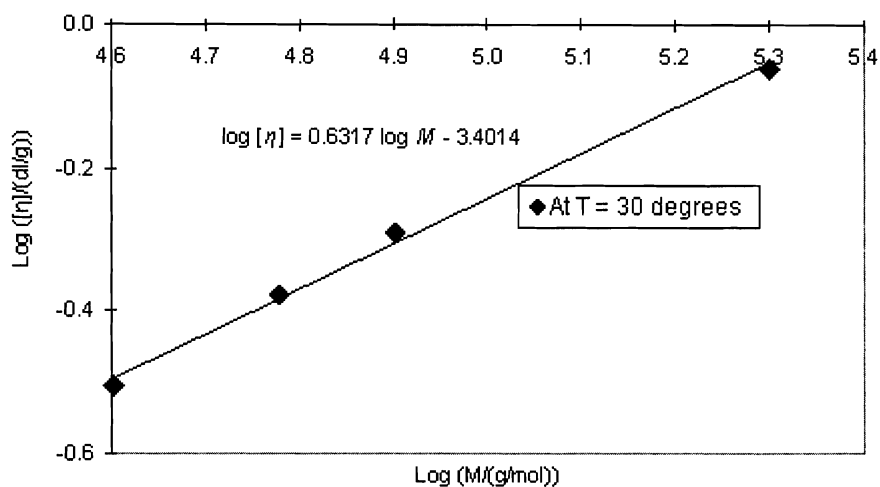


Figure 14. A plot of $\log [\eta]$ versus $\log M$ for terpolymers at 30 °C.

The equation of the graph is

$$\log[\eta] = a \log M + \log k$$

$$\log[\eta] = 0.8821 \log M - 4.5559$$

$$\Rightarrow a = 0.88 \text{ and } \log k = -4.5559$$

$$\Rightarrow a = 0.9 \text{ and } k = 2.78 \times 10^{-5} \text{ mol}^{0.9} \text{ dL/g}^{1.9}$$

The primary goal of these $[\eta]$ experiments was to compare the molecular weights of the original pre-ball milled polymers to the post-ball milled polymers after the additives are extracted from the powders. It turned out that the post-ball milled T-4 powders had similar intrinsic viscosities to the original polymer. Considering that the standard

deviation from the mean $[\eta]$ was found to be 0.0277 dl/g for T-4, it is concluded that the molecular weights of the pre- and post-ball milled powders are about the same.

Table 9. Intrinsic viscosities of original polymer T-4 and post-ball milled polymers (T4-51, T4-52 and T4-58) at 30 °C.

Polymer	Intrinsic viscosity, $[\eta]/(\text{dL/g})$
T-4	1.3431
T4-51	1.3254
T4-52	1.3448
T4-58	1.3464

Hence the fractional standard deviation of M for T-4 can be calculated.

$$\left(\frac{\delta_M}{M}\right)^2 = \left(\frac{1}{M} \frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2 = \left(\frac{1}{\left(\frac{[\eta]}{k}\right)^{1/a}} \times \left(\frac{1}{a} \times \frac{[\eta]^{\frac{1}{a}-1}}{k^{\frac{1}{a}}}\right)\right)^2 \times \delta_{[\eta]}^2 = \left(\frac{k^{1/a}}{[\eta]^{1/a}} \times \left(\frac{1}{a} \times \frac{[\eta]^{\frac{1}{a}-1}}{k^{\frac{1}{a}}}\right)\right)^2 \times \delta_{[\eta]}^2$$

$$\left(\frac{\delta_M}{M}\right)^2 = \left(\frac{1}{a}\right)^2 \left(\frac{\delta_{[\eta]}}{[\eta]}\right)^2 \quad (20)$$

From table 8, $M_{T-4} = 200,000$ g/mol and $[\eta]_{T-4} = 1.3431$ dl/g

$$\left(\frac{\delta_M}{M}\right)^2 = \left(\frac{1}{0.9}\right)^2 \left(\frac{0.0277}{1.3431}\right)^2 = 5.2643 \times 10^{-4}$$

$$\frac{\delta_M}{M} = 0.023$$

$$\delta_M = 0.023 \times 200,000 \text{ g/mol} = 4,600 \text{ g/mol}$$

Hence the standard deviation of M for T-4 is 4,600 g/mol as a result of the error in the intrinsic viscosity measurements.

Another approach can be used to calculate the standard deviation of M for the polymer, T-4 by plotting a graph of M versus $[\eta]$ using the values in table 8.

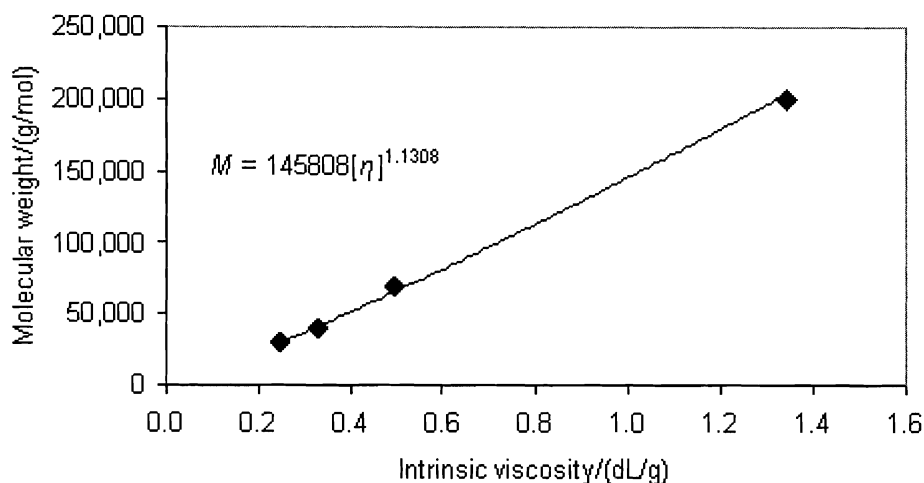


Figure 15. Molecular weight versus intrinsic viscosity for terpolymers at 30 °C.

The Mark-Houwink equation can be re-written as,

$$M = \left(\frac{[\eta]}{k} \right)^{1/a}$$

which can be compared to the equation of the graph above given as

$$M = 145808[\eta]^{1.1308}$$

$$\Rightarrow \frac{1}{a} = 1.1308 \text{ and } \left(\frac{1}{k}\right)^{1/a} = 145808$$

$$\Rightarrow a = 0.9 \text{ and } k = 2.71 \times 10^{-5} \text{ mol}^{0.9} \text{ dL/g}^{1.9}$$

$$\frac{\partial M}{\partial [\eta]} = (1.1308)(145808)[\eta]^{0.1308} = 164880[\eta]^{0.1308}$$

$$\delta_M^2 = \left(\frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2 = (164880[\eta]^{0.1308})^2 (7.6920 \times 10^{-4}) = (164880 \times 1.3431^{0.1308})^2 (7.6920 \times 10^{-4})$$

$$\delta_M^2 = 2.2589 \times 10^7$$

$$\delta_M = \sqrt{\left(\frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2} = \sqrt{2.2589 \times 10^7} = 4,752 \cong 4,800 \text{ g/mol}$$

$$\frac{\delta_M}{M} = \frac{4,800 \text{ g/mol}}{200,000 \text{ g/mol}} = 0.024$$

B. Error Analysis for Intrinsic Viscosity of Copolymer, C-4

The procedure to find the error built into the intrinsic viscosity measurements of the copolymers will basically be the same as that for the terpolymers but the variances in M and $[\eta]$ will be different from those of the terpolymers. This is because the copolymers have different k and a values hence they show different solubility characteristics in DMF.

1. Error contribution from concentration measurements of C-4 solutions

The intrinsic viscosity, $[\eta]$, at 30°C was measured for four different solutions of the C-4 polymer at different concentrations. Table 10 shows the intrinsic viscosities calculated at different concentrations of C-4 in N, N – Dimethylformamide (DMF).

Table 10. Intrinsic viscosities of C-4/DMF solutions at different concentrations.

Concentration/(g/dL)	d_i	d_i^2	$[\eta]/(\text{dL/g})$
0.066	-0.040	0.001580	0.8599
0.077	-0.029	0.000827	0.8520
0.129	0.023	0.000541	0.8610
0.151	0.045	0.002048	0.8989

$$N = 4$$

$$\bar{c} = \frac{1}{4} \sum_{i=1}^4 c_i = \frac{(0.066 + 0.077 + 0.129 + 0.151)}{4} = 0.106 \text{ g/dL}$$

$$d_i = \text{deviation} = \Delta c_i = c_i - \bar{c}$$

$$\sum_{i=1}^4 d_i^2 = 0.004995 (\text{g/dl})^2$$

Hence the variance and standard deviation of concentration for the C-4 solutions can be calculated.

$$\delta_c^2 = \frac{1}{N} \sum_{i=1}^N (\Delta c_i)^2 = \frac{0.004995}{4} = 0.001248 (\text{g/dl})^2$$

$$\delta_c = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta c_i)^2} = \sqrt{0.001248} = 0.035 \text{ g/dL}$$

By plotting the values in table 10, we obtain a relationship between $[\eta]$ and c .

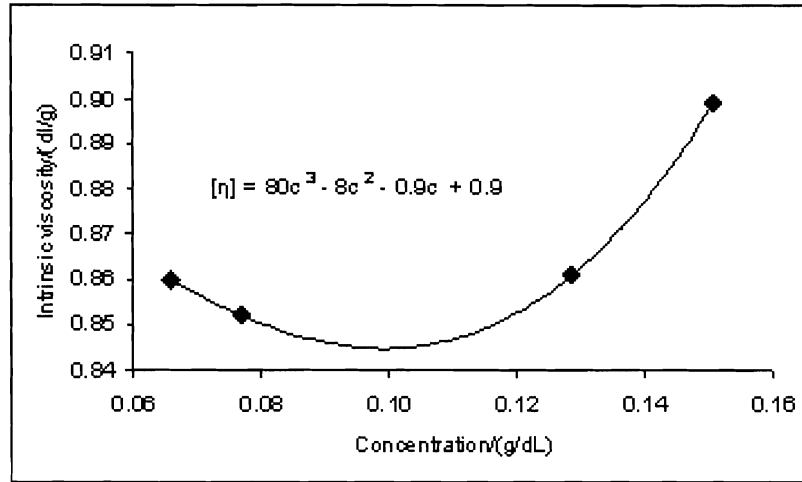


Figure 16. Relationship between intrinsic viscosity and concentration of C-4 at 30 °C.

From the graphical representation above,

$$[\eta] = 80c^3 - 8c^2 - 0.9c + 0.9$$

$$\frac{\partial[\eta]}{\partial c} = (3)(80)c^2 - (2)(8)c - 0.9, \text{ but } \bar{c} = 0.106$$

$$\text{So, } \frac{\partial[\eta]}{\partial c} = (3)(80)(0.106)^2 - (2)(8)(0.106) - 0.9 = 0.1006$$

2. Error contribution from differences in time measurements of C-4

Four consecutive measurements of time were taken for a 0.066 g/dL C-4/DMF solution and the intrinsic viscosities at 30 °C for each time were calculated.

Table 11. Intrinsic viscosities from four consecutive time measurements of a 0.066 g/dL C-4/DMF solution.

Efflux time, t /mins.	d_i	d_i^2	$[\eta]/(\text{dL/g})$
1.2793	-0.0017	3.0625×10^{-6}	0.8487
1.2803	-0.0008	5.6250×10^{-7}	0.8607
1.2805	-0.0006	3.0250×10^{-7}	0.8631
1.2841	0.0031	9.3025×10^{-6}	0.8727

$$N = 4$$

$$\bar{t} = \frac{1}{4} \sum_{i=1}^4 t_i = \frac{(1.2793 + 1.2803 + 1.2805 + 1.2841)}{4} = 1.2811 \text{ minutes}$$

$$d_i = \text{deviation} = \Delta t_i = t_i - \bar{t}$$

$$\sum_{i=1}^4 d_i^2 = 1.3230 \times 10^{-5} (\text{minutes})^2$$

Hence the variance and standard deviation of time for the C-4 solutions can be calculated below.

$$\delta_t^2 = \frac{1}{N} \sum_{i=1}^N (\Delta t_i)^2 = \frac{1.3230 \times 10^{-5}}{4} = 3.3075 \times 10^{-6} (\text{minutes})^2$$

$$\delta_t = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta t_i)^2} = \sqrt{3.3075 \times 10^{-6}} = 0.0018 \text{ minutes}$$

The linear relationship between t and $[\eta]$ for this 0.066 g/dL C-4/DMF solution is plotted in the graph below.

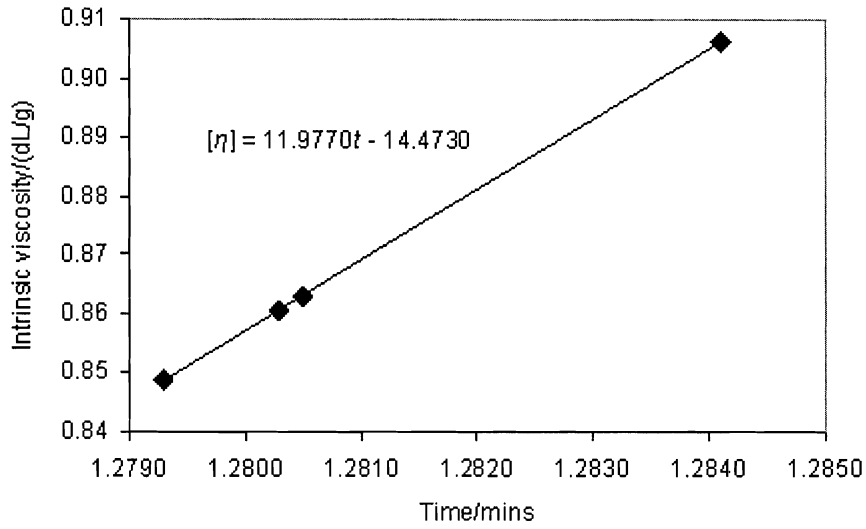


Figure 17. A graph of intrinsic viscosity versus time for a 0.066 g/dL C-4/DMF solution at 30°C.

The equation of the line can be obtained from the graph above.

$$[\eta] = 11.9770t - 14.4730$$

$$\text{So, } \frac{\partial[\eta]}{\partial t} = 11.9770$$

3. Calculating the standard deviation for intrinsic viscosity measurements of C-4

From equation (16),

$$\delta_{[\eta]}^2 = \left(\frac{\partial[\eta]}{\partial c} \right)^2 \delta_c^2 + \left(\frac{\partial[\eta]}{\partial t} \right)^2 \delta_t^2 = (0.1006)^2 (0.001248) + (11.9770)^2 (3.3075 \times 10^{-6}) = 4.8709 \times 10^{-4}$$

$$\delta_{[\eta]}^2 = 1.2630 \times 10^{-5} + 4.7445 \times 10^{-4} = 4.8709 \times 10^{-4} \text{ (dl/g)}^2$$

$$\delta_{[\eta]} = \sqrt{\left(\frac{\partial[\eta]}{\partial c}\right)^2 \delta_c^2 + \left(\frac{\partial[\eta]}{\partial t}\right)^2 \delta_t^2} = \sqrt{4.8709 \times 10^{-4} (\text{dl/g})^2} = 0.0221 \text{ dl/g}$$

But $[\eta]_{C-4} = 0.8709 \text{ dl/g}$, so the fractional standard deviation for C-4 can be calculated.

$$\frac{\delta_{[\eta]}}{[\eta]} = \frac{0.0221}{0.8709} = 0.025$$

4. Calculating the standard deviation in the molecular weight of C-4 due to error from $[\eta]$ measurements

The variance for M can be obtained by equation (19) and is given below as

$$\delta_M^2 = \left(\frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2$$

From equation 20,

$$\left(\frac{\delta_M}{M}\right)^2 = \left(\frac{1}{M} \frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2 = \left(\frac{1}{a}\right)^2 \left(\frac{\delta_{[\eta]}}{[\eta]}\right)^2$$

The value of ‘ a ’ for the copolymers (C-1, C-2, C-3 and C-4) can be obtained by plotting a graph of $\log M$ versus $\log [\eta]$. All four copolymers consist of VDF and HFP in the ratio 78:22 but have different molecular weights. The intrinsic viscosity value obtained for the post-ball milled C-4 polymer (0.8558 dl/g) was very similar to that of the pre-ball milled C-4 polymer (0.8709 dl/g). Considering the standard deviation from the mean $[\eta]$ has a value of 0.0221, it is possible to conclude that these numbers are practically the same and the molecular weight of the

C-4 polymer did not change significantly after ball milling.

Table 12. Intrinsic viscosities of VDF/HFP copolymers with different molecular weights at 30 °C

Polymer	Molecular weight M /(g/mol)	Intrinsic viscosity $[\eta]$ /(dL/g)	Log (M /(g/mol))	Log ($[\eta]$ /(dL/g))
C-1	40,000	0.3117	4.6021	-0.5063
C-2	60,000	0.4194	4.7782	-0.3774
C-3	80,000	0.5117	4.9031	-0.2910
C-4	200,000	0.8709	5.3010	-0.0600

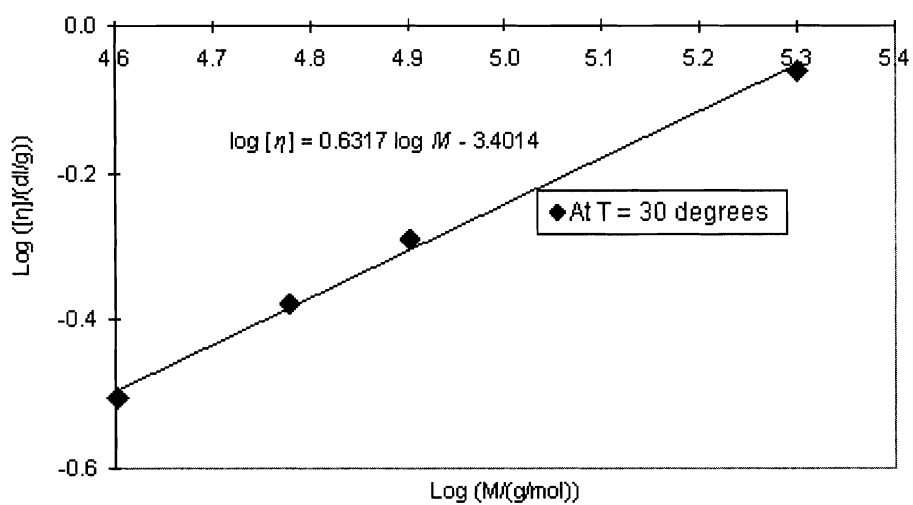


Figure 18. A plot of $\log [\eta]$ versus $\log M$ for copolymers at 30 °C.

The equation of the graph is given as

$$\log[\eta] = a \log M + \log k$$

$$\log[\eta] = 0.6317 \log M - 3.4014$$

$$\Rightarrow a = 0.63 \text{ and } \log k = -3.4014$$

$$\Rightarrow a = 0.6 \text{ and } k = 3.97 \times 10^{-4} \text{ mol}^{0.6} \text{ dL/g}^{1.6}$$

Substituting $a = 0.6$ and $[\eta] = 0.8709$ into equation 10 gives,

$$\left(\frac{\delta_M}{M}\right)^2 = \left(\frac{1}{M} \frac{\partial M}{\partial [\eta]}\right)^2 \delta_{[\eta]}^2 = \left(\frac{1}{a}\right)^2 \left(\frac{\delta_{[\eta]}}{[\eta]}\right)^2 = \left(\frac{1}{0.6}\right)^2 \left(\frac{0.0221}{0.8709}\right)^2 = 1.7887 \times 10^{-3}$$

$$\frac{\delta_M}{M} = \sqrt{1.7887 \times 10^{-3}} = 0.042$$

$$\delta_M = 0.042 \times 200,000 \text{ g/mol} = 8,500 \text{ g/mol}$$

Hence the standard deviation of M for C-4 is close to 8,500 g/mol as a result of the error in the intrinsic viscosity measurements. Table 13 below gives a brief summary of the standard deviations calculated in this section.

Table 13. Standard deviation values for T-4 and C-4.

Deviation Polymer	δ_c (g/dL)	δ_t (mins.)	$\frac{\delta_{[\eta]}}{[\eta]}$	$\frac{\delta_M}{M}$
T-4	0.011	0.0039	0.021	0.023
C-4	0.035	0.0018	0.025	0.042

C. Fraction of Chains Broken

It is important to determine the effect the variance in intrinsic viscosity has on the molecular weight of these polymers. The calculated fractional standard deviation in molecular weight, $\frac{\delta_M}{M}$, due to deviations in intrinsic viscosity, was approximately 2 % for the terpolymer T-4 and 4 % for the copolymer C-4. Hence it is possible that 2 % of T-4 chains or 4 % of C-4 chains may have been broken during the ball milling process.

Suppose the fluoropolymers, C-4 and T-4, have an average degree of polymerization, \bar{x}_n , and a repeat unit molecular weight of M_o g/mol. It is possible to estimate the average molecular weight, \bar{M}_n , at a given time during ball milling.

Let N_o = total moles/g of repeat units in fluoropolymer

N = moles of chains/g at some time during ball milling

Using 1 g of polymer as a basis,

$$N_o = \frac{1 \text{ g}}{M_o \text{ g/mol}} = \frac{1}{M_o} \text{ moles of repeat units}$$

$$\Rightarrow M_o = \frac{1}{N_o}$$

By definition, at any given time, the degree of polymerization, \bar{x}_n , and the number average molecular weight, \bar{M}_n , are given below.

$$\bar{x}_n = \frac{N_o}{N}$$

$$\bar{M}_n = \bar{x}_n M_o = \left(\frac{N_o}{N} \right) \left(\frac{1}{N_o} \right) = \frac{1}{N}$$

Initially, before any chains break,

$$\bar{M}_n^o = \frac{1}{N^o}$$

where \overline{M}_n^o = initial average molecular weight of chains before ball milling

N^o = initial moles of chains before ball milling

Thus, $N^o = \frac{1}{\overline{M}_n^o}$

Let f be the fraction of initial chains broken such that when

$f = 1$ when 100 % of chains are broken to half their initial average molecular weight;

$f = 0$ when no chains are broken.

The number of chains/g, N , that will result when a fraction, f , of chains are broken from the initial number of chains, N^o , at any given time during ball milling will be given by

$$N = N^o + N^o f = N^o(1 + f) = \left(\frac{1}{\overline{M}_n^o} \right) (1 + f) = \frac{(1 + f)}{\overline{M}_n^o}$$

But $N = \frac{1}{\overline{M}_n}$

So, $\overline{M}_n = \frac{\overline{M}_n^o}{(1 + f)}$ (21)

Using equation (21), we can find the average molecular weights for the polymers when $0 \leq f \leq 0.11$. Substituting \overline{M}_n in equation 5 from chapter 3, intrinsic viscosity values for the polymers can be calculated. Figure 19 shows the relationship between average molecular weight of the polymers during ball milling and the fraction of the initial number of chains broken from table 14.

Table 14. Average molecular weight and intrinsic viscosity values resulting from polymer chain breakage during ball milling. Take note that the initial average molecular weight of both C-4 and T-4 before ball milling was 200,000 g/mol.

f	\overline{M}_n	$[\eta]_{\text{C-4}}$	$[\eta]_{\text{T-4}}$	$\Delta[\eta]_{\text{C-4}}$	$\Delta[\eta]_{\text{T-4}}$
0.00	200000	0.885	1.319	0.000	0.000
0.01	198000	0.880	1.308	0.006	0.012
0.02	196000	0.874	1.296	0.011	0.023
0.03	194000	0.869	1.285	0.016	0.034
0.04	192300	0.864	1.274	0.022	0.045
0.05	190400	0.859	1.264	0.027	0.056
0.06	189000	0.853	1.253	0.032	0.066
0.07	187000	0.848	1.243	0.037	0.076
0.08	185000	0.843	1.233	0.042	0.087
0.09	183000	0.839	1.223	0.047	0.097
0.10	182000	0.834	1.213	0.052	0.106
0.11	180000	0.829	1.203	0.056	0.116

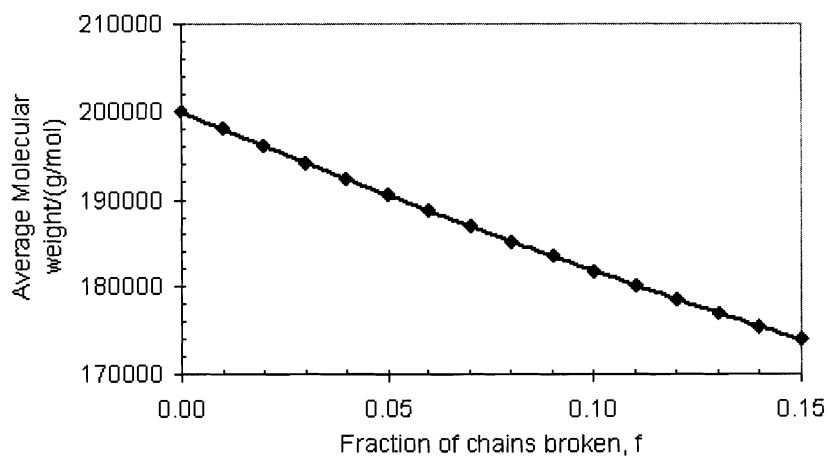


Figure 19. Relationship between average molecular weight, \overline{M}_n , and fraction of chains broken, f (where $0 \leq f \leq 0.11$).

The intrinsic viscosity values obtained for C-4 and T-4 were (8.871 ± 0.022) dl/g and (1.343 ± 0.028) dl/g respectively. Variations in intrinsic viscosity values will also cause variations in molecular weight as seen in table 14. Figure 19 makes it possible to relate different molecular weights of the fluoropolymers with the fraction of chains broken.

Let's examine the change in intrinsic viscosity of the fluoropolymers when 10 % of the chains are broken ($f = 0.1$) in table 14.

$$\Delta[\eta]_{C-4, f=0.1} = (0.885 - 0.834) \text{ dl/g} = 0.052 \text{ dl/g}$$

$$\Delta[\eta]_{T-4, f=0.1} = (1.319 - 1.213) \text{ dl/g} = 0.106 \text{ dl/g}$$

The change in intrinsic viscosity values for both C-4 and T-4 when $f = 0.1$ from table 14, is greater than the standard deviation values ($\delta_{[\eta]_{C-4}} = 0.022$ dl/g and $\delta_{[\eta]_{T-4}} = 0.028$ dl/g) obtained in the error analysis for the viscosity studies of C-4 and T-4 done earlier in this chapter. Hence we conclude that not more than 10 % of the chains were broken from the ball milling process.

Another study was performed to estimate the fraction of chains that may have broken during ball milling. A solution containing a mixture of C-3 (80,000 g/mol) and C-1 (40,000 g/mol) in DMF was made as well as a mixture of C-4 (200,000 g/mol) and C-1 (40,000 g/mol) in DMF. A solution containing a mixture of the terpolymers T-3 (70,000 g/mol), T-2 (40,000 g/mol), and T-1 (30,000 g/mol) in DMF was also prepared. Intrinsic viscosity studies were done at 30 °C for these polymer mixtures and compared to the intrinsic viscosity of the original polymer in solution with the highest molecular weight.

The purpose of these experiments was to find out how much change in intrinsic viscosity will result by decreasing the molecular weight of the polymer. If the change in intrinsic viscosity between the original polymer and the polymer with reduced molecular weight is greater than the standard deviation for the intrinsic viscosity values calculated in the error analysis section, then we can conclude that the molecular weight of the polymer after ball milling was greater than the reduced molecular weight value. The intrinsic viscosity values for C-4, C-3, C-1, T-3, T-2, and T-1 were obtained from table 2 and 3.

Table 15. Intrinsic viscosities of copolymer mixtures in DMF at 30 °C.

Polymers	$[\eta]_{\text{polymers}}$	$\bar{M}_{\text{polymers}} / (\text{g/mol})$	Weight % of polymers in solution		
C-4	0.8709	200,000			95
C-3	0.5117	80,000	95	90	
C-1	0.3117	40,000	5	10	5
$\delta_{[\eta]} / (\text{dl/g}) = 0.0221$	$\bar{M}_{\text{polymer mix in solution}} / (\text{g/mol})$		78,000	76,000	198,400
	$[\eta]_{\text{polymer mix in solution}} / (\text{dl/g})$		0.4819	0.4805	0.7673
	$\Delta[\eta] / (\text{dl/g}) = [\eta]_{\text{C-3 or C-4}} - [\eta]_{\text{polymer mix in solution}}$		0.0298	0.0312	0.1036

If 5 % of C-3 chains (80,000 g/mol) break in half (to 40,000 g/mol) as a result of ball milling, table 15 shows that the intrinsic viscosity of C-3 will reduce from 0.5117 dl/g to 0.4819 dl/g, and to 0.4805 dl/g as a result of 10 % chain breakage. If 5 % of C-4 chains (200,000 g/mol) break into 5 parts (to 40,000 g/mol), table 15 shows a reduction in intrinsic viscosity from 0.8709 dl/g to 0.7673 dl/g. The change in intrinsic viscosities that resulted from all three solutions in table 15 is higher than the standard deviation calculated for the intrinsic viscosity of the copolymers from the error analysis. Therefore, it is possible to conclude that less than 5 % of copolymer chains broke during the ball milling process.

If 5 % of T-3 chains (70,000 g/mol) break to 30,000 and 40,000 g/mol, table 16 shows that the intrinsic viscosity of T-3 reduces from 0.4963 dl/g to 0.4784 dl/g, and to 0.4608 dl/g because of 10 % chain breakage. The change in intrinsic viscosity that resulted from the solution with 5 % chain breakage was less than the standard deviation calculated for the intrinsic viscosity of the terpolymer while the change in intrinsic viscosity that resulted from 10 % chain breakage was greater. Therefore, it is possible to conclude that 5 % of terpolymer chains may have broken during the ball milling process but less than 10 % of these chains were affected.

Table 16. Intrinsic viscosities of terpolymer mixtures in DMF at 30 °C.

Polymers	$[\eta]_{\text{polymers}}$	$\bar{M}_{\text{polymers}} / (\text{g/mol})$	Weight % of polymers in solution	
T-3	0.4963	70,000	95	90
T-2	0.3296	40,000	2.5	5
T-1	0.2476	30,000	2.5	5
$\delta_{[\eta]} / (\text{dl/g}) = 0.0277$	$\bar{M}_{\text{polymer mix in solution}} / (\text{g/mol})$		68,250	66,500
	$[\eta]_{\text{polymer mix in solution}} / (\text{dl/g})$		0.4784	0.4608
	$\Delta[\eta] / (\text{dl/g}) = [\eta]_{\text{T-3}} - [\eta]_{\text{polymer mix in solution}}$		0.0179	0.0355

Equation 21 was used to estimate the fraction of chains broken. From the results obtained, it was possible to conclude that less than 10 % of chains may have broken during the ball milling process. These results are consistent with the results obtained from intrinsic viscosity studies. Hence we conclude that not more than 10 % of the chains were broken during the ball milling process and the rest of the chains were simply disentangled.

Thermogravimetric Analysis (TGA)

TGA measurements were carried out on a TGAQ500 from TA instruments. TGA curves were recorded for the polymers C-4 and T-4, the additive BTPPC and the ball milled powders # 45 (from C-4), # 49 and # 51 (from T-4) at a heating rate of 20 °C/min under a nitrogen atmosphere (40 mL/min).

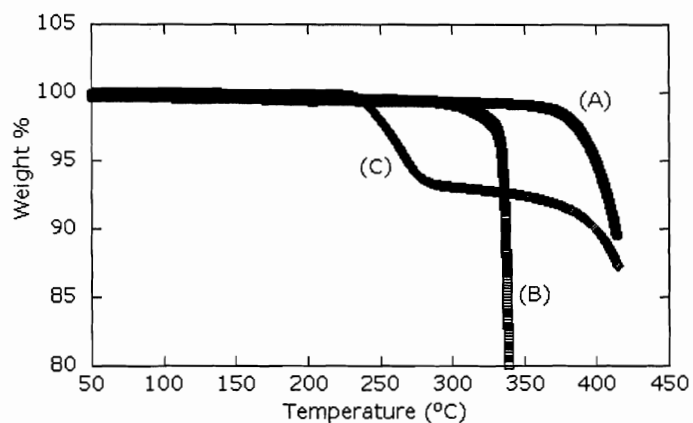


Figure 20. TGA for (A) C-4, (B) BTPPC and (C) powder # 45.

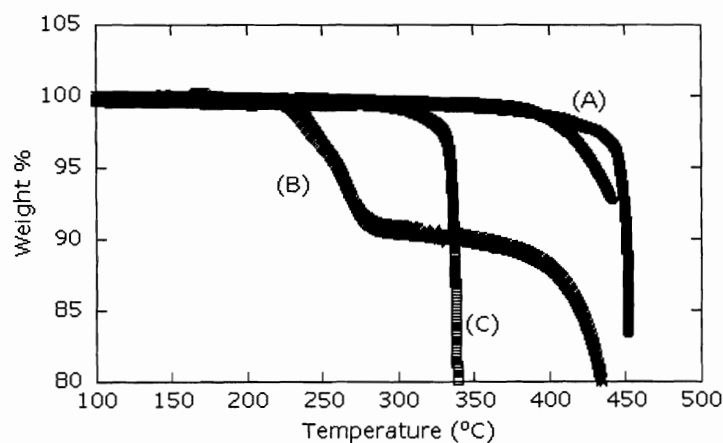


Figure 21. TGA for (A) T-4, (B) powders # 49 and # 51. The curves for both powders overlapped such that both curves are seen as one. (C) BTPPC.

As can be seen from the TGA analysis, these fluoropolymers all exhibit thermal stability at high temperatures and start degrading at temperatures above 400 °C. The copolymer C-4 starts degrading at a slightly lower temperature of 400 °C than the terpolymer T-4 which starts degrading at 450 °C. The additive, BTPPC, in all three powders (# 45, # 49 and # 51) starts to decompose at temperatures slightly lower than 250 °C, though virgin additive does not start decomposing until approximately 350 °C. This

degradation temperature of BTPPC in the powders is lowered due to the presence of polymer. The degradation temperature for the polymer was not affected by the presence of additive.

In figure 20, there was a weight loss of 6 % from powder # 45 corresponding to the amount of BTPPC that was present in the powder. This is slightly higher than the 5 wt% of BTPPC expected to be present when these powders were weighed at the beginning of the ball milling process. Figure 21 shows a 9 wt % loss from the powders # 49 and # 51 corresponding to the amount of BTPPC that was present in the powder. Once again, these TGA values are slightly higher than the 6 wt% obtained gravimetrically at the beginning of the ball milling process for both # 49 and # 51. The slight discrepancy may be due to error that results from weighing the substances before ball milling.

Differential Scanning Calorimetry (DSC)

DSC measurements were conducted on a DSCQ1000 calorimeter from TA instruments. Sample masses of 10 mg were used in aluminum pans. The DSC was purged with nitrogen and heated at a rate of 10 °C/min. DSC traces were obtained for the original fluoropolymers, the additives and the ball-milled powders as shown in figure 22 and 23 below. Figure 22 shows the thermographs for sample # 49 while figure 23 shows the thermographs for sample # 51. About 0.3 g of the ball milled powders (# 49 and # 51) were washed with a 95 % water and 5 % methanol solution and the DSC thermographs for these samples (# 49 W and #51 W) were also obtained as shown in figure 23 and 24, respectively.

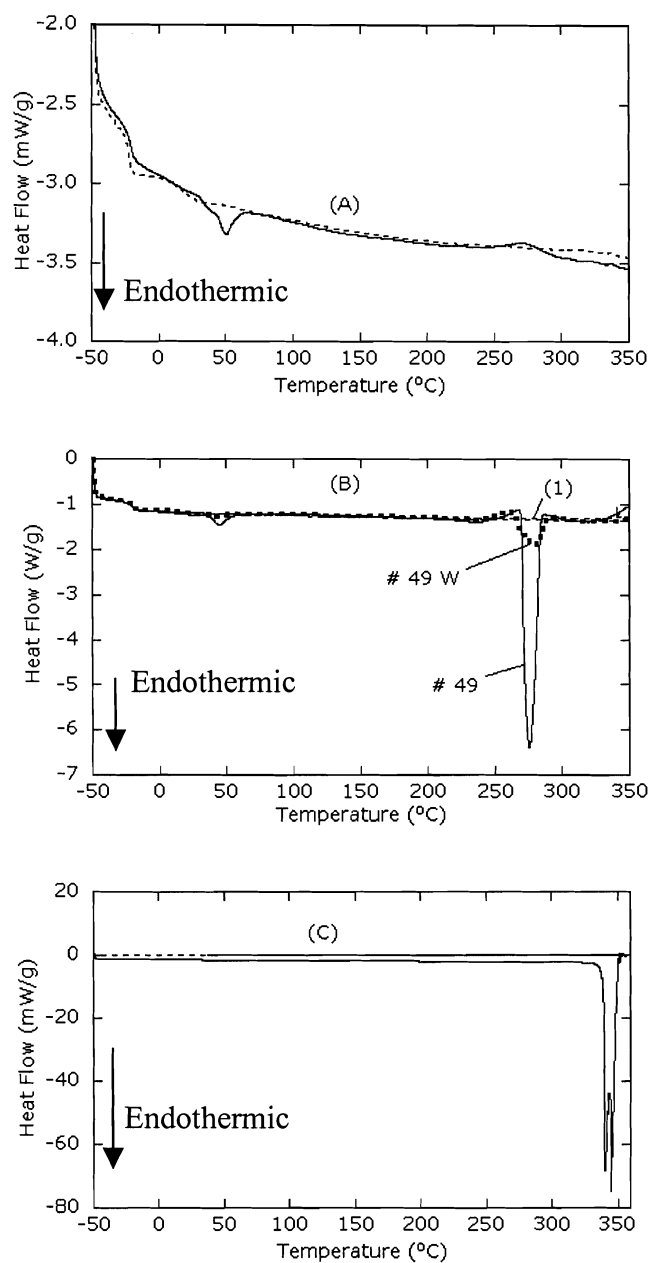


Figure 22. DSC scans for T-4, the ball milled powder (# 49), powder # 49 that was washed with a methanol/water mixture (# 49 W) and the additive BTPPC. (A) T-4 polymer. The solid line corresponds to the first heating process while the dotted line represents the second heating. (B) The first heat for # 49 is represented by the solid line.

The bold dotted line corresponds to the first heating process for # 49 W. The dotted line labeled (1) corresponds to the second heating for both # 49 and # 49 W. (C) First heat for BTPPC (solid line) and second heat (dotted line).

Figures 22(B) and 23(B) of the powders showed the appearance of two endothermic peaks due to the polymer ($-22\text{ }^{\circ}\text{C}$ and $50\text{ }^{\circ}\text{C}$) and one endothermic peak due to BTPPC at $\sim 275\text{ }^{\circ}\text{C}$ in the powders. The endothermic peak due to BTPPC can be identified as the melting temperature which reduces by about $70\text{ }^{\circ}\text{C}$ in the powders compared to the melting temperature of pure BTPPC shown in figures 22C and 23C. There is no change in the glass transition temperature (which can be identified as the inflexion point for the slope at the lowest temperature $-22\text{ }^{\circ}\text{C}$ for T-4 and the T-4 powders.

The endothermic peaks due to melting of the polymer at $50\text{ }^{\circ}\text{C}$ in figures 22 and 23 were very visible in the first heating scan for all the powder samples, but were very much suppressed during the second heating scan. The melting peak present in the first heating scan may be due to a small degree of crystallinity in the polymer²². After the sample was cooled at $10\text{ }^{\circ}\text{C}/\text{min}$ and re-heated, the endothermic peak at $50\text{ }^{\circ}\text{C}$ became very small and was shifted to $40\text{ }^{\circ}\text{C}$. This is most probably because the sample was cooled too fast such that it was not possible to obtain the same amount of crystallization present in the polymer as before²² DSC analysis. The melting peak for BTPPC does not appear for the second heating because it decomposed after the first heating process which was heated to $350\text{ }^{\circ}\text{C}$. The TGA showed that BTPPC starts to decompose at $350\text{ }^{\circ}\text{C}$.

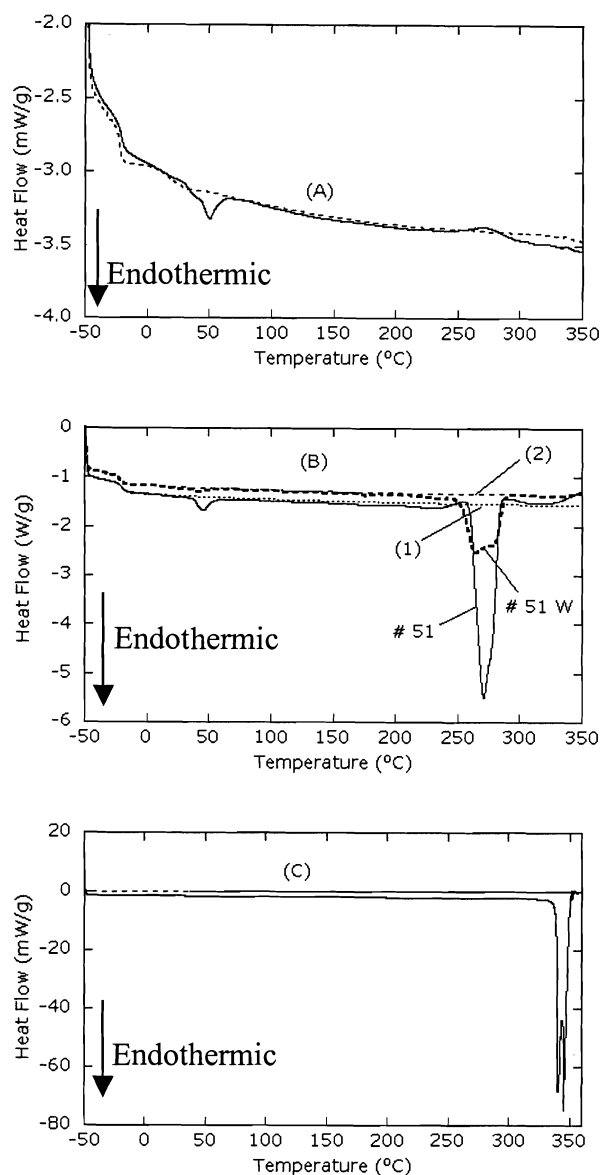


Figure 23. DSC scans for T-4, the ball milled powder (# 51), powder # 51 that was washed with a methanol/water mixture (# 51 W) and additive BTPPC. (A) T-4 polymer. The solid line corresponds to the first heating process while the dotted line represents the second heating. (B) The first heating process for # 51 is represented by the solid line. The bold dotted line corresponds to the first heating for # 51 W. The dotted line labeled (1)

corresponds to the second heating for # 51, and the dotted line labeled (2) is the second heating for # 51 W. (C) First heat for BTPPC (solid line) and second heat (dotted line).

Figures 22(A) and 23(A) show a small exothermic peak at 275 °C for the T-4 terpolymer and is most probably due to a small amount of decomposition of the polymer. This peak is not very visible in Figures. 22(B) and 23(B) for the T-4 powders because the melting peak for BTPPC is at this temperature and it dominates. It is possible though to see the ends of the exothermic peak on the melting peak of BTPPC. Notice that the melting peak for BTPPC does not start decreasing on the first scan immediately; it first goes in an upward direction towards exothermic energies, then starts decreasing as BTPPC melts. At the end of the melting peak for BTPPC, the thermograph goes up towards exothermic energies again and then drops.

Figure 24 compares the glass transition temperature for the virgin fluoropolymer T-4, and the fluoropolymer present in powders # 42 and # 49. The glass transition temperature is about the same for all three samples.

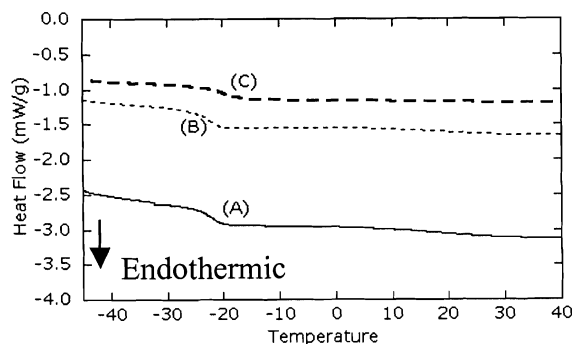
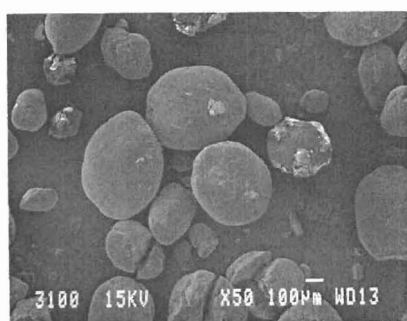


Figure 24. Glass transition temperature ($T_g \sim 22$ °C) for (A) T-4, (B) powder # 42 and (C) powder # 49.

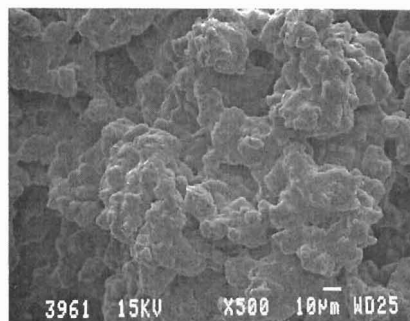
Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was done for T-4, BTPPC and the ball milled powders # 49 and # 51. About 0.3 g of the ball-milled powders was washed with a 95 % water and 5 % methanol solution and the scanning electron micrographs for these samples (# 49 W and # 51 W) were obtained. The reason for washing the powder samples in this solution was to remove of any BTPPC particles that may be present on the surface of the powder particles. This solution was chosen because it will dissolve BTPPC but will not dissolve, melt or soften the fluoropolymer.

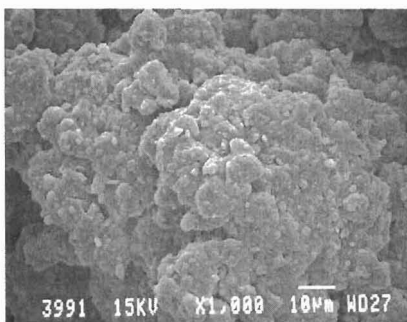
The SEM results are shown in the figures 25 and 26. The micrographs for the powders # 49 in figure 25(C) and # 51 in figure 26(C) showed the presence of additive on the surface of the powder particles. When these powders were washed in a water/methanol solution, the micrographs for # 49 W and # 51 W in figure 25(D) and figure 26(D) respectively showed powder surfaces with no additive speckles. When DSC studies were done on # 49 W and # 51 W, as shown in figure 22(B) and figure 23(B), both thermographs showed melting peaks for BTPPC at 275 °C though the intensity of these peaks were very much reduced compared to the unwashed powder. This tells us that some of the BTPPC was coated by the polymer while the rest remained on the surface.



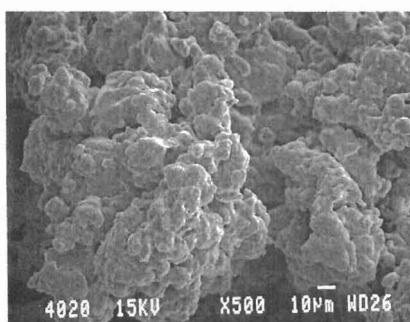
(A)



(B)

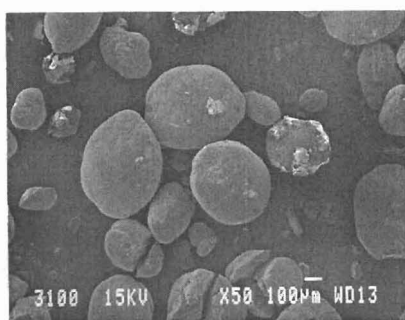


(C)

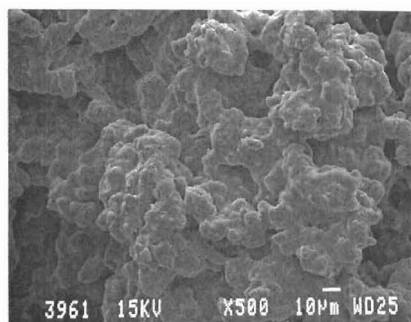


(D)

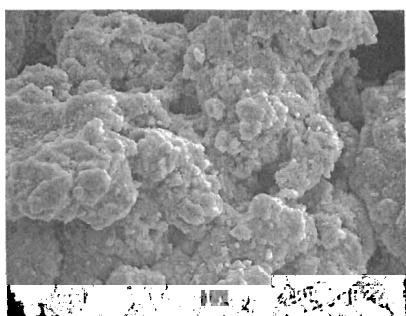
Figure 25. Scanning electron micrographs for (A) additive BTPPC, (B) terpolymer T-4, (C) powder # 49, notice what seems to be tiny speckles of additive particles on the surface of the polymer particle, and (D) # 49 W which was obtained from washing powder # 49 with a water/methanol mixture.



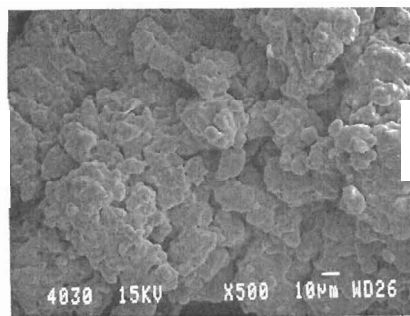
(A)



(B)



(C)



(D)

Figure 26. Scanning electron micrographs for (A) additive BTPPC, (B) terpolymer T-4, (C) powder # 51, notice what seems to be tiny speckles of additive particles on the surface of the polymer particle, and (D) # 51 W which was obtained from washing powder # 51 with a water/methanol mixture.

The micrographs obtained for samples # 49 W and # 51 W look very similar to that for T-4, except that there seems to be more continuity or connectivity of the polymer, T-4,

than the washed powders, # 49 W and # 51 W. DSC studies for # 49 W and # 51 W showed the presence of BTPPC in these samples.

Very little additive was used for these ball milling experiments compared to the amount of polymer used. From the calculations, more than 0.1 g of additive is needed to completely titrate the VDF in the fluoropolymers. This poses the question why all the additive used for ball milling in such little amounts was not completely coated by the polymer.

Both BTPPC and BAF are bulky molecules that contain more than one bulky phenyl group. It is possible that an additive molecule that interacts with a VDF repeat group screens other additive molecules from interacting with the VDF groups near the group interacting with the additive. It may also be possible that the polar site from the additive interacts with more than one polar site from the polymers such that the amount of additive needed to titrate polar sites in the polymer is reduced. The amount of energy needed to melt BTPPC in # 49 was 6 mW/g while an energy of 2 mW/g was needed to melt the BTPPC in # 49 W. This means that approximately 33 % of 0.1 g of BTPPC used for making powder # 49 ended up being coated by polymer (2 g of T-4). For future work, it will be worth finding out whether powder will be formed using quantities close to 0.033 g of BTPPC in 2 g of polymer. The amount of energy needed to melt the BTPPC in # 51 was 5.5 mW/g as opposed to 2.5 mW/g in # 51 W. Hence, approximately 45 % of 0.1 g of BTPPC used ended up being coated by T-4.

CHAPTER 4 Conclusions

When fluoropolymers containing vinylidene fluoride were ball milled with crystalline solid additives in the presence of CO₂ at temperatures close to room temperature and pressures between 1500 psig and 2000 psig, powder particles in which the additive was coated by the polymer were produced. Some of the additive particles remained on the surface of the powder particles but when the surface of these powder particles were washed with a 95 % water and 5 % methanol solution the DSC studies showed the presence of additive inside the polymer matrix. When the additives were extracted out of the polymer powders, viscosity studies showed that the intrinsic viscosity of the fluoropolymer in the powders and, hence, the molecular weight was the same as that for the original fluoropolymer within the experimental error limits. The ball milling process was gentle such that not more than 10 % of polymer chains got broken during the process, and no great change in molecular weight was observed. This implies that most of the polymer chains were not broken into smaller chains but simply disentangled during the milling process.

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APPENDIX 1

DSC for T-4, # 42, # 52 and BAF

Figure 27 shows the DSC results for the T-4/BAF powders # 42 and # 52 with the original polymer T-4 and the additive BAF. Figure 27(B) and (C) above showed the appearance of two endothermic peaks due to the polymer (-22 °C and 50 °C) and one endothermic peak due to BAF (~ 150 °C in the powders and 160 °C in the plain additive). The endothermic peak due to BAF can be identified as the melting temperature which reduces by about 10 °C in the powders compared to the plain additive. The glass transition temperature for T-4 and the T-4 powders remained almost the same (-22 °C).

The second endothermic peak due to the polymer at 50 °C was very visible in the first heating scan while it was very much suppressed in the second scan and was shifted to a lower temperature of 40 °C. This is most probably because the polymer was cooled too fast for it to obtain the same amount of crystallization present as before. It is possible that this endothermic peak may increase if the sample is left to set for a while or is cooled very slowly.

An exothermic peak for T-4 and the T-4/BAF powders (# 42 and # 52) is observed at 275 °C due to slight decomposition of the polymer. This peak was not very visible for the T-4 powders made with BTPPC (# 49 and #51) since the melting peak for BTPPC dominates at this temperature.

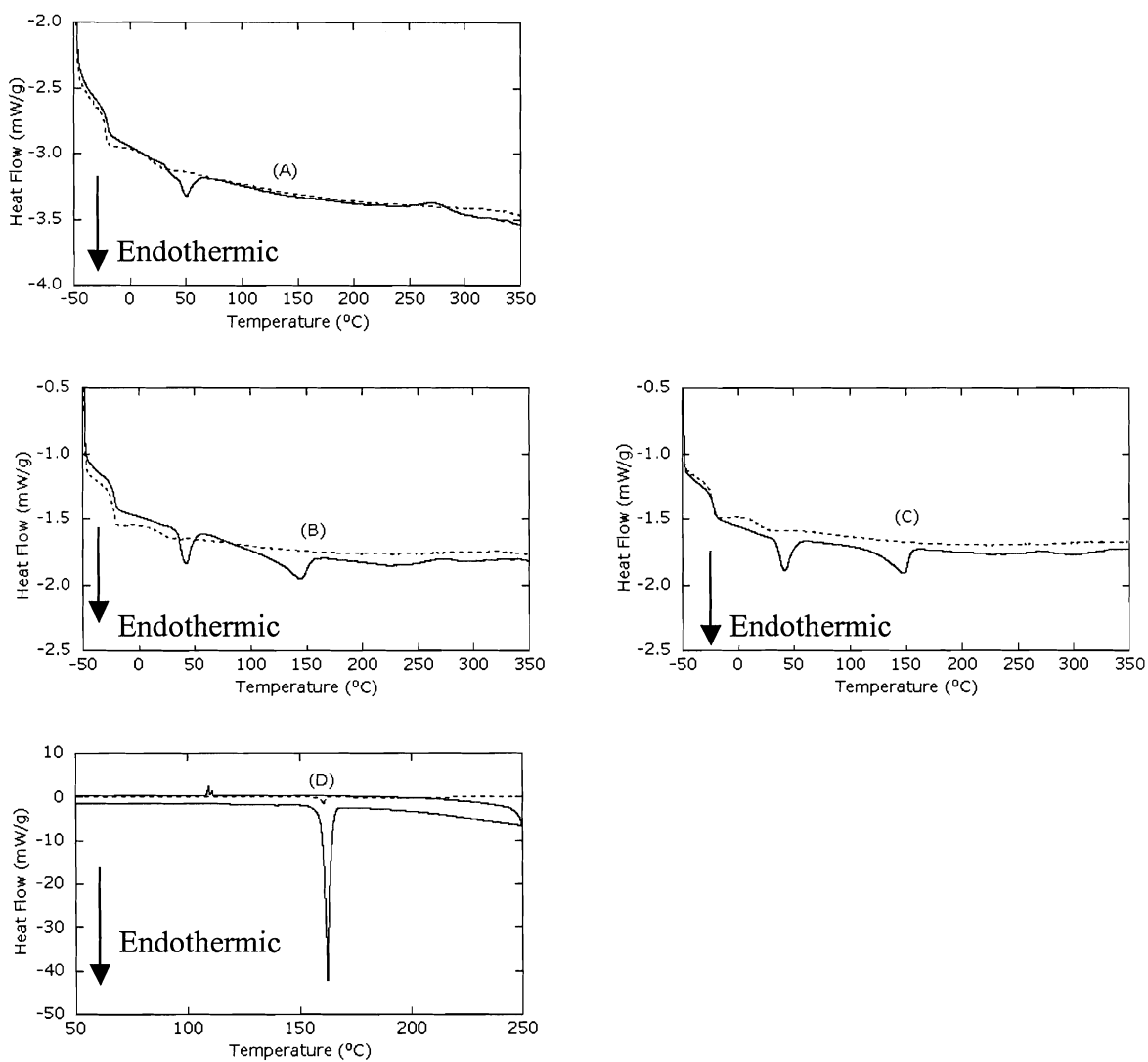


Figure 27. DSC for (A) T-4, (B) # 42, (C) # 52 and (D) BAF. The solid lines represent the first heat while the dotted lines were a result of the second heating process.

APPENDIX 2A

Thermogravimetric Analysis for Fluoropolymers (C4-45, T4-51, T4-52 and T4-58)

In order to carry out intrinsic viscosity studies on the fluoropolymer present in the powders after ball milling, the additives used in the powder making process had to be extracted. The additives were extracted using 95 % water and 5 % methanol mixture. It was very important to verify that all of the additives were extracted and that the resulting samples were totally dried of water or methanol. The fluoropolymers that remained after extraction were dried and thermographs of the dried samples were obtained. TG analysis on these dried samples showed no weight loss at 60 °C (due to the presence of methanol) and 100 °C (due to the presence of water) in figure 28 on the next page. DSC results (appendix 2B) showed that the additives were completely extracted.

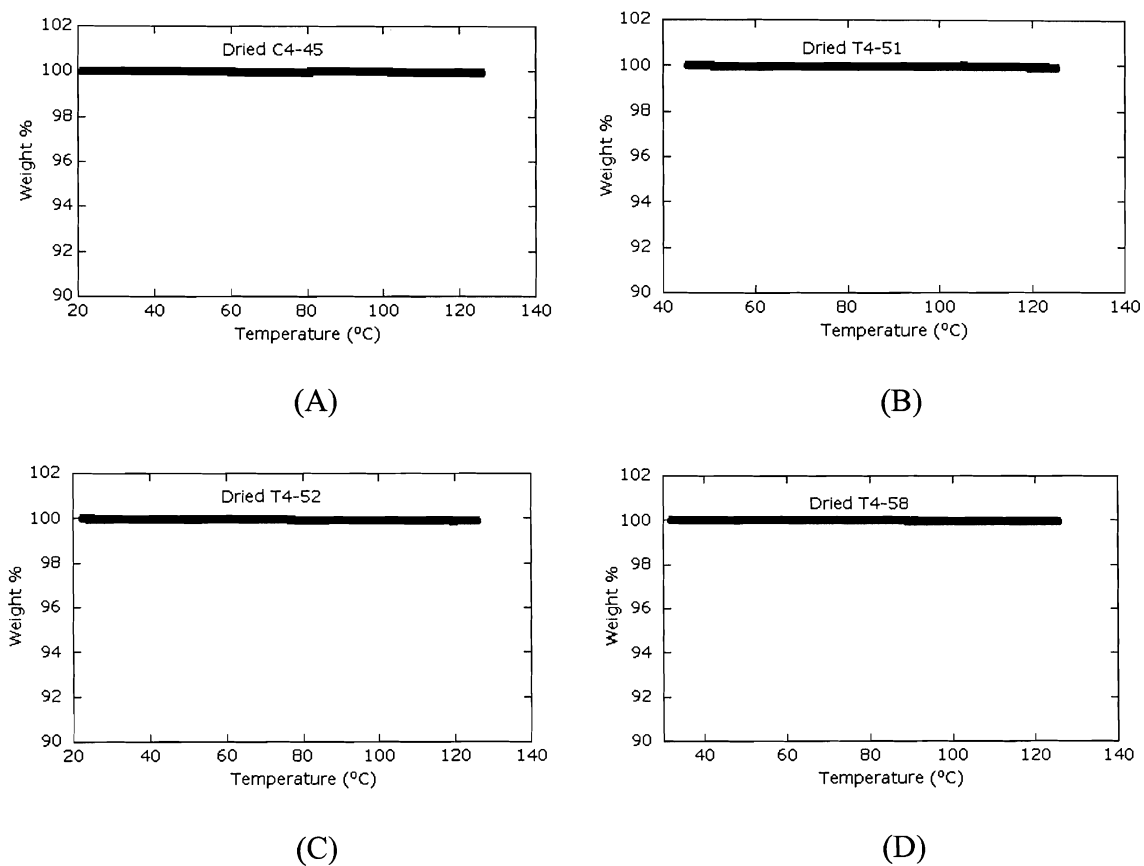


Figure 28. TG analysis for dried fluoropolymers after extraction. (A) C4-45, (B) T4-51, (C) T4-52 and (D) T4-58. No weight loss of samples was observed at 60 and 100 ° C.

APPENDIX 2B

DSC for Fluoropolymers (T4-51 and T4-52)

DSC traces were also obtained for the dried fluoropolymers that remained after BTPPC had been extracted from powders # 51 (sample called T4-51) and BAF had been extracted from # 52 (sample called T4-52). The results showed that there were no additives present in these polymers that could have affected the intrinsic viscosity values obtained. There were no visible exothermic peaks observed methanol at 67 °C or water at 100 °C due to evaporation of solvent. This supports the fact that these polymers were thoroughly dried.

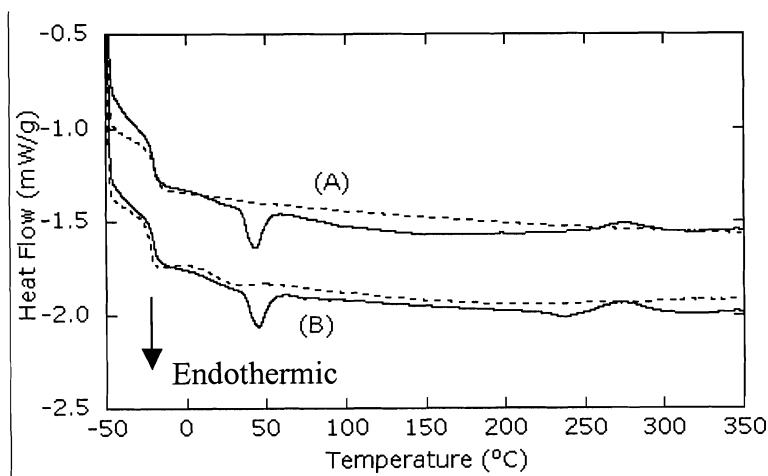


Figure 29. DSC scans for (A) T4-51 and (B) T4-52. The solid line represents the curves obtained from the first heating while the dashed lines are from the second heating process.

The thermographs for these powders in which the additives were extracted look very similar to that of the original polymer showing a T_g at $-22\text{ }^{\circ}\text{C}$, an endothermic peak at $50\text{ }^{\circ}\text{C}$ and a small exothermic peak at $275\text{ }^{\circ}\text{C}$ (due to a small amount of decomposition) in the first heating process. There are no visible endothermic peaks for BTPPC at $275\text{ }^{\circ}\text{C}$ or $345\text{ }^{\circ}\text{C}$ in figure 29(A) and for BAF at $150\text{ }^{\circ}\text{C}$ or $160\text{ }^{\circ}\text{C}$ in figure 29(B).

APPENDIX 3A

SEM for T-4, # 42 and BAF

SEM was done for T-4, BAF, powders # 42 and # 52. The results showed the presence of BAF on the surface of the powder particles. The ball milling process for the T-4/BAF powders resulted in particle diameters between 100 μm and 200 μm . Comparison of the micrographs for T-4, BAF, # 42 and # 52 can be seen in figure 30 and 31 below.

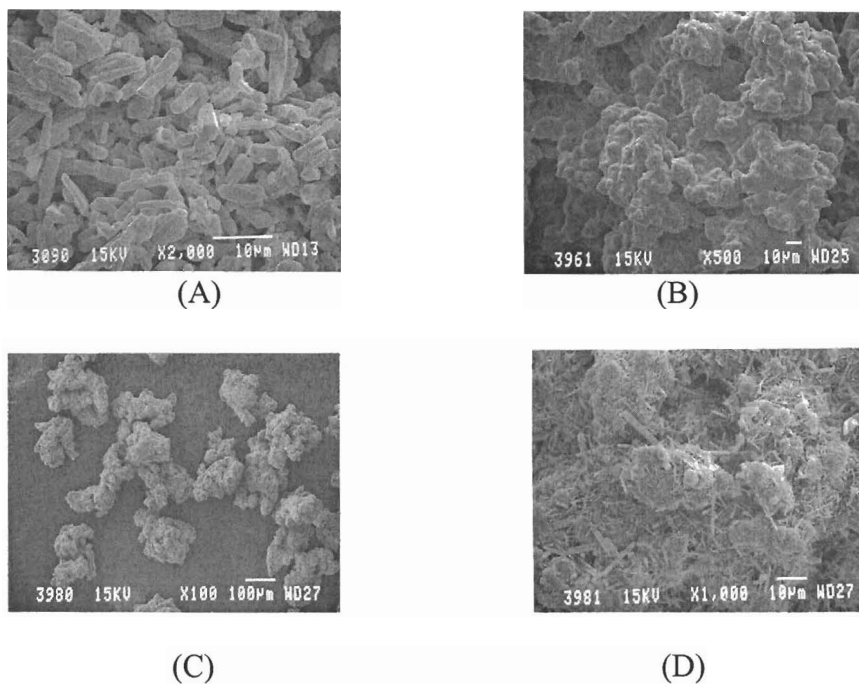


Figure 30. Scanning electron micrographs for (A) BAF, (B) T-4, (C) powder # 42 and (D) one powder particle of # 42. Notice the presence of BAF on the surface of the powder particle.

APPENDIX 3B

SEM for T-4, # 52 and BAF

Comparison of the micrographs for T-4, BAF and # 52 can be seen below. Notice the presence of BAF particles on the surface of the powder in figure 31(D).

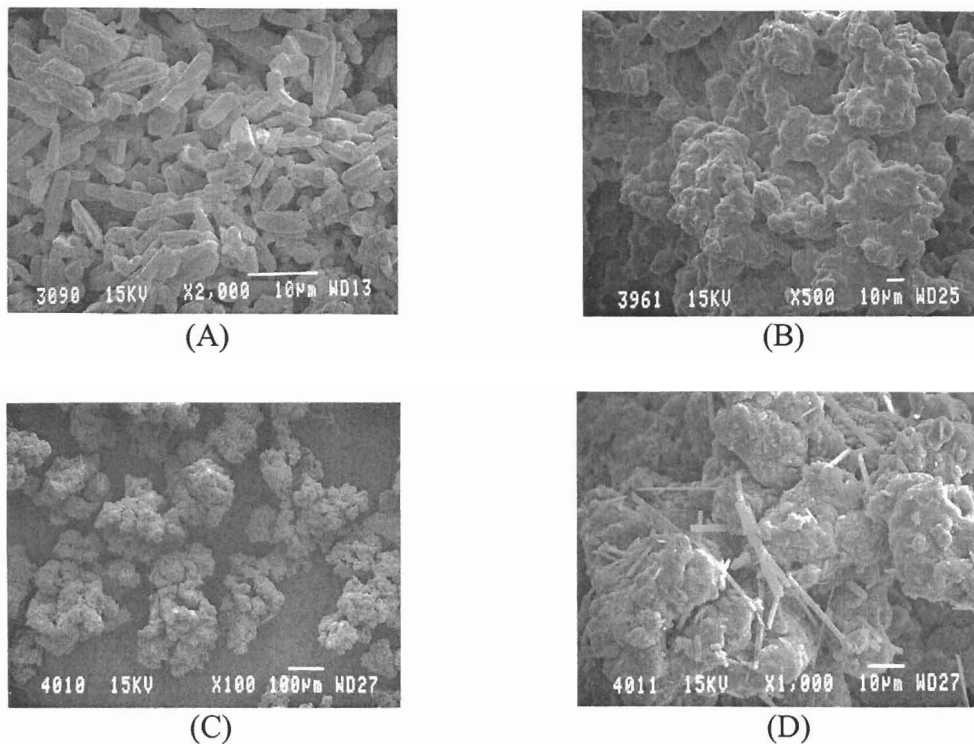


Figure 31. Scanning electron micrographs for (A) BAF, (B) T-4, (C) powder # 52 and (D) one powder particle of # 52. Notice the presence of BAF on the surface of the powder particle.

VITA

Ntoh Atem-Tambe born on February 24, 1980, in Alexandria, Virginia returned to Cameroon, West Africa, with her family in 1985, where she grew up and completed her Primary, Secondary and High School Education. She obtained a Bachelor of Science in Chemistry, with a minor in Chemical Process Technology in the University of Buea, Cameroon, in 2001. Ntoh left her family in Africa to return to the United States in 2002 with a primary goal of obtaining a graduate degree in Chemical Engineering. While trying to get admission into graduate school, she worked as a certified and registered Pharmacy Technician for NeighborCare Pharmacy in Chantilly, VA; then as a Vision Center Technician at Wal-mart SuperCenter, Richmond, VA. She finally got admitted to the Graduate School of Engineering at Virginia Commonwealth University, Richmond, VA, in the fall of 2003 where she was a Teaching/Research Assistant under the supervision of Dr. Mark McHugh and Dr. Gary Huvard. Ntoh's research efforts focused on blending studies of polymers and additives in the presence of supercritical fluids which earned her a Master of Science in Chemical Engineering from Virginia Commonwealth University in December, 2005. She currently works as a Process Shift Engineer at Boehringer Ingelheim Chemicals, Inc.