

# Radiation Grafting of Vinyl Monomers onto Poly(tetrafluoroethylene) Powder Produced by $\gamma$ Irradiation and Properties of Grafted Poly(tetrafluoroethylene) Filled Low Density Polyethylene

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**ABSTRACT:** Scrap poly(tetrafluoroethylene) (PTFE) was  $\gamma$  irradiated under an ambient atmosphere in order to produce extensive chain scission and oxidative degradation. After irradiation the PTFE was ground into a fine powder (2°-PTFE) and grafted with styrene (St), vinyl acetate (VAc), and 4-vinylpyridine (4-VP) by using the direct irradiation technique. The grafted PTFE were then blended with low density polyethylene (LDPE). The study covered the characterization of irradiated PTFE and grafted 2°-PTFE powder with various methods. Mechanical grinding was found to reduce trapped radicals formed during the irradiation process faster than the annealing process. Grafting on 2°-PTFE was followed by gravimetric analysis, TGA, and the change in the particle size of the samples. Although we reached almost 20% grafting by weight in the St and 4-VP monomers, VAc grafting was found to be maximum at around 8% by weight at the maximum absorbed dose. The addition of VAc grafted 2°-PTFE into LDPE produced better final mechanical properties with a fine dispersion. However, as may be expected, the incorporation of the other two 2°-PTFEs into LDPE showed low film quality and poor mechanical properties. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 816–826, 2001

**Key words:** grafting;  $\gamma$  irradiation; poly(tetrafluoroethylene); poly(tetrafluoroethylene) filled low density polyethylene

## INTRODUCTION

Although poly(tetrafluoroethylene) (PTFE) has outstanding thermal and chemical stability, it is very sensitive to high energy radiation. The dominant effect of ionizing radiation on PTFE is a molecular weight decrease through a chain scission process.<sup>1–5</sup> Radiation induced chain scission

is responsible for the increasing crystallinity of PTFE while decreasing the molecular weight. Chain scission can also act to relieve intramolecular stresses of molecules in the amorphous phase. The crystallinity is found to be greater when PTFE is irradiated in the presence of oxygen rather than irradiated under a vacuum. A further increase in crystallinity can also be observed by  $\gamma$  irradiation at a temperature just below the melting point of PTFE.<sup>1–5</sup> So, the dramatic decrease in the polymer molecular weight changes its melting and crystallization behaviors. The melting temperature of PTFE decreases with irradiation,<sup>2</sup> but the elevation in crystallization

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temperature of PTFE after irradiation is also indicated as being due to increased molecular mobility.<sup>6</sup> This result is explained by two competing processes: the crystallization of the molecules in the amorphous phase and the introduction of defects in the crystalline phase such as chain branching reactions.<sup>1-12</sup>

The changes in crystalline content upon irradiation of PTFE can also be determined by increases in density and heat of fusion, the reduction and/or increase in intensity of absorption bands in the IR spectrum whose intensities are proportional to the amorphous content (775, 375, and 270  $\text{cm}^{-1}$ ) and crystalline chain folding (286  $\text{cm}^{-1}$ ),<sup>2</sup> and the change in the crystalline peaks in the X-ray diffraction.<sup>6,13</sup> The low crystalline PTFE was found to have higher  $G$  values for chain scission in comparison to high crystalline PTFE, because radiation induced chain scission mostly proceeded in the amorphous region of the polymer.<sup>1,11</sup> Chain degradation was shown to be affected by the dose rate; but, particularly at very low dose rates, the rate of chain scission was reduced.<sup>1</sup> Radiation induced changes in the number-average molecular weight ( $M_n$ ), and hence the chain scission, can be followed by melt viscosity and heat of crystallization measurements.<sup>1</sup> It was also found that radiation induced crosslinking of PTFE could only be produced by irradiation with high energy radiation under a vacuum in the molten state at around 340°C.<sup>14-17</sup>

It was demonstrated in the literature that PTFE radicals reacted rapidly with oxygen to give the corresponding peroxy radicals under ionizing radiation.<sup>1,2,4,18-20</sup> Electron spin resonance (ESR) spectroscopy showed that midchain and end-chain radicals were produced by high energy radiation under a vacuum and air irradiation. These radicals react with oxygen to yield corresponding peroxy radicals, which are then followed by carboxylation of the molecules. The appearance of an IR absorption band at 1880  $\text{cm}^{-1}$  was identified with the acid fluoride end group.<sup>2</sup> The oxygen associated absorbance band at 1880  $\text{cm}^{-1}$  and other carbonyl bands at 1810 and 1780  $\text{cm}^{-1}$  were absent in the spectra of samples irradiated in a vacuum. The growth of the absorption band at 1790  $\text{cm}^{-1}$  was identified as the formation of the olefin end group.<sup>4</sup> Besides these functional groups, the appearance of the 980  $\text{cm}^{-1}$  band most probably corresponds to the formation of trifluoromethyl end groups.<sup>1-4</sup> High energy irradiation under a vacuum showed that an absorption appears between 1735 and 1715  $\text{cm}^{-1}$ , which

is characteristic of olefin formation in the polymer chain and is responsible for the possible branching or crosslinking reactions.<sup>1,2,4,18,20</sup>

Surface modification methods were proposed to modify the surface of PTFE to use its remarkable properties for further applications that require good bonding ability to other materials such as in polymer blends and composites. Some of these blend and composite applications of PTFE with polyacetal, polyethylene (PE), poly(ether ether ketone), and polypropylene were summarized in our previous study.<sup>21</sup>

Ionizing or high energy radiation was also studied for radiation grafting of monomers onto PTFE in particular by either direct or preirradiation grafting techniques. The details of radiation induced grafting of vinyl monomers into PTFE films are summarized in the literature.<sup>22,23</sup> Although PTFE does not swell in any monomer or solvent, grafting is initially localized on the surface and then the grafted layers swell in the reaction medium and the monomer diffuses through this layer and reaches the depth of the film by successive steps of grafting and diffusion.<sup>22,23</sup> Acrylic acid,<sup>22-27</sup> methacrylic acid,<sup>27,28</sup> 4-vinylpyridine (4-VP),<sup>22,23,26,29</sup> styrene (St),<sup>30,31</sup> *N*-vinylpyrrolidone,<sup>22,23,32</sup> acrylonitrile,<sup>33</sup> acrylamide,<sup>34</sup> and vinylimidazol<sup>24,35</sup> are some examples of these monomers. One of the most widely used hydrophilic monomers is acrylic acid. Under appropriate conditions, for example, at a 10 Gy/min dose rate, 50% (v/v) acrylic acid/water with high grafting ratios of about 125% was obtained on the PTFE membranes.<sup>26-30</sup> Graft polymerization of vinyl fluoride onto the surface of PTFE powder, which was produced from  $\gamma$  irradiation of PTFE scrap particles, was also studied.<sup>36,37</sup> The yield of grafted vinyl fluoride was reported as 3 and 10% grafting yield in the gas phase and liquid phase  $\gamma$  irradiation, respectively.

Our objective in this study was divided into three sections. The first was to prepare and characterize the fine powder PTFE (2°-PTFE) from scrapped PTFE with oxidative and chain scission degradation produced by  $\gamma$  irradiation under an oxygen atmosphere. In the second part St, 4-VP, and vinyl acetate (VAc) monomers were grafted onto the surface of the 2°-PTFE powder by using the direct irradiation technique. After the amount of grafting was characterized by direct gravimetric analysis and TGA, the third part of our work to achieve our main objective was to ascertain the effects of surface treatment on the 2°-PTFE that changed its surface properties and increased the

interactions between surface treated 2°-PTFE and low density PE (LDPE). Surface treated and untreated 2°-PTFE powder filled samples were than tested mechanically and SEM analysis was also used on the fractured surface of the film samples.

## EXPERIMENTAL

### Materials

The PTFE powder used in the study was obtained by  $\gamma$  irradiation of scrapped PTFE in the form of turnings and ribbons from the reshaping procedure of PTFE blocks. The oxidative and chain scission degradation of PTFE induced by a cobalt-60  $\gamma$  irradiation source (GAMMACELL 200, Atomic Energy of Canada Ltd.) continued until a 70-kGy absorbed dose was found to be the optimum dose. Finally, degraded, brittle PTFE was ground into powdered PTFE (secondary, 2°-PTFE). The other details of the 2°-PTFE blended with LDPE were discussed in our previous study.<sup>21</sup>

The LDPE was supplied by the Turkish Petrochemical Industry G03-5-PETKIM. The melt flow index and density of the polymer were 0.3 g/10 min and 0.921 g/mL, respectively.

The VAc (Merck), St (PETKIM), and 4-VP (Merck) were grafted onto the surface of 2°-PTFE powder in order to modify the surface characteristics of the filler. The VAc and 4-VP contained hydroquinone stabilizer. The 4-VP was a Sigma product and was inhibited with 4-*tert*-butylcatechol. They were used without further purification.

### Grafting

Approximately 2.5 g of 2°-PTFE powder was placed in a 10 × 150 mm (diameter × length) Pyrex tube with a 14/20 brand in one end. About 30% (w/w) of St, VAc, and 4-VP monomers with respect to the powder were added for a complete wetting of the 2°-PTFE powder. Tubes were vacuum sealed before  $\gamma$  irradiation. The absorbed doses of 10, 20, 30, and 40 kGy were studied for each of the samples. After the desired dose was reached, the tubes were immediately immersed in boiling water for 15 min to destroy any of the living radicals after irradiation. The tubes containing the 2°-PTFE powder and polymer were then opened to the air and transferred to a cellu-

lose extraction thimble (Whatman, 25 × 80 mm, diameter × length). The extraction of unbound homopolymer from the monomer grafted 2°-PTFE powder was carried out in an extraction funnel with the proper solvents, which were methanol for poly(4-VP) (P4-VP), acetone for poly(VAc) (PVAc), and toluene for polystyrene (PS). All solvents were supplied by Merck.

### Grafting Analyses

The UV analysis was performed with a Shimadzu 160 UV-vis spectrophotometer on the liquid samples taken from the extraction funnel to follow the existence of homopolymer that was not grafted to the surface of the 2°-PTFE powder. The complete cleaning of the unbound homopolymer usually took more than 3 days. After each data set was taken, the solvent in the extraction system was refreshed. Almost zero absorbance was obtained in the corresponding absorbance wavelength; the extraction thimble was dried in a vacuum oven at 50°C until a constant weight was achieved. The percentage of grafting was then determined by the following equation:

$$\% \text{ grafting} = (W_g - W_0)/W_g \times 100$$

where  $W_0$  and  $W_g$  represent the weight of the initial and grafted 2°-PTFE powders, respectively.

The amount of grafting was also followed by TGA (Dupont, TGA-951). Tests were carried out between 100 and 500°C, and no significant weight loss originated from the degradation of the 2°-PTFE powder. Therefore, the weight loss obtained in the grafted samples was directly related to the amount of copolymer that was grafted onto the surface of the 2°-PTFE powder. The percentage of grafting was then also determined by the following equation:

$$\% \text{ grafting} = W_L/W_g \times 100$$

where  $W_L$  and  $W_g$  represent the amount of weight loss resulting from the TGA and the initial weight of the grafted 2°-PTFE powder, respectively.

A further determination of grafting was also followed by the change in the particle size distribution of the 2°-PTFE in the grafting process. The particle size distributions with respect to the total volume of nonmodified and vinyl monomer grafted surfaces of 2°-PTFE particles were ob-

tained by using a MASTERSIZER S particle size analyzer.

### ESR and DSC Studies

The effects of  $\gamma$  irradiation on PTFE and changes on the surface of the 2°-PTFE powder due to grafting of vinyl monomers were also examined by using a Shimadzu IR-470 IR spectrometer. The ESR spectra of PTFE were also obtained from 70-kGy irradiation of scrapped and powdered samples with a Varian T-12 ESR spectrometer. All measurements were carried out at room temperature with 10-kHz modulation and a microwave power of 5 mW in a 3-min scan time.

In the thermal properties part of the work, we tried to follow the maximum melting peak temperatures and the enthalpies of heating and cooling curves of different dose  $\gamma$ -irradiated PTFE samples and polymer grafted 2°-PTFE powders. In addition to these, the radiation induced changes in the  $M_n$  of PTFE were determined by a thermal analysis DSC 910 S instrument. The heating and cooling rates and the amount of samples used in all of the measurements were 10°C/min and 3–10 mg, respectively. The molecular weight of the different doses of  $\gamma$ -irradiated and nonirradiated PTFE samples was calculated by using Suwa's equation in which  $H_c$  is the heat of crystallinity (cal/g).<sup>10,11</sup>

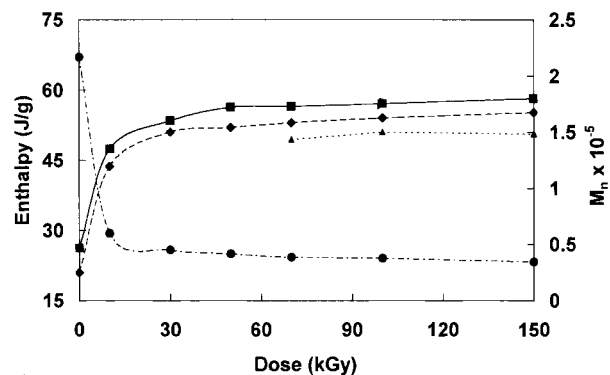
$$M_n = 2.1 \times 10^{10} H_c^{-5.16}$$

### 2°-PTFE Filled LDPE Studies

A single screw extruder was used to obtain 0.5, 1.5, 3, and 5% (w/w) monomer grafted 2°-PTFE powder filled LDPE films at  $200 \pm 20 \mu\text{m}$  thickness. Films were cut off using a standard dumb-bell-shaped die along the flow direction of the extruded films. The details of the film preparation were discussed in our previous study.<sup>21</sup>

SEM analysis was made on both monomer grafted 2°-PTFE powder samples and tensile fractured surfaces of the monomer grafted 2°-PTFE powder filled LDPE film samples at various magnifications after gold plating by using a Jeol JSM-6400 SE microscope.

Tensile properties, stress, and elongation at break of the modified and nonmodified 2°-PTFE powder filled films were determined with an Instron tensile testing machine (model TM 1102). The crosshead speed and gauge length in the measurements were 5.0 cm/min and 3.5 cm, re-



**Figure 1** The variations in the heat of fusion ( $\Delta H_m$ ), heat of crystallization ( $\Delta H_c$ ), and number-average molecular weight ( $M_n$ ) of scrapped and powdered PTFE with the absorbed dose: (■)  $\Delta H_m$  of scrapped PTFE, (◆)  $\Delta H_c$  of scrapped PTFE, (▲)  $\Delta H_m$  of powdered PTFE, and (●) the variation of the  $M_n$ .

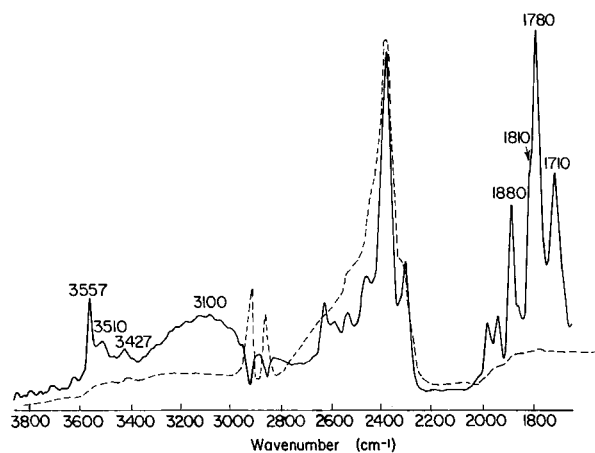
spectively. Tests were performed at room temperature, and the average of at least five samples was reported.

## RESULTS AND DISCUSSION

### Radiation Induced Physical Changes in PTFE

The increases in the heat of fusion ( $\Delta H_m$ ) and heat of crystallization ( $\Delta H_c$ ) and the decrease in the  $M_n$  of PTFE with the absorbed dose are shown in Figure 1. Because the  $\Delta H_m$  and  $\Delta H_c$  are directly proportional to the crystallinity, a sharp increase in the total crystallinity of PTFE occurs in the early stage of irradiation and the  $M_n$  of PTFE decreases dramatically as calculated by using Suwa's equation because of the enhanced crystallization ability of smaller chains. Because radiation induced chain scission proceeds predominantly in the amorphous region (including defects within the crosslinked parts and the amorphous parts bridging the crystallites) of the polymer, the relief of stress built up in this phase permits further crystallization.<sup>1–13</sup> The melting and crystallization peaks of PTFE arose at about 327 and 317°C, respectively. The heat of fusion of the 2°-PTFE was found to have values lower than that of scrap PTFE (Fig. 1). Because the mechanical grinding process may cause further mechanical degradation, especially in the more rigid parts of the polymer, the crystalline phases of PTFE therefore appear to be highly affected compared to the amorphous part during the grinding



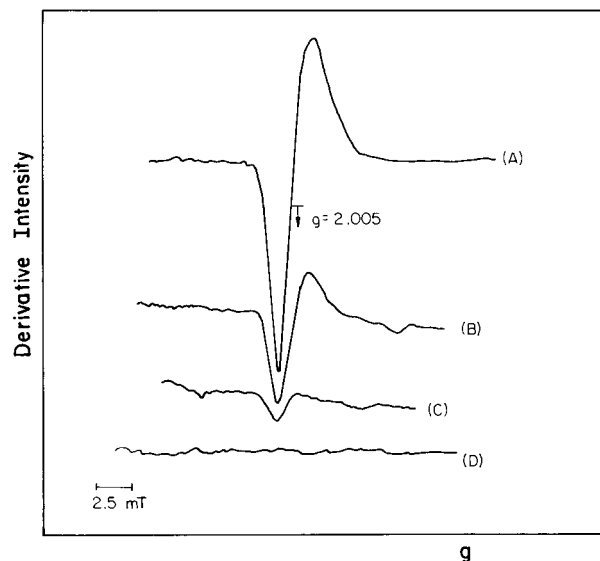


**Figure 2** The difference FTIR spectrum of 70 kGy irradiated PTFE from pure PTFE. (---) The FTIR spectrum of pure PTFE is shown. Some bands with negative absorbance are due to the thickness difference between pure PTFE and irradiated PTFE.

process. The  $\gamma$ -irradiated PTFE samples resulted in almost a 10% decrease in the crystallinity of the powdered polymer compared to that of the corresponding scrapped film samples.

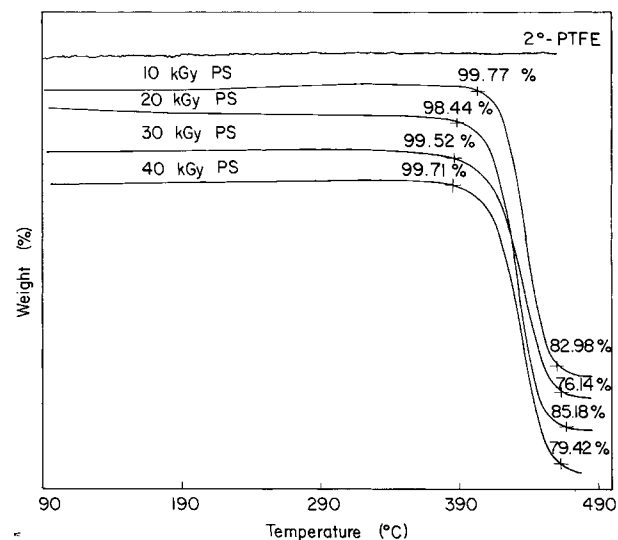
#### Structural Changes of PTFE upon $\gamma$ Irradiation

The difference FTIR spectrum of 70 kGy irradiated PTFE from pure PTFE is represented in Figure 2. The carboxylation of PTFE with irradiation is clearly visible. Note that the OH-stretching vibrations of the acid group above  $3000\text{ cm}^{-1}$ , a band of the terminal carboxylic acid fluoride group at  $1880\text{ cm}^{-1}$ , the carbonyl vibrations at  $1780\text{ cm}^{-1}$ , and isolated carboxyl groups at  $1810\text{ cm}^{-1}$  are in good agreement with other previous works.<sup>1,2</sup> The ESR spectrum of the 70 kGy  $\gamma$ -irradiated scrapped PTFE sample is shown in Figure 3(A). The decrease in the intensity after 24-h annealing of the same sample at  $150^\circ\text{C}$  is represented in Figure 3(B). This result is well correlated with the result of Lunchwitz et al.<sup>1</sup> They had already assigned the single nearly symmetric line to the end-chain peroxy radicals. However, the concentration of these radicals decreased slightly with annealing, but it was not sufficient to remove these end-chain peroxy radicals.<sup>1</sup> These radicals were most probably trapped in the sample. However, in our case a fast decrease in the concentration of these radicals was observed with the mechanical grinding process of the irradiated scrapped PTFE [Fig. 3(C)], noting that the mechanical grinding process took about 1 or 2 min.

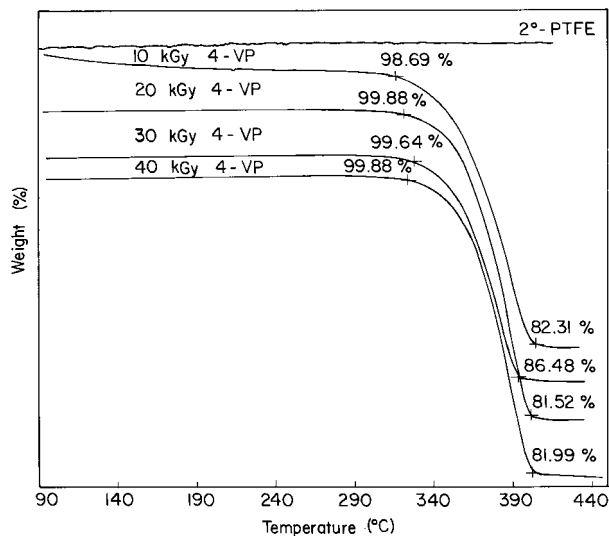


**Figure 3** ESR spectra of 70 kGy irradiated scrapped PTFE (spectrum A), scrapped PTFE annealed for 24-h at  $150^\circ\text{C}$  (spectrum B), powdered PTFE after the mechanical grinding process (spectrum C), and the empty tube (spectrum D).

Hence, we can conclude that most of the trapped radicals can be removed by the grinding process in a shorter time compared to annealing at high temperature for longer periods.



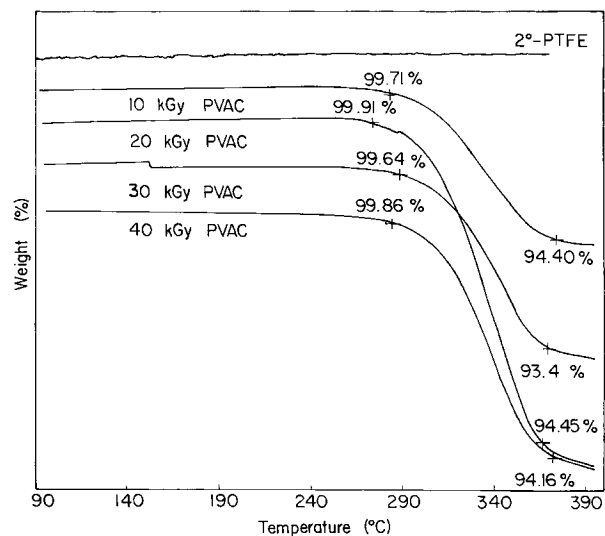
**Figure 4** TGA of the St grafted  $2^\circ$ -PTFE powder at different absorbed doses. (+) The onset temperature of the weight loss in the experiment and the percentages indicate the remaining weight at these temperatures.



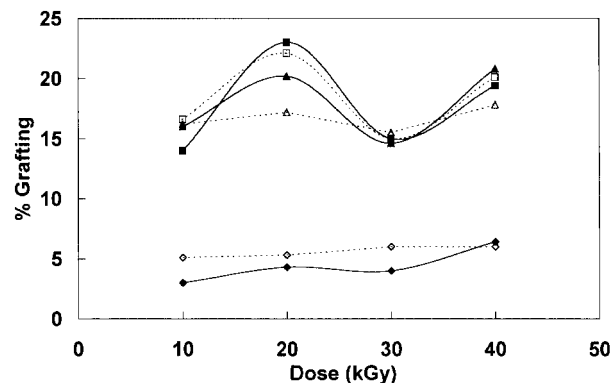
**Figure 5** TGA of the 4-VP grafted 2°-PTFE powder at different absorbed doses. (+) The onset temperature of the weight loss in the experiment and the percentages indicate the remaining weight at these temperatures.

#### Radiation Grafting Surface Treatments on 2°-PTFE Powder

The St, 4-VP, and VAc monomers were grafted onto the surface of the 2°-PTFE powder and better interfacial interaction was obtained when it was used as a filler in the polymer matrix. The direct radiation grafting method was used as a



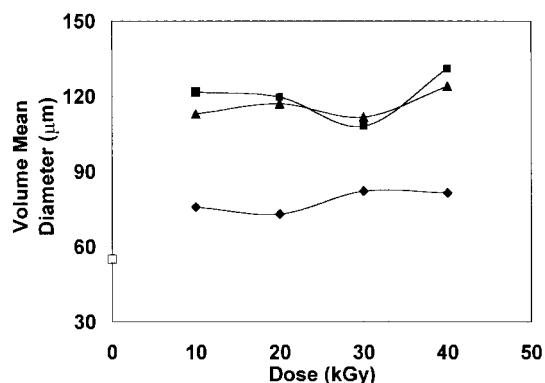
**Figure 6** TGA of the VAc grafted 2°-PTFE powder at different absorbed doses. (+) The onset temperature of the weight loss in the experiment and the percentages indicate the remaining weight at these temperatures.



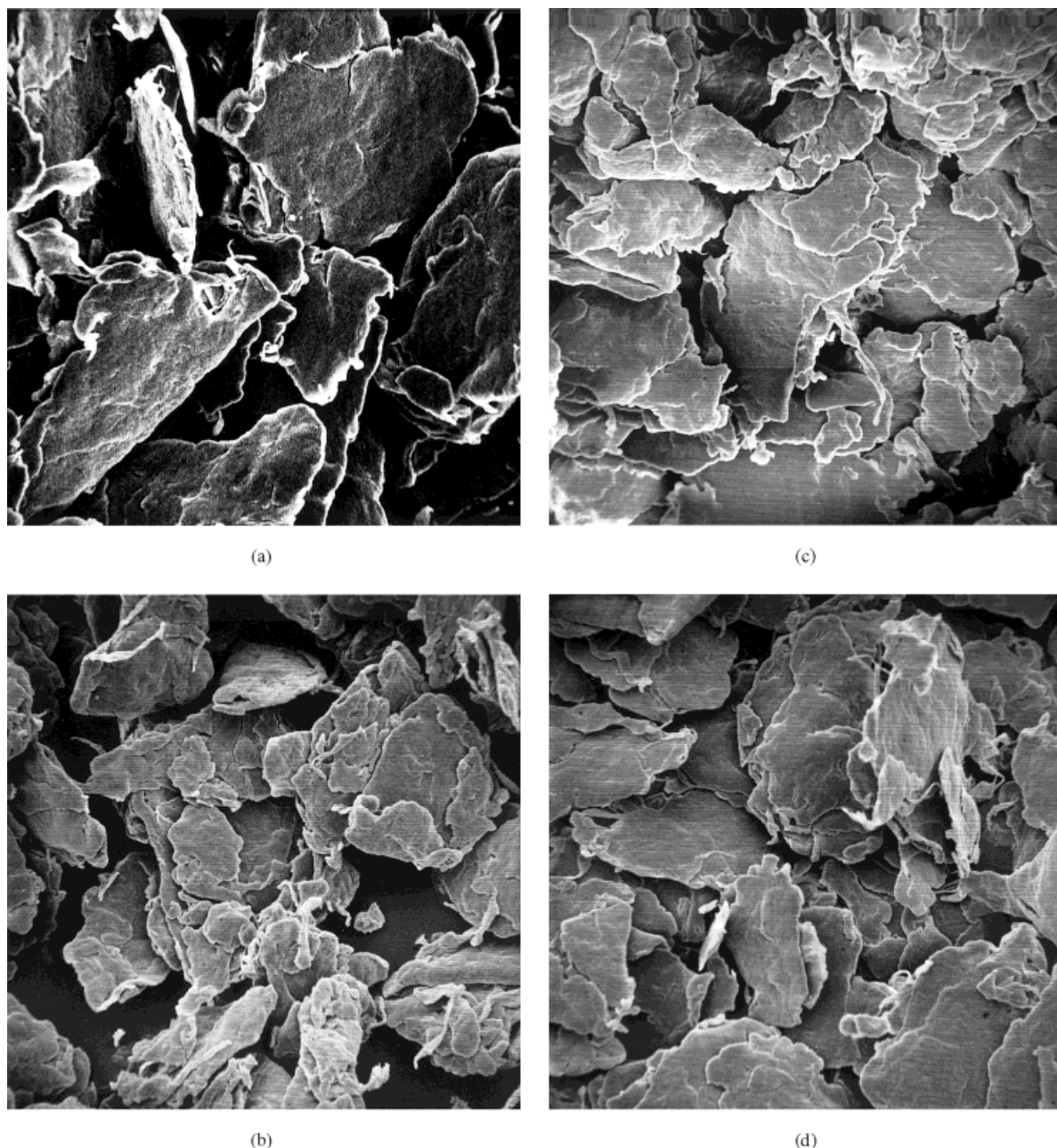
**Figure 7** The variations of the percentages of grafting of the monomers with the absorbed dose (kGy) measured by gravimetric analysis (filled symbols) and TGA (unfilled symbols): ( $\Delta$ ,  $\blacktriangle$ ) St grafted 2°-PTFE, ( $\diamond$ ,  $\blacklozenge$ ) VAc grafted 2°-PTFE, and ( $\square$ ,  $\blacksquare$ ) 4-VP grafted 2°-PTFE.

technique in which the powder and monomer solution were subjected to ionizing radiation at different absorbed doses (10, 20, 30, and 40 kGy) under a vacuum.

The gravimetric method and thermal gravimetric analysis (TGA) were used to determine the degree of grafting of the monomers. In the latter technique, we observed that there was almost no weight loss originating from the 2°-PTFE powder within the given temperature range; hence, the amount of weight loss in the grafted samples probably arose from the polymers grafted onto the surface of the 2°-PTFE (Figs. 4–6). The degree of grafting measured by using these two different techniques was found to very similar for both



**Figure 8** The change of the average particle size (mean diameter) of the monomer grafted 2°-PTFE powder with respect to the absorbed dose: ( $\square$ )  $\gamma$ -irradiated ground 2°-PTFE, ( $\blacksquare$ ) St grafted 2°-PTFE, ( $\blacktriangle$ ) 4-VP grafted 2°-PTFE, and ( $\diamond$ ) VAc grafted 2°-PTFE.

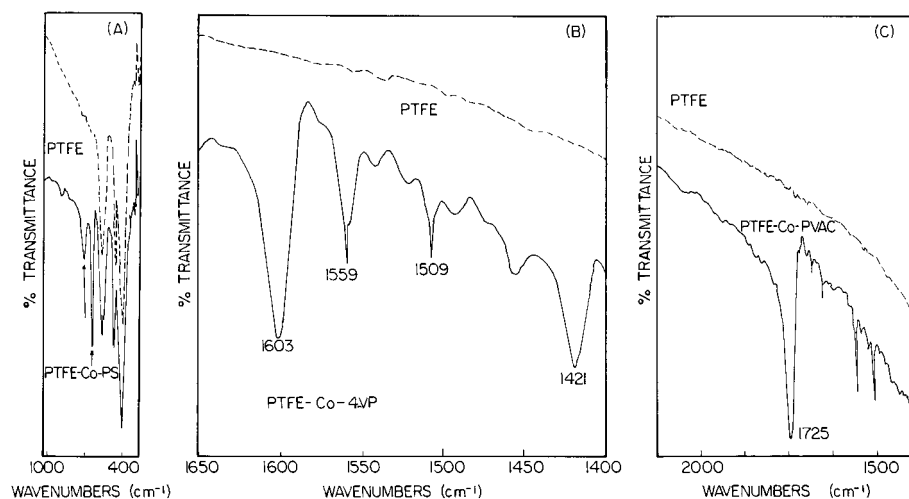


**Figure 9** SEM photographs of (A) 2°-PTFE powder, (B) St grafted 2°-PTFE powder, (C) 4-VP grafted 2°-PTFE powder, and (D) VAc grafted 2°-PTFE powder.

(Fig. 7). The amount of VAc monomer grafted onto the 2°-PTFE remained almost constant with an increasing absorbed dose. However, threefold higher grafting was achieved onto the surface of the powder in the PS and 4-VP cases compared to that of VAc grafting. The gravimetric and TGA results both showed the increase in the amount of grafting of St and 4-VP from 10 to 20 kGy. It was then followed by an observable decrease in graft-

ing at 30 kGy. The increase in the rate of homopolymerization compared to that of grafting may be responsible for this decrease, in addition to a possible chain scission. After the 30-kGy dose, an increase was observed in the grafting of these monomers but not as much as measured in the 20-kGy dose results.

Particle size analysis was also carried on the nongrafted and monomer grafted 2°-PTFE pow-



**Figure 10** IR spectra of 2°-PTFE powder grafted with (A) St, (B) 4-VP, and (C) VAc.

ders. The changes in the mean diameter of the powders with respect to absorbed dose are shown in Figure 8. Mean diameter is defined from the overall average of the particle size distribution curve of the particles that represents 80% of the volume of all particles that fall in that range. Good similarity was found between the change in the particle size curves and the amount of grafting (Fig. 7). Any increase or decrease in the amount of grafting can be directly followed by the changes in the average particle size of the powders. Therefore, this technique can be successfully applied on the monomer grafted samples as an indication to follow the changes of the grafting ratio in the powder samples.

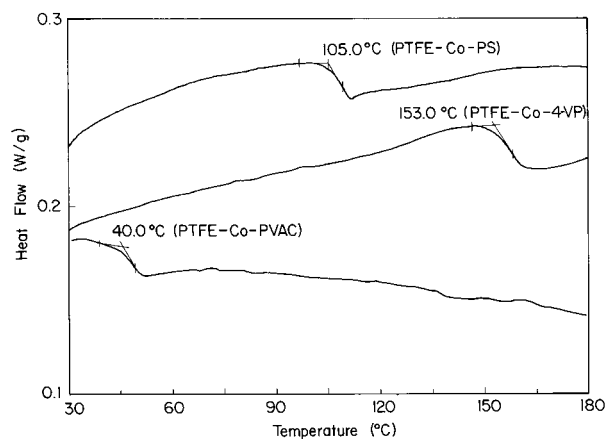
#### SEM, IR, and DSC Analysis of Monomer Grafted 2°-PTFE Powder

Surface analysis of the 2°-PTFE powder and monomer grafted powders were carried out by SEM [Fig. 9(A–D)]. After grafting a new laminating surface appeared on the surface of the 2°-PTFE powder [Fig. 9(B–D)] compared to that of the nongrafted powder surface [Fig. 9(A)].

IR analysis was carried on the St, 4-VP, and VAc grafted 2°-PTFE powder samples after the homopolymers of the corresponding monomers were removed by solvent extraction. Two strong peaks between 690 and 770  $\text{cm}^{-1}$  indicated a monosubstituted benzene ring in the St grafted 2°-PTFE powder [Fig. 10(A)]. Pyridine showed four IR bands in the region between 1300 and 1600  $\text{cm}^{-1}$ , corresponding to the ring-stretching vibrations of 4-VP grafted 2°-PTFE powder [Fig.

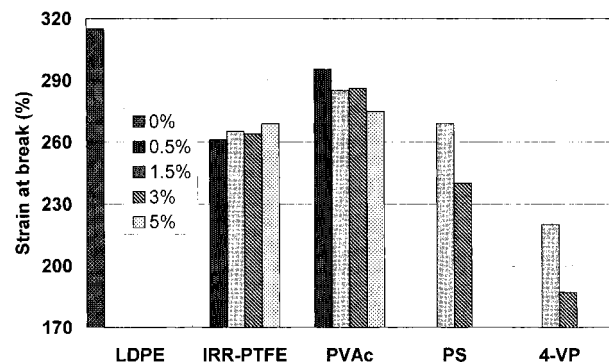
10(B)]. The appearance of a strong 1725  $\text{cm}^{-1}$  carbonyl absorption was assigned to a VAc carbonyl [Fig. 10(C)], which was grafted onto the surface of the 2°-PTFE powder.

DSC thermograms of St, 4-VP, and VAc grafted 2°-PTFE powder after solvent extraction of the homopolymers is shown in Figure 11. The onset temperatures in the DSC curves correspond to the glass-transition temperatures ( $T_g$ ) of the grafted polymers. When these values were compared with the  $T_g$  values of corresponding homopolymers available elsewhere, we observed that there was a 5–10°C higher  $T_g$  in the grafting polymers than that of their homopolymers. This increase in the  $T_g$  of the grafting polymers may arise not only from the differences in the experimental condi-



**Figure 11** DSC curves of St, 4-VP, and VAc grafted 2°-PTFE powders and the corresponding  $T_g$  values of the grafted polymers.



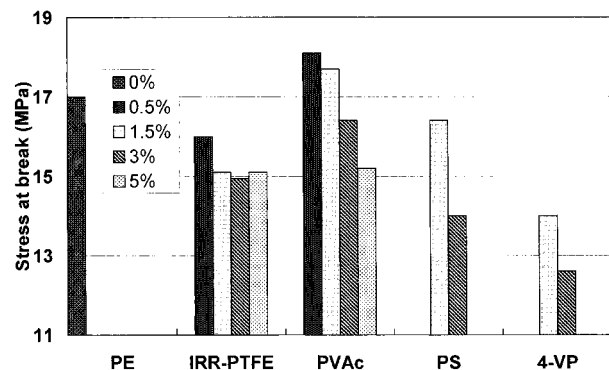


**Figure 12** The variation of the strain at break of different monomer grafted 2°-PTFE powder filled LDPE samples. The percentage values next to the bar keys represent the weight percentage of 2°-PTFE and grafted 2°-PTFE (PVAc, PS, and 4-VP) added to the LDPE.

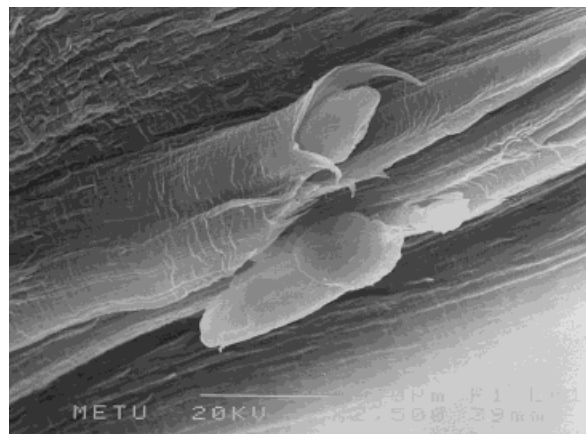
tions such as the heating rate, but also from restrictions in the chain mobility of the grafted polymers and possible crosslinking, which is most probably responsible for the increase in the  $T_g$  in the grafted polymers.

#### Mechanical Properties of Grafted 2°-PTFE Powder Filled LDPE and SEM Studies

The variations in the strain and stress at break of monomer grafted (St, 4-VP, and VAc) and ungrafted 2°-PTFE powder filled LDPE films are presented in Figures 12 and 13, respectively. The VAc grafted 2°-PTFE powder filled samples showed higher ultimate properties compared to



**Figure 13** The variation of the stress at break of different monomer grafted 2°-PTFE powder filled LDPE samples. The percentage values next to the bar keys represent the weight percentage of 2°-PTFE and grafted 2°-PTFE (PVAc, PS, and 4-VP) added to the LDPE.



**Figure 14** An SEM fractograph of 4-VP grafted 2°-PTFE powder filled LDPE.

that of ungrafted and the other grafted 2°-PTFE powder filled samples. This increase is clearer in the 0.5, 1.5, and 3% compositions. The stress at break at 0.5 and 1.5% addition of VAc grafted 2°-PTFE represents an even higher value than that of pure LDPE. There are almost no differences in the strain at break in all compositions of VAc grafted 2°-PTFE filled LDPE, but the ultimate elongation is lower than pure LDPE as given in Figure 12. Although it is well known that PE and PVAc blends are immiscible, PVAc forms fine domains in the PE matrix and improves the compatibility and hence the mechanical properties of the final polymer blend.<sup>38</sup> In addition to this, because of the excellent transparency and high UV stability resulting from the chemical structure of the polymer, ethylene-VAc copolymer films are very suitable for greenhouse applications. So, VAc grafting onto the surface of the 2°-PTFE powder not only increased the mechanical properties but also enhanced the UV stability of the powder filled LDPE films when compared to 2°-PTFE filled LDPE. There was no improvement in the ultimate properties of the 1.5 and 3% St grafted 2°-PTFE powder because of the complete immiscibility between PS and PE. In the 4-VP grafted case, although an adhesion between LDPE and 4-VP grafted PTFE powder was observed (Fig. 14), coagulation of the 4-VP grafted powders resulted in a sharp decrease in the mechanical properties of the 4-VP grafted 2°-PTFE powder filled samples.

The fractured surface SEM fractographs of the 4-VP, VAc, and St grafted 2°-PTFE powder filled LDPE films are shown in Figures 14–16, respectively. No adhesion was observed between the St

grafted 2°-PTFE powder and the LDPE matrix (Fig. 15). However, it was clear that an adhesion existed between the VAc grafted powder and LDPE, which was reflected in the mechanical properties of the filled samples (Fig. 16). The adhesion between 4-VP grafted 2°-PTFE powder and LDPE appeared to be stronger than these two former ones, but the coagulation of the powder particles resulted in a sharp decrease in the mechanical properties (Fig. 14). In all cases, splitting of LDPE films was observed along the mechanical testing direction around the grafted 2°-PTFE particles.

## CONCLUSIONS

High energy irradiation of PTFE produced a great number of active sites on the PTFE surface, as expected, which could be used for the grafting of vinyl monomers. It appeared that the mechanical grinding process of the scrapped irradiated PTFE reduced the active radicals in a shorter time than any common annealing process at high temperatures. Grafting of these three vinyl monomers was rather successful with the radiation doses applied. However, VAc grafting yielded lower values compared to the others. The two methods, the traditional gravimetric and TGA, showed good agreement in measuring the grafting amount. Furthermore, with the determination of the change of the hydrodynamic volume, the variation of the particle size of the grafted 2°-PTFE, also represented a similar result but this method apparently produced a qualitative result rather than the quantitative results of the other two



**Figure 15** An SEM fractograph of St grafted 2°-PTFE powder filled LDPE.



**Figure 16** An SEM fractograph of VAc grafted 2°-PTFE powder filled LDPE.

methods. The addition of the VAc grafted 2°-PTFE into LDPE produced better final mechanical properties with a good and transparent film than the others and 2°-PTFE filled LDPE. The SEM studies showed good interaction between PVAc and 4-VP grafted 2°-PTFE and LDPE, but the coagulation of 4-VP grafted 2°-PTFE produced a low film quality and poor mechanical properties.

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