# Influence of physical parameters on mutual polymer grafting by electron beam irradiation

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## ARTICLE INFO

## ABSTRACT

Grafting is a good method for modifying a polymer matrix and radiation induced grafting is an advantageous technique for chemical grafting because it does not require an initiator. In this work, mutual radiation grafting was performed and physical parameters like vacuum, pressure of air or inert gas and temperature were studied to verify their influences on styrene grafting onto hydrocarbon and fluorinated polymers. We observed that vacuum and temperature are determinant parameters to be considered in mutual radiation grafting besides the backbone polymer, monomer molecules and solvent. The optimization of these parameters for a specific polymer/monomer system contributes to a good performance and allows mutual radiation grafting to be an attractive technique even if it is performed in commercial accelerators.

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## 1. Introduction

Polymer grafting is a process where monomer molecules are covalently bonded to polymer chains through chemical reactions between the reactive species and the substrate during matrix modification (Bhattacharya, 2000). This process differs from curing where the polymerization process occurs for an oligomer mixture and the coating formed adheres physically to the polymer substrate.

Grafting is a process that allows for the development of new materials that feature unique properties. The introduction of new functional groups on a substrate surface improves properties such as hydrophilicity, adhesion, biocompatibility, conductivity and antifogging, among others. The first studies about grafting appeared in the 1950s dealing with chemical-, photochemical- and radiation-induced grafting. Such studies included the chemical grafting for vinyl monomers onto distinct polymers (Smets and Claesen, 1952), photochemical grafting from polyacrylamide onto natural rubber (Oster, 1957) and the radiation grafting of styrene and methacrylate monomers onto PTFE (Chapiro, 1959).

In the radiation grafting process, the high energy level is responsible for homolytic bond scission of molecules and release of free radicals (Wojnárovits, 2003). Compared to chemical and photochemical grafting, radiation grafting is fast, occurs in the absence of an initiator and produces low byproduct levels, costs and hazards.

The term radiation grafting comprises the following techniques: pre-irradiation, peroxidation and mutual (simultaneous) irradiation (Bhattacharya and Misra, 2004).

The pre-irradiation technique is carried out in two steps: first, the polymer is irradiated under vacuum or an inert gas; in the second step, the irradiated polymer is treated with the monomer that can be present as a liquid, as a vapor or as a solute dispersed in a suitable solvent.

The peroxidation technique is also performed in two steps: initially the polymer is irradiated under air atmosphere or oxygen flux to form hydroperoxides or diperoxides, depending on the nature of the polymeric backbone and irradiation conditions. This peroxidated polymer is treated with the monomer at high temperature in the second step, whence the peroxides decompose to generate radicals, which initiate the grafting process. This method has the advantage of allowing the peroxidized polymer obtained in the first step to be stored for long periods of time, well before the actual grafting takes place. A disadvantage of both pre-irradiation methodologies is that scissioned chains in the polymer substrate, due to direct irradiation, can result in the formation of block copolymers.

Mutual irradiation takes just one step to perform the grafting process, since the polymer and monomer are irradiated simultaneously with the subsequent formation of free radicals, which result in the formation of chemical bonds at the polymer substrate (Kaur et al., 1994). Although homopolymer is a byproduct of this process, and this phenomenon has not been observed in the previous techniques discussed, this one-step

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process has advantages: it is faster than the pre-irradiation methods and, most importantly, also leads to low chain scission levels—a clear advantage when the final product requires adequate mechanical properties.

In the literature, it is known that the success of irradiation grafting reactions depends on the polymer backbone, monomer molecules, solvent and temperature (Dargaville et al., 2003; Geraldes et al., 2008; Bucio and Burillo, 2009). Another important parameter in the irradiation process is dose rate, which is determinant for the chemical reactions that take place (Sutton and Rotblat, 1957; Sabharwal et al., 1999). The optimization of these parameters depends on a knowledge of chemical mechanisms; they must be studied for each polymer/monomer system to improve new materials for specific applications.

In this work, mutual radiation grafting of styrene was performed and some physical parameters (vacuum, pressure of air or inert gas and temperature) were studied to verify their influence on grafting of hydrocarbon and fluorinated polymers. The grafting yield was measured by gravimetric determination and qualitative/semi-quantitative styrene analysis was made by infrared spectrometry. These results are discussed based on chemical mechanisms proposed in the literature.

## 2. Experimental

The mutual irradiation grafting was performed using a Job 188 Dynamitron® Electron Beam Accelerator with 1.5 MeV energy, the beam current was 25 mA, the beam power was 37.5 kW and the scan was 50–120 cm. The irradiation conditions comprised a dose of 100 kGy and a dose rate of 22.4 kGy/s. A preliminary study of absorbed dose related to grafting yield for each polymer substrate is presented in Table 1.

The polymer substrates used in this study were polypropylene (PP) as a non-fluorinated polymer, polyvinilidenefluoride (PVDF) as a fluorinated polymer and polytetrafluoroethylene (PTFE) and polytetrafluoroethylene co-perfluoropropylvinylether (PFA) as perfluorinated polymers. All polymeric substrates were purchased from Goodfellow. Before irradiation, polymer samples of $30 \times 30 \times 0.05$–$0.10$ mm$^3$ were washed in analytical grade ethanol

and dried at room temperature; the monomer used for grafting was commercial grade styrene pre-treated by inhibitor removal with molecular sieves. The grafting media was a 1:1 styrene/butanol-1 mixture.

The influence of solvent on grafting yield for the hydrocarbon and the perfluorinated polymers were preliminarily verified and these results are shown in Table 2. The physical conditions for the irradiation system were a tight irradiation chamber (Manzoli et al., 2008; Cardozo Jr. et al., 2009), pressure/vacuum of $8.0 \times 10^3$–$1.8 \times 10^5$ Pa and temperature of 25 or 60 °C. During the experiments, the chamber contained either atmospheric air or argon (99.99%, Praxair).

The post-irradiation treatment of the samples was homopolymer extraction by toluene immersion (2 days), followed by ethanol washing (several times) and finally vacuum drying at 50 °C. The styrene grafted samples were analyzed by gravimetry to determinate the grafting yield; the final values have been averaged from a series of three measurements. Finally, mid-ATR-FTIR was the spectrophotometric technique used for qualitative/semi-quantitative styrene analysis.

## 3. Results

The value of absorbed dose at 100 kGy was conveniently chosen function of styrene grafting yield and its handling integrity. Table 1 shows the yield of grafting process for absorbed doses from 30 to 200 kGy at room temperature and pressure and at 22.4 kGy/s dose rate. These results show in some cases an increase of yield values at absorbed doses above 100 kGy; however, when submitted to such high doses, the samples lost their mechanical properties: they became fragile and broke easily when touched or handled.

Table 2 shows a large grafting yield when the grafting media is the 1:1 styrene and butanol-1 mixture. In Fig. 1a, we observe a grafting yield of 8% for polypropylene samples irradiated at room pressure under air atmosphere; grafting yield around 3% can be observed when irradiation is performed either under vacuum or under inert gas. The presence of air in small concentration ($4.7 \times 10^4$ Pa) increases grafting yield. The transmittance FTIR

**Table 1**
Average grafting yield of styrene grafting process in mutual polymer irradiation under several absorbed doses at 22.4 kGy/s performed under atmospheric air and room conditions (temperature and pressure).

| Polymer | Absorbed dose (kGy) | | | | |
|---|---|---|---|---|---|
| | 30 | 50 | 100 | 200 | 300 |
| Polypropylene (PP) | 3.97 (0.45)[a] | 4.92 (0.10) | 7.89 (0.60) | 8.53 (0.32) | – |
| Poly(vinylidene fluoride) (PVDF) | 0.42 (0.08) | 0.67 (0.04) | 1.17 (0.30) | 1.07 (0.11) | 1.11(0.45) |
| *Poly*(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) | – | 0.30 (0.10) | 1.00 (0.03) | 1.16 (0.08) | 2.10 (0.17) |

[a] The standard deviations of grafting yields are in brackets.

**Table 2**
Average grafting yields at 100 kGy and at 22.4 kGy/s dose rate in distinct styrene grafting media and polymer substrates. Grafting process performed under atmospheric air and room conditions (temperature and pressure).

| Polymer | Average grafting yield (%) | | | |
|---|---|---|---|---|
| | Styrene | Styrene/toluene 1:1 | Styrene/methanol 1:1 | Styrene/butanol-1 1:1 |
| Polypropylene (PP) | 4.86 (0.23)[a] | 3.1(0.59) | 5.77 (0.70) | 7.89 (0.60) |
| *poly*(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) | 0.63 (0.06) | 0.19 (0.02) | 0.34 (0.06) | 1.00 (0.03) |

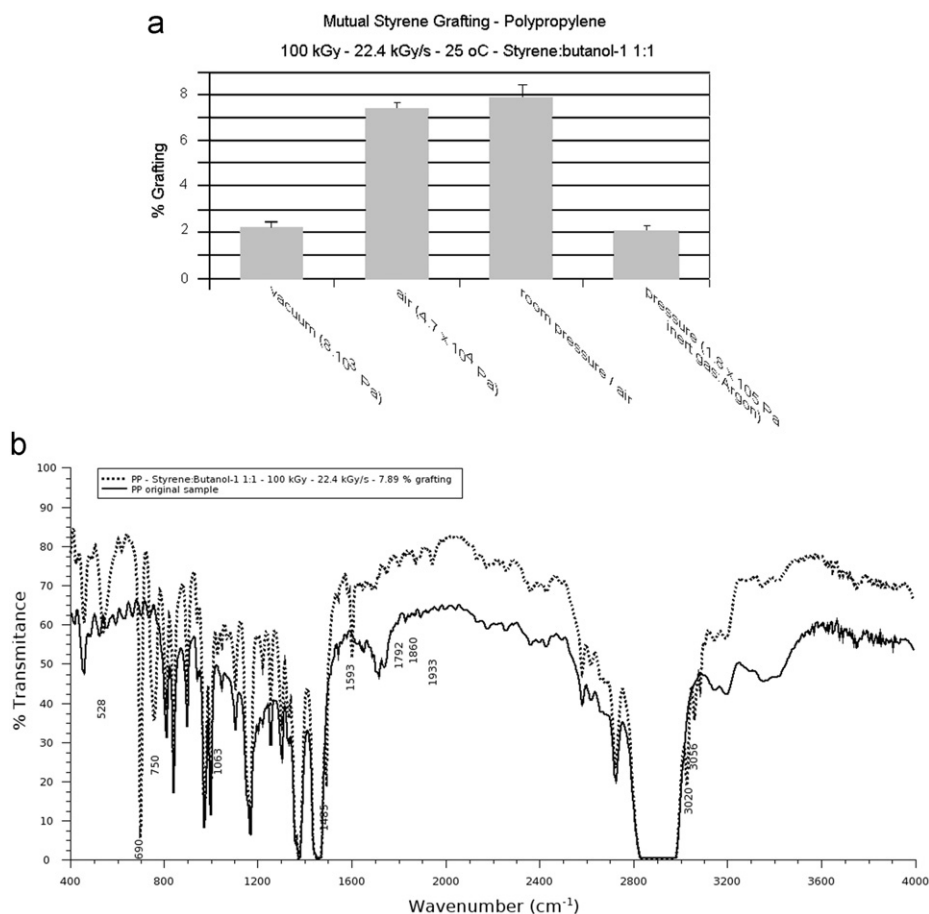[a] Standard deviations of grafting yields are in brackets.

**Fig. 1.** (a) Styrene grafting yield for polypropylene for mutual electron beam irradiation (100 kGy, 22.4 kGy/s, 25 °C, grafting medium: 1:1 styrene/butanol-1 mixture) under several conditions of pressure/vacuum. (b) Transmission mid-FTIR of original and grafted polypropylene samples under these conditions.

spectra of grafted and non-grafted polypropylene samples are shown in Fig. 1b. The absorption bands at 690 and $750\,cm^{-1}$ arise from grafted aromatic rings (Colthup et al., 1990) and the absorption band at $1060\,cm^{-1}$ is assigned to the C–H in-plane band of the aromatic ring (Hershenson, 1964). These absorption bands are important evidences of the presence of styrene in the polymer matrix.

The PFA perfluorinated polymer (Fig. 2a), gives the same qualitative result at room temperature and we observed a successful grafting when irradiation occurs at room pressure in the presence of air. The 1:1 styrene/butanol-1 mixture is the grafting medium that produces the largest grafting values under these conditions (Table 2). However, the mutual grafting performed under air pressure did not increase grafting yield values (around 1%) and the process performed under vacuum provided intermediate performance results. The mid-ATR-FTIR spectra of these samples (Fig. 2b) show styrene absorption bands at 690 and $750\,cm^{-1}$ and a broadening of the band at $1060\,cm^{-1}$; both are evidences of the presence of styrene in the polymer substrate at this grafting level.

Table 3 shows the averages of final and initial weight differences and grafting yields of the fluorinated (PVDF) and the perfluorinated (PFA) polymer samples compared to the hydro-carbon sample (PP). In the performed grafting conditions (atmospheric air, room temperature and pressure), a large weight gain is observed for a PP sample in comparison to fluorinated/perfluorinated polymer samples; similar grafting yields among the fluorinated/perfluorinated polymers were observed under the same irradiation conditions (100 kGy, 22.4 kGy/s, 25 °C, under

atmospheric air and room pressure), and their grafting yields are low. The mid-ATR-FTIR (Fig. 3) confirms the presence of styrene in the PVDF grafted samples.

When the mutual grafting is performed at 60 °C under vacuum, these results change. Table 4 shows grafting yield for PVDF films of around 15.5%, and for PFA and for PTFE yields of 6.2% and 3.3% are observed, respectively. The polypropylene films presented no good response, grafting yield decreased and values near 2.8% were observed. The mid-ATR-FTIR spectra of the fluorinated and perfluorinated polymers (Fig. 4) show the presence of styrene as evidenced by the absorption bands at 690 and $1060\,cm^{-1}$ regions; the low distinctness of these regions in the spectra for PTFE can be related to matrix effects in the frequency range analyzed.

## 4. Discussion and conclusion

According to the presented results, physical state of the grafting media is an important experimental condition. In this work, it was performed in both liquid and vapor phases.

In the liquid phase, where polypropylene had the highest grafting yield, it is known the interaction of photons of ionizing radiation with the polymer results in the polymer radiolysis process with the consequent generation of radicals from the substrate. Additionally, the radiolysis process occurs in all components under ionizing radiation. The radiation chemistry of organic liquids is not simple, but a simplified chemical mechanism can be proposed that can be described in three steps as
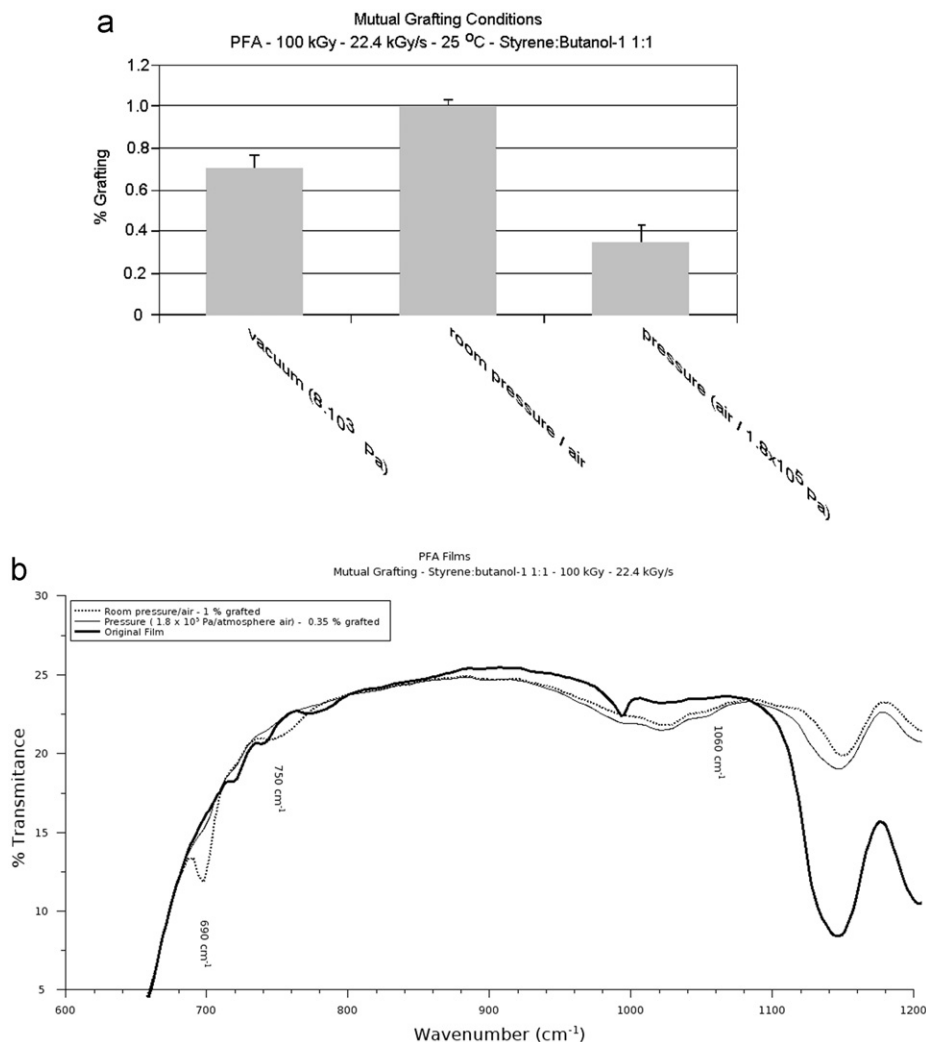
**Fig. 2.** (a) Styrene grafting yield for PFA at mutual electron beam irradiation (100 kGy, 22.4 kGy/s, 25 °C, grafting medium: 1:1 styrene/butanol-1 mixture) under several conditions of pressure/vacuum. (b) mid-ATR-FTIR spectra of original and grafted PFA samples under these conditions.
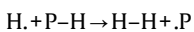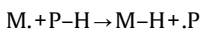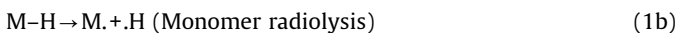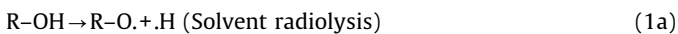
**Table 3**

Results of styrene grafting process in simultaneous polymer irradiation at 100 kGy and 22.4 kGy/s performed under atmosphere air, room temperature and pressure and 1:1 styrene/butanol-1 mixture.

| Polymer | Average of differences from final to initial weights (mg) | Yield (%) |
|---|---|---|
| Polypropylene (PP) | 3.90 (0.20)[a] | 7.89 (0.60) |
| Poly(vinylidene fluoride) (PVDF) | 0.30 (0.20) | 1.17 (0.30) |
| Poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) | 1.60 (0.12) | 1.00 (0.03) |

[a] Standard deviations of grafting yields are in brackets.

follows:

$$R\text{–}OH \rightarrow R\text{–}O.+.H \quad \text{(Solvent radiolysis)} \tag{1a}$$

$$M\text{–}H \rightarrow M.+.H \quad \text{(Monomer radiolysis)} \tag{1b}$$

$$R\text{–}O+P\text{–}H \rightarrow R\text{–}OH+.P \tag{2}$$

$$M.+P\text{–}H \rightarrow M\text{–}H+.P$$

$$H.+P\text{–}H \rightarrow H\text{–}H+.P$$

$$.P+.M \rightarrow P\text{–}M \tag{3}$$

In the first step, radiolysis of the solvent (butanol-1) and the monomer (styrene) occurs and their respective radicals appear (Eqs. (1a) and (1b)). In the second step, there is a transfer of the H atom from the polymer molecule (P–H) to the organic media; as a consequence, radicals are formed on the polymer chains. These two steps are well discussed by Lehrle and Pattenden (1999) and it is mentioned by Xu et al. (2007) who compared the mutual and pre-irradiation grafting methods. In this case, a simple analysis of chemical activity of the radicals produced from each solvent may be proposed to explain the second step.

A measure of chemical activity of each of these radicals can be derived from a comparison of bond dissociation energies. The hydrogen atoms and alkoxy radicals are the most reactive species in the experimental media because of their highest hydrogen bond dissociation energies (H–H: 436 kJ/mol and RO–H: 430–440 kJ/mol ; West, 1978) and these species act as hydrogen atom scavengers on polymer chains. However, the styryl radicals ($C_6H_5\text{–}\dot{C}\text{=}CH_2$) have low reactivity (styr–H: 324.5 kJ/mol ; Walling, 1960; Cardona et al., 2003) and hydrogen scavenging on the substrate has a low occurrence in this system.

In the last step, addition of monomer radicals to free radicals on the polymer occurs. In this way, the termination mechanism pathways may involve the interaction of polymer–polymer radicals and styryl–styryl radicals, where homopolymerization occurs in this last case.
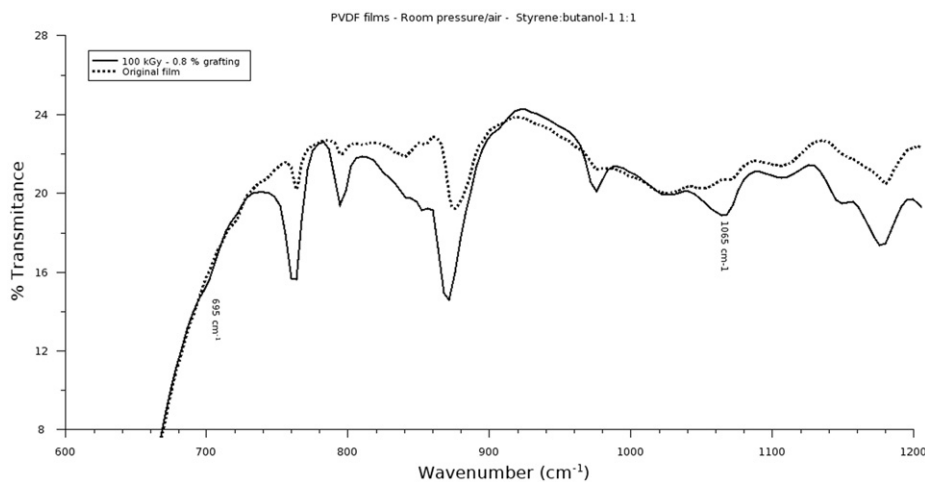
**Fig. 3.** Mid-ATR-FTIR spectra of original and grafted PVDF samples for mutual electron beam irradiation (100 kGy, 22.4 kGy/s, 25 °C and grafting medium: 1:1 styrene/butanol-1 mixture).

**Table 4**
Grafting yield of styrene grafting process in simultaneous polymer irradiation at 100 kGy and 22.4 kGy/s performed under 60 °C, $8.0 \times 10^3$ Pa and 1:1 styrene/butanol-1 mixture.

| Polymer | Yield (%) |
|---|---|
| Polypropylene (PP) | 2.79 (0.24)[a] |
| Poly(vinylidene fluoride) (PVDF) | 15.42 (0.74) |
| Polytetrafluoroethylene (PTFE) | 3.29 (0.11) |
| *Poly*(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) | 6.18 (1.09) |

[a] Standard deviations of grafting yields are in brackets.

However, low yields of grafting have been observed for the fluorinated and perfluorinated polymers for mutual radiation styrene grafting in the liquid phase. In this case, a distinct mechanism for the polypropylene substrate occurs.

As a first remark, the generation of substrate radicals by interaction with radiation photons results in a specific radiolysis process for each polymer that requires distinct energies. The C–H bond dissociation energy on polypropylene requires 368.9 kJ/mol (Zuquan, 1985) and the C–F bond dissociation energy on PTFE requires from 490 to 540 kJ/mol (Dixon et al.,1995). The mechanism of radical generation in polypropylene is related to H atom removal from the *tert*-carbon atom of the main chain (the lowest energy process) and a polymer molecule degradation by β-scission reaction, where two species are generated—a chain end radical and an unsaturated end group (Rätzsch et al., 2002). In irradiated perfluorinated polymers, trifluoromethyl radicals, radicals on the main chain and chain ends appear; this indicates scission of both the C–C and C–F bonds. Polymer molecule degradation by β-scission reaction is also observed, which results in low molecular weight perfluoroolefins and their radicals (Forsythe and Hill, 2000). Radicals originated by C–H bond dissociation in PVDF fluorinated polymer have been observed; however, they are very unstable and consequentially have high reactivity (Makuuchi et al., 1976).

In these conditions, the grafting mechanism proposed above in the liquid phase does not take place for perfluorinated and fluorinated polymers. It is known that the influence of monomer concentration increases the grafting yield (Trommsdorff's effect); however, changes in monomer concentration of grafting media did not improve the grafting yield magnitudes, as seen in Table 2. Here the grafting mechanism is classic and once radicals are generated on the polymer, the monomer radicals are added on it.

However, in the case where the grafting media constitute a styrene and butanol-1 mixture, a competition could happen between highly reactive alkoxy radicals and styryl radicals, this hinders effective collisions of these last radicals and thus a very low grafting yield can be observed besides homopolymer byproducts.

Grafting mechanism is distinct in the vapor phase. Competition of the reactive species did not prevent the grafting process for fluorinated/perfluorinated polymers. The monomer diffusion effects are very important because grafting occurs initially on the polymer surface, this process continues through the bulk of the substrate when the monomer gradually swells this grafted zone (Yamamoto et al., 1978).

Kamel et al. (1972) discussed that polyolefin materials may have a high resistance to monomer diffusion at the polymer–vapor interface. By analogy, this can be the reason for the lowest grafting yields observed for polypropylene by irradiation under vacuum and 60 °C.

For the fluorinated and perfluorinated polymers under the vapor phase grafting, PTFE had a grafting yield three times greater than that for the liquid phase, although this perfluorinated polymer always had the lowest grafting yield and PVDF had the highest grafting yield, where it was around 15 times greater than that for the liquid phase. These behaviors can be related to the observations of Chapiro (1959), where PTFE swells slightly in styrene and this monomer diffuses into the partially grafted layers. Similarly, PVDF should have a low monomer diffusion resistance at the polymer–vapor interface.

Also, reactivity of radicals formed on each of the polymer substrates and G values (number of species formed or number of chemical changes of a particular type induced on the deposition of 16 aJ (100 eV) of energy) for radical formation are important factors to explain the experimental results in this work; for example, some typical G values for radical formation on γ-radiolysis under vacuum at ambient temperature are PTFE, 0.14 (Oshima et al., 1997), PFA, 0.93 (Dargaville et al., 2001) and PVDF, 3.3 (Dargaville et al., 2003; Seguchi et al., 1974). By analogy, the high grafting yield onto PVDF and the observed decrease in grafting yields for PFA and PTFE could be related to the number of radicals generated on these polymer matrices.

It was observed that the grafting process is enhanced by the presence of atmospheric oxygen for all studied polymer samples, and high values of grafting yields have been verified for polypropylene samples. As described in the literature (Nasef, 2001), oxygen generally must be absent in grafting reactions if
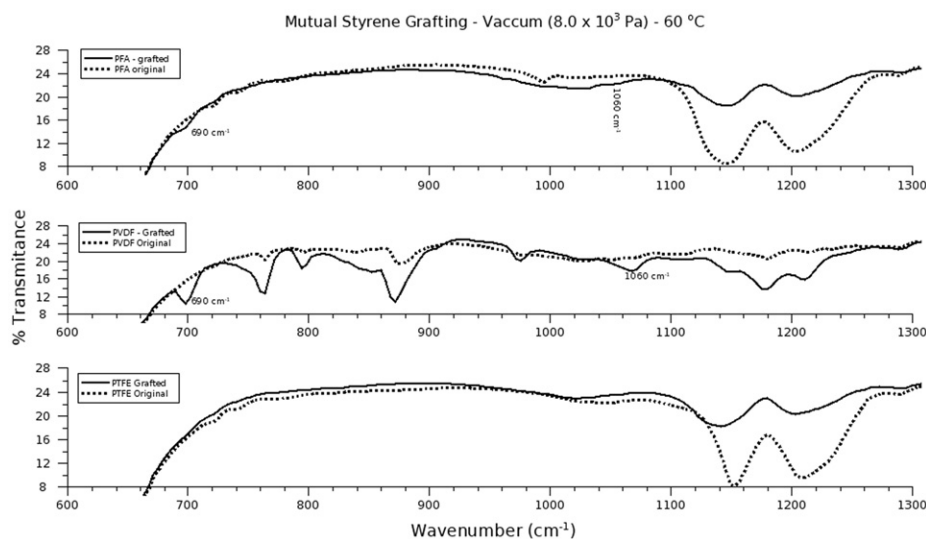
**Fig. 4.** Mid-ATR-FTIR spectra of original and styrene grafted hydrocarbon, fluorinated and perfluorinated polymers at mutual electron beam irradiation under vapor phase condition.

grafting is performed by the pre-irradiated or peroxidated methods for polymer films. The high values of grafting yield for mutual grafting of polypropylene under the studied conditions (100 kGy, 22.4 kGy/s, 25 °C, under atmospheric air and room pressure) are attributed to hydroperoxides, formed because of the large amount of tertiary hydrogen atoms, whose C–H homolysis occurs at low bond dissociation energy (Kaur et al., 1998). Once these highly reactive species are formed, the grafting reaction takes place immediately.

Dose rate should be considered when performing grafting reactions; high dose rates increase concentration of radicals by changes in life-time of solute radicals and their ability to diffuse in the media (Sutton and Rotblat, 1957); on the other hand, Nasef et al. (1999) have shown that low dose rates give an adequate time for polymer radicals to survive and to react with monomer molecules. An observed effect is enhancement of monomer diffusibility to the internal layers; thus, low dose rates are adequate for utilization in simultaneous irradiation.

Our experimental approach could not tune extensively the electron beam accelerator for grafting, since it is a commercial model and it is the only one available. Thus, the used dose rates were two or three orders of magnitude above those described in the literature for electron beam irradiation (Nasef et al., 2006). However, regardless of this limitation and the adverse grafting media, we obtained adequate and reproducible results. It will be possible to decrease the dose rate values in order to optimize vapor phase mutual grafting in a future work.

## 5. Summary

In this work the importance of monomer phase on the grafting process has been reported. Moreover, the high dose rate present in commercial accelerators was not a limiting factor in the grafting process. Mutual grafting is an attractive technique since it has shown good reaction yields, which depend on the parameters chosen besides the polymer/monomer system.

## Acknowledgements

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