ABSTRACT

MELT HYDROPEROXIDATION OF POLYPROPYLENE WITH POTENTIAL APPLICATIONS IN POLLUTION CONTROL

by
Zeena Cherian

The primary objective of this study is to introduce tertiary hydroperoxide functional groups into polypropylene (PP) melt by injecting air. This was done first by mixing additive free polypropylene powder with air in a batch mixer. The influence of air flow rate, temperature, mixing time and rotor RPM on the concentration of hydroperoxide groups were studied. Iodometric analysis and fourier transform infrared spectroscopic analysis were the techniques used to detect and quantify the concentration of hydroperoxide groups. In the second phase of the study, hydroperoxide groups were introduced in polypropylene through reactive processing in a single screw extruder. It was possible to incorporate hydroperoxide groups at concentration as high as 0.089 mole/kg of PP. The viscosity changes of the modified polypropylene corresponding to molecular weight reduction were studied using a capillary rheometer.

Preliminary scrubbing experiments were carried out to study the reactivity of one hydroperoxidized polypropylene sample towards NO and further experiments are recommended to establish suitable testing protocol. It has been shown in the past that organic hydroperoxides react with NO to form nitrites and nitrates. It was also demonstrated that γ-ray irradiated PP in moist air produced hydroperoxides that could be made to react with NO. The ultimate objective of this research is to use hydroperoxidized polypropylene for selective NO removal for pollution control.

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by
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To my dear family

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CHAPTER 1

INTRODUCTION

Hydroperoxidation of polypropylene has been done in the past by dissolving the polymer in a suitable solvent and reacting with oxygen. Some studies were also carried out by irradiating polypropylene films or fibers with e-beam or γ-rays. However hydroperoxidizing polypropylene in bulk through a solventless and less energy intensive method could be more realistic and cost effective. Hence the primary objective of this study is to introduce hydroperoxide functional groups on polypropylene in melt phase, by injecting air which is readily available.

Derivatization reactions by NO and SO_2 have been used as techniques to detect and quantify the level of hydroperoxide functional group in oxidized polyolefins. The efficient reaction of NO and SO_2 with hydroperoxide sites results from the ease of reaction of each hydroperoxide group with a small gas molecule which can diffuse through the solid polymer. Quantitative reaction between NO and polymer hydroperoxides occurs to produce nitrate groups which are readily measured by their IR absorption. This technique has been used to quantify hydroperoxide groups in polymers.

The above concept can also be applied to remove NO_x using hydroperoxidized polymers. Earlier research suggested that polypropylene containing hydroperoxide groups produced by surface modification of films through UV or γ- radiation could be used to remove NO_x compounds.

Nitrogen oxides (NO_x) are mixtures of compounds of nitrogen and oxygen generally found in effluents from combustion sources. The predominant NO_x compounds are NO and NO_2. They are formed as a result of the reactions of atmospheric oxygen and nitrogen at high temperatures. Also, large quantities of NO_x are formed from the combustion of nitrogen compounds found in fuels, or in wastes being incinerated. More than 90% of NO_x emitted from stationary combustion sources, consist of NO. Although relatively insoluble in water, NO continues to react slowly in the atmosphere to form NO_2, an acid rain precursor. NO_2, in the presence of sunlight and hydrocarbons forms ozone, a strong oxidizing agent that causes respiratory diseases. Finding a way to control NO is essential for the prevention of NO_x and ozone pollution.

Selective removal of nitric oxide (NO) from gas streams has been studied in the past by various researchers using low molecular weight commercially available organic hydroperoxides such as cumene hydroperoxide, pinane hydroperoxide, etc. For example, the influence of different variables such as temperature, gas stream flow rate and concentration of tertiary hydroperoxide compounds on rate of NO removal was evaluated. (Perlmutter, et. al., 1993). The NO reacted with hydroperoxides to produce alkyl nitrates.

The objectives of this research are (a) to modify polypropylene through melt hydroperoxidation in bulk by injecting air, in the absence of solvents, in batch mixers or continuous extruders, and (b) to investigate the effects of process parameters on the degree of reaction. The ultimate objective is to evaluate the modified material as a possible absorbent of NO_x compounds in pollution control applications.

CHAPTER 2

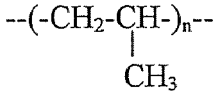
LITERATURE REVIEW

2.1 Polypropylene

2.1.1 General Characteristics

Polypropylene (PP) is a thermoplastic material-it softens and melts when heated, rather than charring or burning. With its low density of 0.9g/cc., polypropylene is one of the lightest of all thermoplastics. It is 5% lighter than high density polyethylene (HDPE), 14% lighter than polystyrene (PS) and 33% lighter than polyvinylchloride (PVC). The high melting point of polypropylene (165°C-170°C) enables it to be used up to 120°C before it softens. Thus, the automotive industry uses polypropylene in bumpers and in battery cases, while the packaging market uses it for crates and microwaveable containers. The leisure industry uses it for furniture and apparel and the gardener uses it for pots and netting. The medical industry uses it for disposable syringes.

Isotactic polypropylene consists of a regular arrangement of monomer molecules in which all methyl groups are on the same side of the chain. The chemical structure of polypropylene is:

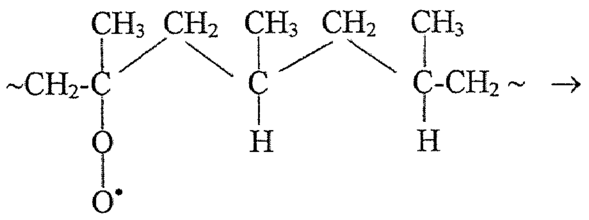


$$\text{--(-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-)}_n\text{--}$$

The stereoregular polypropylene possesses a substantial structural disadvantage, i. e., easy oxidation. This is due to the fact that the hydrogen atom attached to the tertiary carbon atom of the polymer molecule is highly reactive and as a result, the -C-H bond at the asymmetric carbon atom readily reacts with oxygen to form a hydroperoxide group.

This decomposes, forming free radicals that may initiate further oxidation of the material and this causes marked deterioration of the physico-mechanical properties of the polymer. Despite the problems of thermal and photooxidative instability associated with the polymer, polypropylene has found wide commercial application in the form of fibers and films. A partial solution of these problems has been achieved by the development of many ultraviolet (UV) stabilizers and antioxidant systems for use with polypropylene.

The photo- and thermal oxidations of polypropylene have been shown to involve, at least in part, the conventional free radical auto oxidation chain process to give hydroperoxides as initial products. In addition a host of carbonyl products is also formed, probably by secondary processes (Carlsson, D.J, et. al,1969). The mechanism of auto oxidation of polypropylene is the following: there is a slow oxidation during the induction period; intramolecular hydrogen abstraction results in the formation of neighboring hydroperoxides. (Chien, 1967). The reaction sequences are given below.



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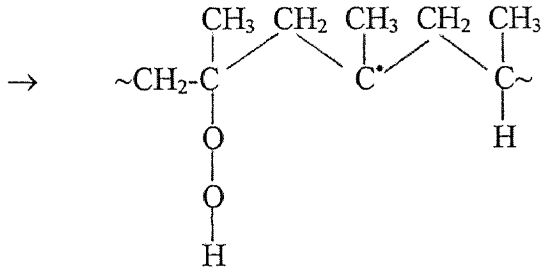

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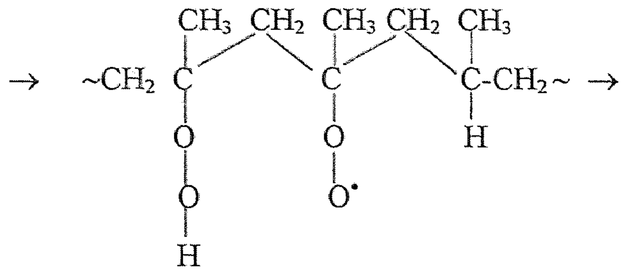

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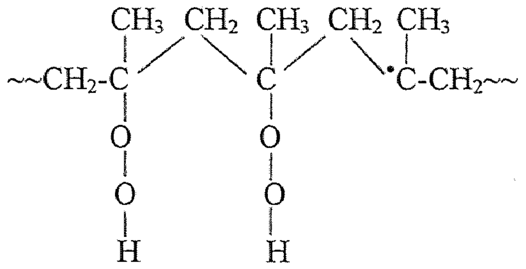
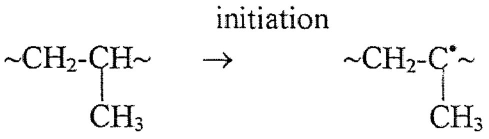


(4)

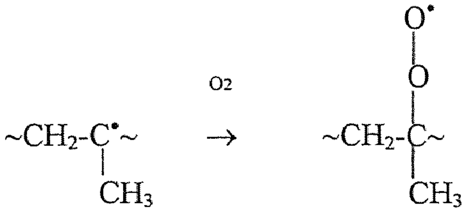
2.1.2 Hydroperoxidation

Several methods are available for modifying polypropylene, and thus, extend its use in several technologically important fields. Functionalization and/or graft co- polymerization have proved attractive because the polymer not only retains most of its original properties but also acquires some additional properties needed for a particular application. Hydroperoxidation and halogenation have been used for introducing the functional groups into the polymer. In the present review, the work reported on hydroperoxidation of polypropylene often followed by grafting of an unsaturated monomer is reviewed.

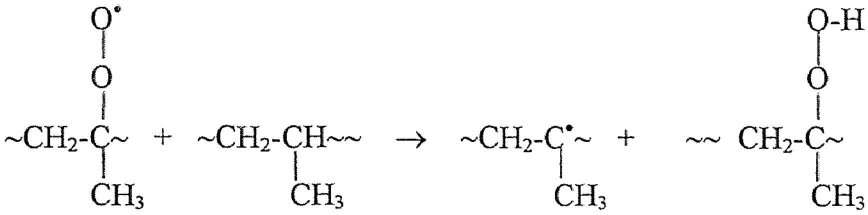
The oxidation of polypropylene is an auto catalytic process and controlled oxidation results in the formation of hydroperoxides. The hydrogen atom on the tertiary carbon atom is highly reactive and hence is the site for reaction with oxygen to form hydroperoxide group, which upon decomposition, results in the formation of free radicals required for graft polymerization. Hence, hydroperoxides in PP are predominantly tertiary (90%), the remainder being essentially secondary ones (Commereuc, 1997). The scissions of these tertiary hydroperoxides lead directly to backbone scissions, giving a mixture of low molecular weight molecules. Thus tertiary hydroperoxy radicals are the intermediate precursors to chain scission (Chien, 1967).



$$\sim CH_2-\underset{CH_3}{CH}\sim \xrightarrow{\text{initiation}} \sim CH_2-\underset{CH_3}{C^{\bullet}}\sim \qquad (5)$$



$$\sim CH_2-\underset{CH_3}{C^{\bullet}}\sim \xrightarrow{O2} \sim CH_2-\underset{CH_3}{\overset{O-O^{\bullet}}{C}}\sim \qquad (6)$$



$$\sim CH_2-\underset{CH_3}{\overset{O-O^{\bullet}}{C}}\sim + \sim CH_2-\underset{CH_3}{CH}\sim\sim \rightarrow \sim CH_2-\underset{CH_3}{C^{\bullet}}\sim + \sim\sim CH_2-\underset{CH_3}{\overset{O-O-H}{C}}\sim \qquad (7)$$

Hydroperoxidation of polypropylene has been extensively used for the graft polymerization of various vinyl monomers onto polypropylene. The surface hydroperoxidation of isotactic polymers makes it possible to modify the surface properties by grafting to produce , e.g., hydrophilic fibers or films, dyeable fibers, etc. A great deal of research work has been carried out by this technique.

Natta, et al., (1959) carried out hydroperoxidation of polypropylene without substantial degradation by heating in air or oxygen flow at 70-80°C. In such conditions, the hydroperoxidation of the crystalline isotactic polymers takes place only on the surface of the crystals or in the intercrystalline amorphous regions next to the external surface.

On the contrary, in less crystalline polymers, containing stereoblock and atactic polymers, the hydroperoxidation takes place deeper, depending on the stereoisomeric composition. However, homogeneous hydroperoxidation has been shown to occur during oxidation in solution in the presence of initiators. This hydroperoxidized polypropylene was used for the graft copolymerization of methyl methacrylate, styrene, and vinyl chloride monomers.

Sirota (1971) reported that heterogeneous oxidation of polyethylene below the melting point of the crystalline phase is faster, the lower the crystallinity. Under these conditions, the oxidation mainly takes place in the amorphous regions, in which oxygen diffuses at a much more rapid rate than in the crystalline phase. Wu et al (1962) were able to graft polymerize vinyl acetate onto hydroperoxidized polypropylene obtained by thermal oxidation in air. In another publication (Wu, 1961), the rate of formation of hydroperoxide groups was studied.

Chien (1967) studied the structure of polypropylene hydroperoxide (PPH). PPH was prepared as follows: commercial polypropylene was extracted with an excess of chlorobenzene at room temperature; the extract was precipitated and vacuum dried. A sample of this polymer was redissolved in 300 ml chlorobenzene. The solution was air-oxidized at 100°C and the reaction was initiated by α-α'azobisisobutyronitrile. The polypropylene hydroperoxide has been shown to consist of sequences of neighboring hydroperoxides. Intramolecular hydrogen abstraction during oxidation could account for the formation of these neighboring hydroperoxides.

Minsker, et al., (1963) carried out the oxidation of polypropylene at 70°C. Polypropylene fiber was thoroughly washed until there was no further loss in weight, first with acetone and then with ether at the boiling points of the solvents in a fractionation apparatus. Then at 70°C, air purified by activated charcoal, calcium chloride, potassium hydroxide and activated alumina, was blown from below through the same apparatus. After oxidation for 6 hours up to 0.3% hydroperoxide groups were detected by iodometric method. The resulting hydroperoxidized polymer was used for modification by graft copolymerization of methyl methacrylate monomer and by treating the polymer with tri-ethyl aluminum in n-heptane. It has been observed that the oxidation of polypropylene, initiated by free radical initiators in a suitable solvent, has provided control over the extent of hydroperoxidation (Bawn, 1968).

Beati, et al., (1963) used tert-butyl peroxide as the initiator during the oxidation of polypropylene and subsequently grafted 2-vinyl pyridine onto hydroperoxidized polypropylene . A similar procedure was followed by Pegoraro, et al., (1964) for the grafting of methyl acrylate onto polypropylene.

Hydroperoxidation of polypropylene in an aqueous slurry has been reported by Jabloner and Mumma (1972). A cationic surfactant and potassium persulfate were used to achieve wetting and initiate oxidation. Oxygen was sparged and heated to 100°C to get hydroperoxidized polypropylene. A surfactant was shown to have a visible impact on hydroperoxide formation. Successful oxidation of polypropylene has been attributed to the formation of the persulfate salt of the quaternary ammonium surfactant on the surface of polypropylene.

Patton (1975) synthesized poly (propylene-g-2-vinylpyridine) by selective hydroperoxidation of polypropylene in an aqueous slurry. A mixture of ozone-oxygen was bubbled at 65-100°C to introduce sufficient hydroperoxide groups. The product was then used for graft copolymerization of 2-vinyl pyridine under a nitrogen atmosphere.

The oxidation of both crystalline and amorphous polypropylene in benzene solution was studied at 100-130°C (Van Sickle, 1972). Tert-Butyl peroxide was used as an initiator. The results showed that 40% of the absorbed oxygen is present as hydroperoxide.

Reactive extrusion has been used to introduce a variety of functional groups into polymers. Hydroperoxide groups was introduced into polyethylene by coextruding the polymer with air at 190°C on a 20 mm (L = 40D) counter rotating twin screw extruder with 3 min residence time at 200 rpm. Air is introduced into an induction zone of the extruder at 25 l/hr at 75 bar and into an oxidation zone at 100 l/hr at 55 bar. A PE with 3200 ppm hydroperoxide groups could be produced. These hydroperoxidized polyethylene could be used for graft reaction with a monomer such as butyl acrylate (Xanthos, 1992).

Photoozonization of polypropylene films to induce surface oxidation was studied by Rabek, et al., (Fettes, 1965). A mixture of ozone and oxygen at flow rate of 500 ml/min and ozone concentration of 4×10^{-3} g/l was passed through a quartz cell, containing polypropylene films (50-70 μm) which could be in addition irradiated with UV. The hydroperoxide (ROOH) concentration was determined iodometrically after decomposition of the ozonides with excess of alcoholic sodium hydroxide.

Environmental photo-oxidation of polypropylene films to study the chemical changes was reported by Carlos De La Cruz, et al., (1996). The films fixed in an aluminum framework were exposed to environmental photo-oxidation in Maracaibo, Venezuela, according to ASTM D 1435-75 between July and August. The Infrared spectroscopic analysis of exposed films showed bands at 3400 cm^{-1} associated to hydroperoxide groups (OOH) and bands at 1715 cm^{-1} associated to carbonyl (C=O) groups.

2.1.3 Detection of Hydroperoxide Groups in Polymers

Although there are usually no problems with the determination of hydroperoxides in polymers soluble at low temperatures, complication arise if the polymer is insoluble or soluble only at high temperature (Scheirs, et al.,1995). Very few methods of hydroperoxide analysis are sufficiently sensitive to measure the very low concentrations of hydroperoxide found in melt processed polymers.

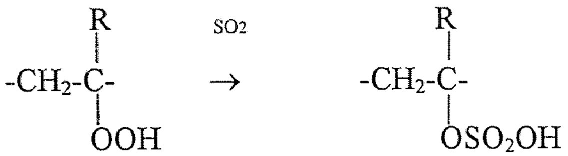
Iodometric method is the most widely used technique for hydroperoxide analysis and accounts for approximately 70% of reported methods of hydroperoxide determination in polymers. Carlsson and Wiles (1969) found that the Iodometric method is capable of determining hydroperoxide concentrations down to 1×10^{-4} mole/kg. The method can be effectively used for polymeric films of thickness less than 200 µm. The reflux times adopted by various workers who have used iodometric methods vary considerably from 3 min to 18 h. The loss of hydroperoxide during refluxing is generally considered negligible.

Nuclear Magnetic Resonance (NMR) Spectroscopy on dissolved samples has superb resolution by this method, but modest sensitivity in the detection of polymer hydroperoxides. The method can detect oxidation products at high levels (≥ 0.1 mole/kg). Despite this limitation, polymer hydroperoxides have been identified and quantified by high-resolution solution NMR.

In direct infrared analysis techniques, weak infrared absorption due to polymer hydroperoxides occur at 3550-3555 cm^{-1} for isolated hydroperoxides and about 3400 cm^{-1}

for hydrogen bonded hydroperoxides (Scheirs, et al., 1995). These can be differentiated from isolated alcoholic groups (3650 cm^{-1}) and all other hydrogen bonded alcohol and hydroperoxide groups (3400 cm^{-1}). However, the hydrogen-bonded species usually dominate. Hydrogen bonded alcohol groups also absorb at around 3400 cm^{-1} , thus IR measurements produce an overestimate of the hydroperoxide concentration, unless the alcohol level can be shown to be insignificant by, for example, the nitric oxide method (Carlsson, et al., 1987). Alcohol groups react with NO to give nitrites.

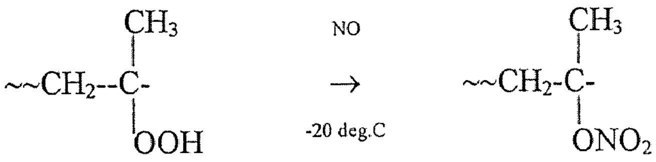
Indirect infrared methods, such as sulfur dioxide and nitric oxide methods relies on the derivatization of hydroperoxide groups. The polymer hydroperoxides can be transformed into alkyl hydrosulfates by treatment with SO_2 [Eq.8] (Carlsson, 1988).



$$-CH_2-\underset{OOH}{\overset{R}{C}}- \xrightarrow{SO2} -CH_2-\underset{OSO_2OH}{\overset{R}{C}}- \qquad (8)$$

Alkyl hydrosulfates absorb at 1195 cm^{-1} in the IR spectrum. However, Carlsson and Wiles (1969) found that the sulfur dioxide method does not work satisfactorily for oxidized PP because the expected IR band at 1195 cm^{-1} is largely masked by the IR absorption of H_2SO_4 produced in the highly hydroperoxidized domain found in oxidized polypropylene.

By careful control of the reaction conditions, polymer hydroperoxides react with NO to produce alkyl nitrates which are readily measured by their IR absorption at 1290 cm^{-1} [Eq. 9] (Carlsson, 1988).



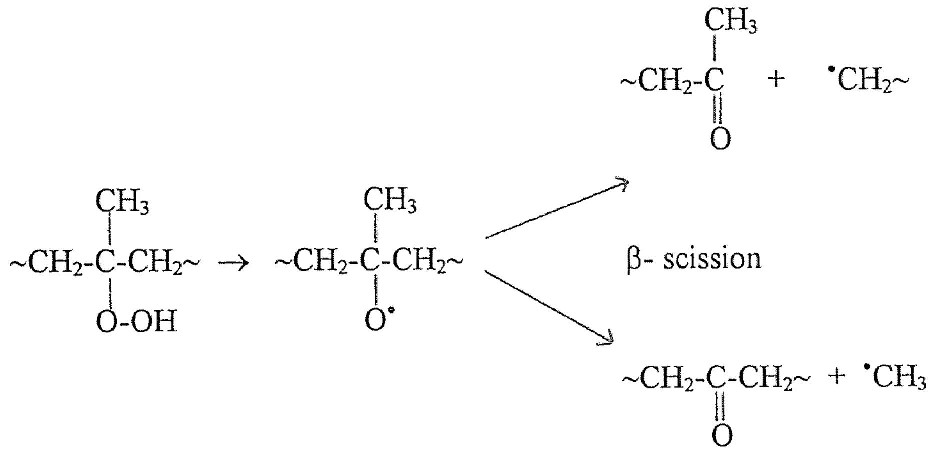
$$\sim\sim CH_2--\underset{OOH}{\overset{CH_3}{C}}- \xrightarrow[-20\ deg.C]{NO} \sim\sim CH_2-\underset{ONO_2}{\overset{CH_3}{C}}- \qquad (9)$$

The poor thermal stability of tertiary nitrate groups at room temperature means that the reaction between oxidized PP and NO should be carried out at -20°C. The reaction is believed to be quantitative up to modest degrees of hydroperoxidation (0.3 mole/kg of PP).

2.1.4 Stability of Polymer Hydroperoxides

The stability of polymer hydroperoxides depends largely on the proximity of neighboring hydroperoxide groups, other oxidation products and the temperature (Scheirs, 1995). The presence of ‘blocks’ of hydroperoxides in PP favors their bimolecular decomposition as this has a lower activation energy than the monomolecular reaction. Thus the initiation rate associated with hydroperoxide “blocks’ is superior to that of isolated hydroperoxides.

Hydroperoxides may undergo thermal, photochemical, or catalytic decomposition to generate free radicals which propagate the oxidative process and ultimately lead to the formation of alcohol and/ or carbonyl groups in the polymer. Mill T. (1973) reported that decomposition of hydroperoxides result in a scission which leads preferentially to carbonyl groups. The reaction sequences are as follows:



$$\sim CH_2-\underset{O-OH}{\overset{CH_3}{C}}-CH_2\sim \;\rightarrow\; \sim CH_2-\underset{O^{\bullet}}{\overset{CH_3}{C}}-CH_2\sim \;\xrightarrow{\beta\text{- scission}}\; \begin{cases} \sim CH_2-\underset{\overset{\|}{O}}{\overset{CH_3}{C}} + {}^{\bullet}CH_2\sim \\ \sim CH_2-\underset{\overset{\|}{O}}{C}-CH_2\sim + {}^{\bullet}CH_3 \end{cases} \qquad (10)$$

The accumulation of alcohol and carbonyl groups are predicted in the reactions (11) to (14) as reported by Lacoste, et al., (1991)

$ROOH \rightarrow RO^{\bullet} + OH \rightarrow R^{\bullet} + H_2O / ROH$ (11)

$R^{\bullet} + O_2 \rightarrow RO^{\bullet}_2$ (12)

$RO^{\bullet}_2 + RH \rightarrow ROOH + R^{\bullet}$ (13)

$2RO^{\bullet}_2 \rightarrow ROH + RC(=O)R + O_2$ (14)

Conventional methods, i.e., the iodometric titration method and direct infrared methods have been used as the tools for detection and quantification of hydroperoxide groups in polypropylene in this research. It is important to preserve the hydroperoxidized polypropylene at low temperatures. It has been found that more than 85% of polypropylenehydroperoxides are rapidly decomposed within the temperature range of 100-135°C. Appreciable decomposition may also occur at temperatures slightly above 30°C (Scheirs, 1995).

2.2 Nitrogen Oxides Formation and Sources

2.2.1 Fuel Combustion

Nitrogen oxides (NO_x) are generated in all combustion processes that employ air as the oxidizer. At flame temperatures, the reaction of atmospheric oxygen and nitrogen results in the formation of nitric oxide (NO). The mechanism of formation of NO from nitrogen and oxygen follows the chain reaction sequence postulated by Zeldovich (1946) and Glich, et al.,(1957). The reaction sequence is shown in Equations (15) through (17).

$O_2 + M \leftrightarrow 2O + M$ (15)

$O + N_2 \leftrightarrow NO + N$ (16)

$N + O_2 \leftrightarrow NO + O$ (17)

Where M is a third body.

2.2.2 Lightning

The major primary source of natural NO_x is caused by the effect of lightning on atmospheric oxygen and nitrogen. The temperature of a column of air surrounding the lightning bolt is a function of energy deposition of the lightning. A typical lightning bolt has a energy deposition of about 10^5 J/m. The column of air immediately surrounding such a bolt will be heated to temperature on the order of 30,000 K. At temperatures above 2,300 K, NO is in thermodynamic equilibrium with N_2 and O_2. As the temperature of the heated air drops below 2,000 K, NO cools down rapidly and does not revert back to oxygen and nitrogen. (Levine, et al., 1984). This is a major natural source of NO_x and accounts for 1/3 of natural NO_x.

2.2.3 Microbial Activity in Soils

It has been found from field flux measurements and laboratory experiments that soil microorganisms also produce appreciable amounts of NO. To quantify the rate of production of NO, a series of laboratory experiments were performed using two of the most common bacteria found in soils named *Nitrosomonas Europaea* and *Acaligenes Faecalis*. The result indicates that nitrification is an aerobic process in which ammonium cations are oxidized to inorganic nitrite and nitrate ions. NO and N_2O are direct or indirect intermediates of this mechanism (Levine, et al.,1984). Soil accounts for about 2/3 of natural NO_x (Bolin, et al.,1983)

2.3 Effects of Nitrogen Oxides

Nitrogen oxides (NO_x) may cause a lot of serious environmental problems, such as tropospheric ozone formation, acid precipitation, respiratory diseases, and associated health effects.

The increasing acidity in poorly buffered soils (Bridgeman, 1990) is having a serious influence on vegetation, surface water, biological systems, and structures of the earth. The U.S. National Acid Precipitation Assessment Program (NAPAP) was implemented in 1980 to conduct research and assess the complex causes and effects of acid deposition. NAPAP had two primary objectives. First, it sought to fill many gaps in the scientific understanding of acid deposition. Second, the program developed methods and evaluated the consequences of alternative acid deposition control strategies (Isom, et al., 1984).

The oxides of nitrogen are not very active biologically. At exposures well above a few ppm, NO_2 causes lung damage of various types, including bronchial damage reminiscent of that from SO_2, though less severe, and acute pulmonary edema, an effect characteristic of ozone. Since atmospheric levels only rarely reach a half ppm (1000 $\mu g/m^3$), there has historically been little concern over the direct health effects of NO_2. However, a major observational study found that certain portions of the population had decreased ventilatory function and increased respiratory illness in neighborhoods near a factory that manufactures TNT. This unusual situation provided a test area with very low NO_2 levels ranging from 0.06 to 0.109 ppm (113-205 $\mu g/m^3$). These NO_2 levels are of the same magnitude as the ambient concentrations experienced in many cities (Lynn, 1976).

Air pollution alerts due to ozone and Peroxy Acetyl Nitrate (PAN, which are formed through incomplete combustion of hydrocarbons such as gasoline) may increase the rate of O_3 formation by releasing NO_2. PAN is thermally unstable and may contribute to O_3 formation downwind of urban areas by transporting NO_x, and then decomposing into peroxy acetyl radicals and NO_2 (Finlayson-Pitts, 1986). Thus, NO_2 is important because it is the precursor to ozone formation. Ozone adversely affects the health of the elderly and the very young through its impact on the respiratory system. The reason NO_2 rather than NO is used as standard for health effect studies is because all NO is oxidized to NO_2 in the atmosphere.

2.4 Absorption of NO using Organic Hydroperoxides

Perlmutter, et al (1993) studied the absorption of NO_x using organic hydroperoxide such as cumyl hydroperoxide. According to the study, a successful NO_x-scrubbing hydroperoxide candidate would have to fulfill the following requirements:

1. Hydroperoxide should be tertiary(R_3COOH). Hydroperoxides (ROOH) as a class of organic oxidizing agents are safer, (i.e., thermally more stable), than peroxides (ROOR).
2. The hydroperoxide should be relatively inexpensive. This is important in order to be competitive with selective catalytic reduction. (selective catalytic reduction is a process where NO_x can be reduced to nitrogen and water by adding NH_3 into the effluent gas from a combustor using a catalyst. The reactions occur at 300 to 400°C.)
3. The components of the NO scrubber solution should be nonvolatile, i. e. , should not be vaporized at flue gas temperatures.
4. The 'spent' scrubbing solution should be easily denitrated and the denitrated organic

material reoxidized to hydroperoxide and / or used in another economically advantageous way.

A possible reaction sequence was postulated for the reaction of ROOH with NO for nitrate formation.

$ROOH + NO \rightarrow ROO^{\bullet} + HNO$

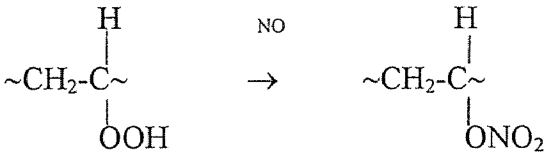
$ROOH + HNO \rightarrow ROO^{\bullet} + H_2 + NO$

$2ROO^{\bullet} + 2NO \rightarrow 2[ROONO] \rightarrow 2RONO_2$, with a net reaction;

$2ROOH + 2NO \rightarrow 2RONO_2 + H_2$

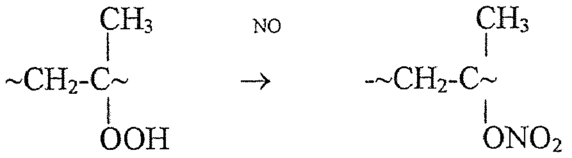
Derivatization reactions by NO and SO_2 have been used as techniques to detect and quantify the level of hydroperoxide functional group in oxidized polyolefins. The efficient reaction of NO and SO_2 with hydroperoxide sites results from the ease of reaction of each hydroperoxide group with a small gas molecule which can diffuse through the solid polymer (Scheirs, et. al.,1995).

By careful control of the reaction conditions, quantitative reaction between NO and polymer hydroperoxide occurs to produce nitrate groups which are readily measured by their IR absorption [Eqs (18) and (19)]. This technique has been used to detect and quantify hydroperoxide groups in polymers.



$$\sim CH_2-\underset{OOH}{\overset{H}{C}}\sim \xrightarrow{NO} \sim CH_2-\underset{ONO_2}{\overset{H}{C}}\sim$$

(IR 1276 cm-1) (18)



$$\sim CH_2-\underset{OOH}{\overset{CH_3}{C}}\sim \xrightarrow{NO} -\sim CH_2-\underset{ONO_2}{\overset{CH_3}{C}}\sim$$

(IR 1290 cm-1) (19)

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Unstabilized Polypropylene Powder

The polypropylene selected for the study was a commercially available, additive free, unstabilized powder PD 6501, supplied by Montell USA. The nominal melt flow index of the material was 4.5 g/10 min. It was assumed that, formation of hydroperoxide groups during processing would be easier with unstabilized rather than with stabilized polypropylene, without the complication arising from antioxidant radical scavengers.

3.1.2 Antioxidant

The antioxidant Irganox 1010 (CIBA GEIGY) was used during the measurement of melt flow index and viscosity to prevent further viscosity changes of polypropylene.

3.1.3 Air

For batch experiments, machine shop compressed air was used. For reactive extrusion, air cylinders were purchased from SOS gases, Inc. and were used directly.

3.1.4 Compounds for Iodometric Titration

Sodium iodide (NaI), Isopropyl alcohol (IPA) and Sodium thiosulfate ($Na_2S_2O_3$) were used for the iodometric titration to determine the concentration of hydroperoxide functional groups in polypropylene. These three compounds were purchased from Aldrich chemical company and used without further purification.

3.2 Processing Equipment

3.2.1 Batch Mixer (Brabender)

A 300 cc capacity electrically heated batch mixer (Brabender) was used for the batch modification of the polymer. Figure 1 shows the photograph of the batch mixing experimental set-up. It consists of a figure-eight-shaped chamber which fits over two sigmoid, counter rotating rotors driven by motor. The rotor speed can be varied from 10 RPM to 100 RPM. It is provided with an opening through which air can be passed during processing. Air supply was connected to the batch mixer via a flow meter. The experimental set up is shown in Figure 1

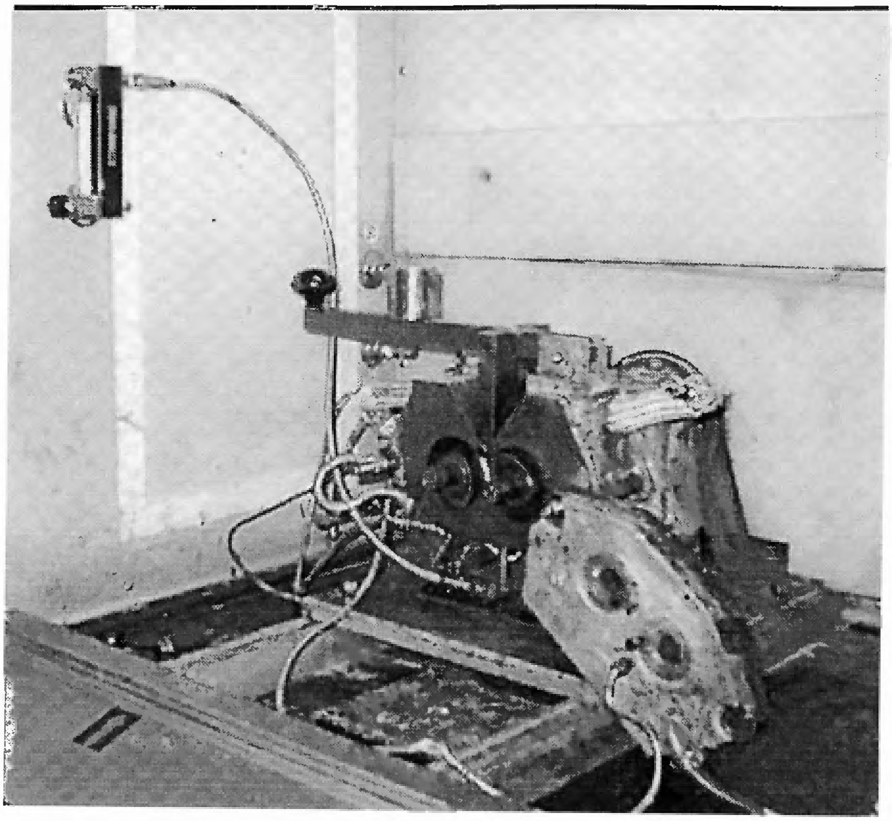


Figure 1 A Photograph of the batch mixing experimental set-up

3.2.2 Extruder

The extruder used was a 31.7mm Killion segmented single screw having a length to diameter ratio of 40:1. The extruder used for this study is provided with an injection nozzle at the reaction zone through which air or any gas can be injected. The temperature of the extruder can be controlled at twelve different places (zones) from feed zone to die zone, including melt and die temperature. The feed rate and screw speed can be varied. A solid metering feeder was used to adjust the feed rate.

In an extrusion process, the polymer is fed into the hopper and then conveyed continuously along a screw through regions of high temperature and pressure where it is compacted and melted, and finally forced through a die. The design of the screw produces positive displacement conveyance.

The screw consists of three main sections. The feed section picks up the finely divided polymer from the hopper and propels it into the main part of the extruder. In the compression section, the loosely packed feed is compacted, melted, and formed into a continuous stream of molten plastic. Some external heat is applied, but much is generated by friction. The metering section contributes to uniform flow rate, and builds up sufficient pressure in the polymer melt to force the plastic through the rest of the extruder and out of the die. Several screw configurations could be used to enhance mixing. The screw used for this experiment is provided with an additional mixing section to facilitate dispersion/ dissolution of air in the polymer melt. A typical screw configuration is shown in Figure 2.

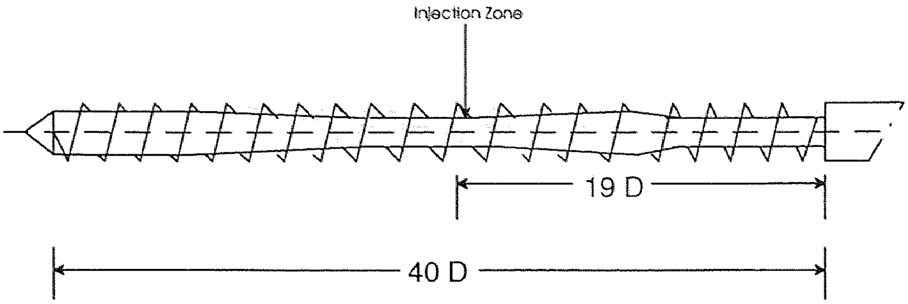


Figure 2 A schematic of a typical screw configuration for gas injection

3.3 Experimental Procedure

3.3.1 Batch Reaction

For the batch mixing experiments, statistical experimental design techniques were used in examining the effects of processing factors on the concentration of the hydroperoxides formed, with only one third of the experimental runs normally required to carry out such study. The processing variables selected were temperature, time of mixing, rotor RPM, air flow rate. The experimental design followed is given in Table 1

About 130 g of polymer were processed at the selected conditions in the batch mixer. After processing, a sample of 30-40 g was taken out from the mixer. To the remaining sample, about 2% of antioxidant, Irganox 1010 was added and mixed for 1 min. This was done to prevent changes in viscosity of the sample during viscosity measurement using a capillary rheometer. The polymer taken out from the mixer was cooled down to room temperature and powdered using a commercial blender. The ground samples were analyzed for hydroperoxide concentration by iodometric titration. All these samples were preserved under refrigerated conditions until the analysis could be carried out.

Missing Page

Table 1 The experimental design for batch mixing

Experiment	Time	Temperature	Air flow	Rotor RPM
1	-	-	-	-
2	+	-	-	-
3	-	+	-	-
4	+	+	-	-
5	-	-	0	-
6	+	-	0	-
7	-	+	0	+
8	+	+	0	+
9	-	-	+	+
10	+	-	+	+
11	-	+	+	+
12	+	+	+	+

Variables	**Minimum (-)**	**Maximum (+)**	**(0)**
Temperature (°C)	190	230	
Time of Mixing (min.)	10	30	
Rotor Speed (RPM)	40	80	
Air Flow (scc/min.)	1000	3000	N_2

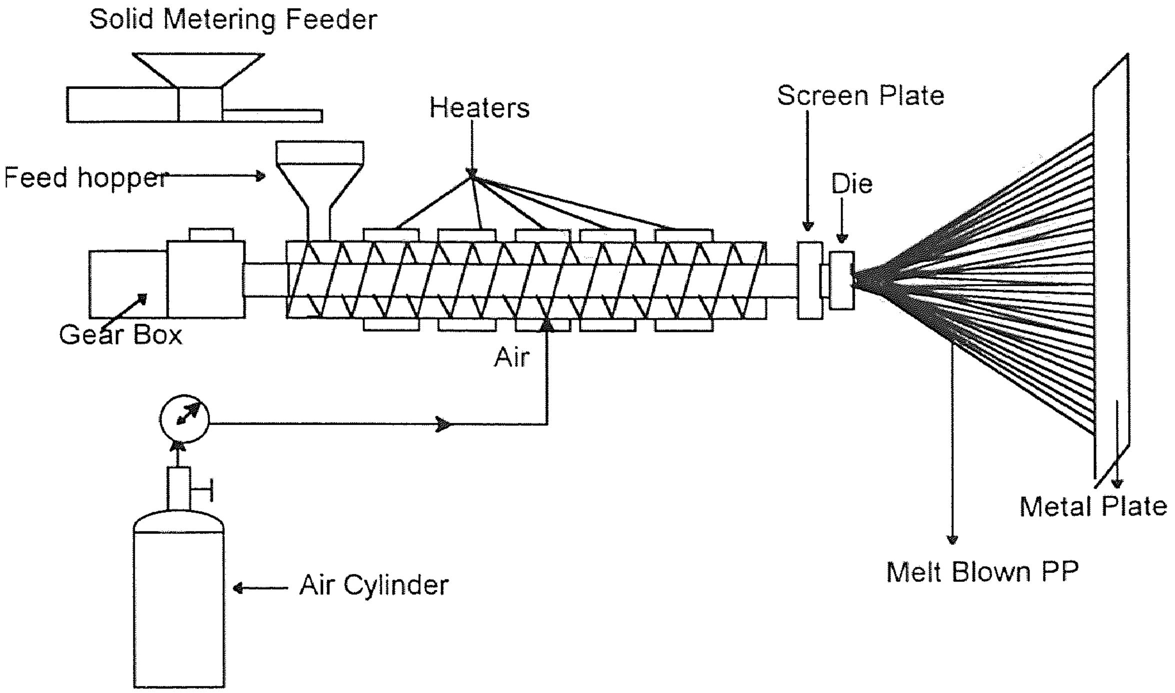


Figure 3 A schematic diagram of the reactive extrusion process

3.4 Analytical Techniques

3.4.1 Iodometric Titration

Iodometric methods are commonly used for determining the concentration of organic hydroperoxides (Scheir, 1995). Carlsson and Wiles (1969) found that the iodometric method is capable of determining hydroperoxide concentration down to 1×10^{-4} mole/kg.

In the presence of acid, polymer hydroperoxides oxidize iodide ions to iodine [Eq. (1)]. The intensely colored triiodide species is subsequently formed via the reaction between iodine and excess iodide [Eq. (2)] during refluxing. The concentration of triiodide can be measured by titrating with sodium thiosulfate. The concentration of the triiodide is directly proportional to the concentration of the analyte (hydroperoxide) in the sample.

Following equations show the sequence of reactions involved.

$$ROOH + 2I^- + 2H^+ \rightarrow ROH + I_2 + H_2O \qquad (1)$$

$$I_2 + I^- \leftrightarrow I_3^- \qquad (2)$$

$$I_2 + 2\,S_2O_3^{\,2-} \rightarrow 2\,I^- + S_4O_6^{\,2-} \qquad (3)$$

2 moles $I_2 \equiv$ 2 mole hydroperoxide $\equiv$1 mole S_2O_3

Thus, the concentration of the analyte in the sample should be equal to:

$$\text{mole analyte /kg} = \frac{(\text{ml titrant} \times \text{its normality}) / 2}{\text{Weight of the sample, in g}}$$

A known amount of sample, ground or in the form of fibres was refluxed for 5 minutes in a 250 ml round bottomed flask with 40 ml of Isopropyl alcohol (IPA) after acidification with 2 ml of acetic acid (Mair et al., 1964). At the end of this period, 10 ml of NaI-IPA reagent is added and refluxing continued for 2 hrs. (NaI-IPA reagent was prepared in advance by refluxing 10 g of NaI in 50 ml IPA till NaI dissolves). Due to the slow penetration of the solution into the polymer sample, a minimum time of 2 hour refluxing was allowed for complete reaction and to allow the accessibility of the reagent into the deeper regions within the solid sample. At the end of refluxing, 5 ml of water is added to wash the condenser. The solution was then titrated while hot against 0.01 N Sodium thiosulfate to a colorless end point. Blank titration was carried out without the sample. A schematic diagram of iodometric titration set up is shown in Figure 4.

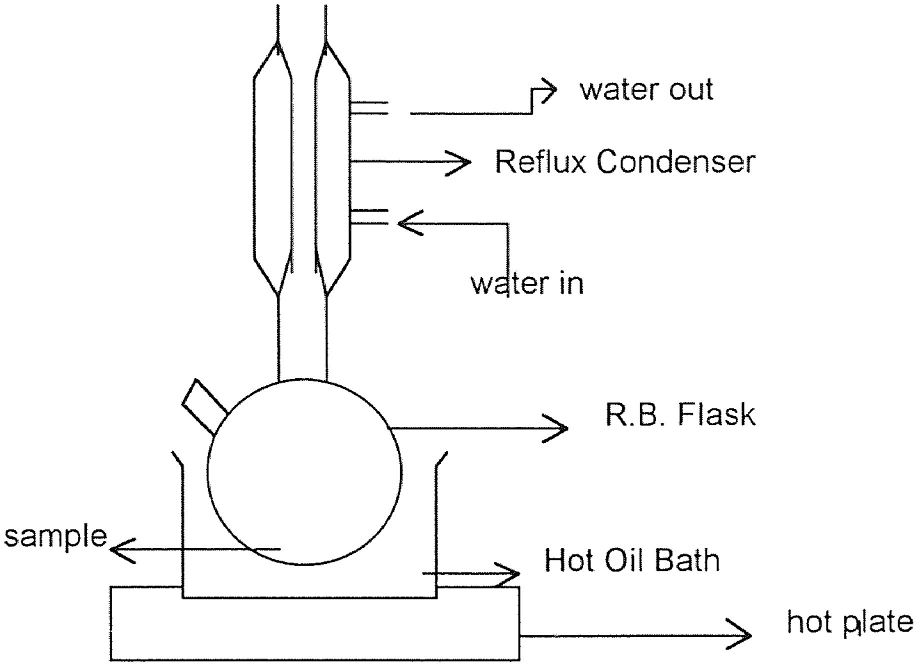


Figure 4 A schematic diagram of iodometric experimental set-up

3.4.2 Fourier Transform Infrared Spectrometer (FTIR)

Analysis by IR spectroscopy is based on the fact that molecules have specific frequencies associated with internal vibrations of groups of atoms. The frequencies occur in the IR region of electromagnetic spectrum: 4000 cm^{-1} to 200 cm^{-1}. When a sample is placed in a beam of IR radiation, it absorbs radiation at frequencies corresponding to molecular vibrational frequencies, but transmits all other frequencies. An IR spectrometer measures the frequencies of absorbed radiation, and the resulting plot of absorbed energy versus frequency is called IR spectrum of the material. The identification of the material is possible because differences in the chemical structure of materials give rise to characteristic vibrations and yield unique IR spectra, i. e., " finger prints" for each material.

An FTIR spectrometer employs an interferometer in place of a monochromator. Figure 5 shows a schematic diagram of a FTIR spectrometer. In continuous scan mode the moving mirror is repetitively scanned as fast as 1/20 second to generate the fourier transform of the IR spectrum (Sibilia, 1996).

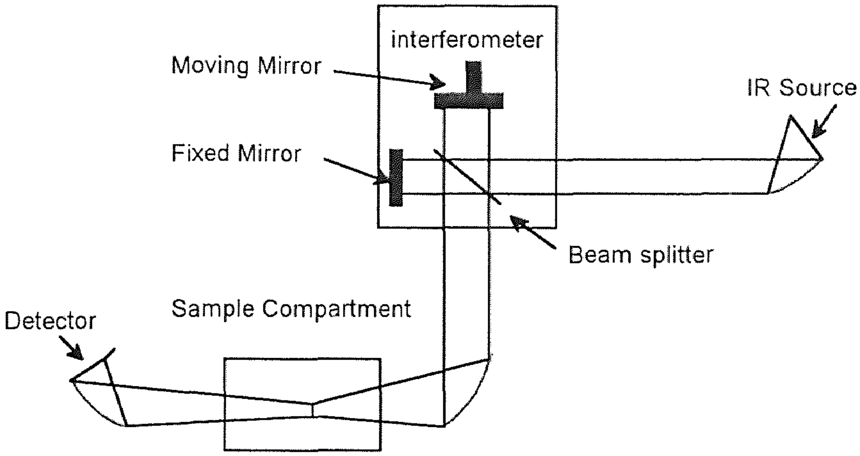


Figure 5 A schematic of FTIR spectrometer

Weak infrared absorption due to polymer hydroperoxides occur at 3550-3555 cm^{-1} for isolated hydroperoxides and about 3400 $cm-^{1}$ for hydrogen bonded hydroperoxides. A broad spectrum centered at 3400 cm^{-1} has been used to monitor the buildup of hydrogen bonded hydroperoxides during thermal oxidation of PP (Carlsson, 1969). Hydrogen bonded alcohol groups also absorb at around 3400 cm^{-1} and IR measurements may produce an overestimate of the hydroperoxide level, unless the alcohol level can be shown to be insignificant by, for example, the nitric oxide method. Despite the low sensitivity, infrared spectroscopic analysis has been used to give a cross-check on the broad level of hydroperoxide groups in a polymer.

3.4.3 Capillary Rheometer

The apparatus used to study the viscosity changes (rheological changes) of polypropylene is a Kayeness Capillary Rheometer equipped with a microcomputer. The viscosity of polymers at various shear rates is an important reflection of the molecular structure of the material. Polymers exhibit " Non-Newtonian" flow which means a non uniform viscosity or flow over a range of shear stresses and shear rate. This tester has a programmable ram speed to provide shear rates from 0.04 in/min to 20.0 in /min and a force transducer provides the force feedback to the computer for computation of shear stress. Thus, one or up to five different shear rate viscosity points may be determined in one test. The melt viscosity values are reported in poise.

Due to the presence of highly reactive tertiary carbon atom on polypropylene, the polymer is thermally unstable, unless antioxidants are added to stabilize the polymer. Hence, the melt viscosity changes were carried out on oxidized polymer in the presence of antioxidant.

3.4.4 Melt Flow Index

The melt flow index (MFI) is a widely used, simplified version of the capillary rheometer.

The rate of extrusion of a polymer melt is determined through a given capillary in a closely defined apparatus as per the ASTM standard D1238. It consists of a heated barrel into which a capillary of diameter 2.09 mm and length 8 mm is fixed. Polymer granules are fed into the barrel and, after being heated to temperature T, forced through the capillary by a pressure induced by a piston of mass M. The flow is obtained by cutting off the length of extrudate which has flowed through the capillary in a certain time. For polypropylene, this flow rate, measured in gram per ten minutes, is the melt flow index when the test is run according to the conditions: T = 230°C; and M = 2.16 kg. The MFI tester was used to determine the nominal melt flow index of polypropylene powder.

3.4.5 Compression Molding

The compression molding press used for making thin films for IR analysis was a laboratory model Carver hydraulic press. It has lower and upper platens with independent temperature controls. The temperature is selected based on the composition of polymer.

In compression molding process, a few grams of polymer sample is placed between the platens. The upper platen is then lowered and the polymer is compressed under a pressure of 15000-20000 psi depending on the thickness desired. The molten polymer is kept under pressure for few minutes. It is then allowed to cool by shutting of the heater and circulating water. After cooling, the polymer film is taken out.

In this study, the samples were pressed at a temperature of 190°C and compressed under a pressure of 15000 psi for 3 minutes with 1 minute preheat time. The thickness of the film obtained was in the range 10-12 microns.

CHAPTER 4

RESULTS AND DISCUSSION

Reactive macroalkyl radicals are formed during stress and thermal initiated scission of the polymer backbone. These radicals are unstable and lead to the formation of hydroperoxides in the presence of oxygen during the initial stages. In isotactic polypropylene, thus, long sequences or 'blocks' of tertiary hydroperoxide groups are usually formed in when the polymer is oxidized. This is because tertiary carbon sites of polypropylene are very reactive and free radicals are formed which act as a potential site for the formation of hydroperoxide group. A schematic diagram of such a molecule is shown in Figure 6.

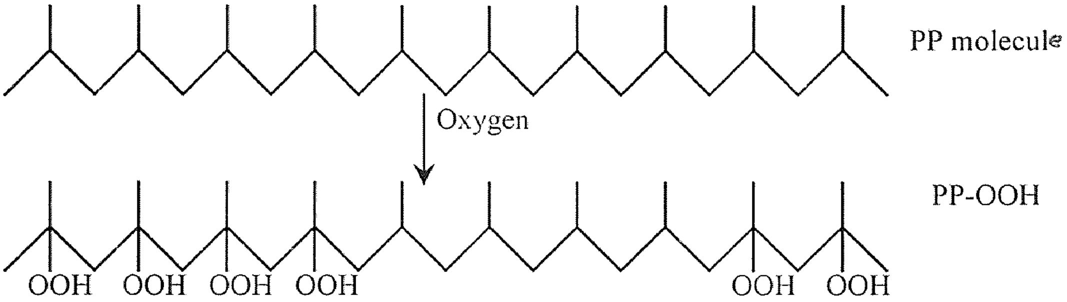


Figure 6 A Schematic diagram of hydroperoxidized PP molecule

4.1 Batch Mixing Experiments

The effects of processing temperature, mixing time, rotor RPM and air flow rate on the hydroperoxide concentration were evaluated. The concentration of hydroperoxide groups in mole/kg was determined by iodometric method. FTIR analysis was used to detect the presence of hydroperoxide groups from films made out of the samples. The effect of processing temperature, mixing time, rotor RPM and air flow rate on hydroperoxide concentration was studied using statistical analysis software. The objective was to maximize the concentration of hydroperoxides groups while keeping the polymer integrity.

Table 2 summarizes the concentration of hydroperoxide groups in mole/kg as obtained from the iodometric method. The reactions carried out under nitrogen atmosphere showed very little concentration of hydroperoxides. These might have formed from trapped or diffused oxygen in the mixing chamber. The influence of each processing variables on the concentration of hydroperoxide is explained in the following sections.

4.1.1 Effect of Temperature on Concentration of Hydroperoxide Groups

The relationship between concentration and mixing temperature is given in Figure 7. It can be seen that, there is tendency to produce more hydroperoxide groups as temperature is increased. This may possibly be due to the formation of more tertiary free radicals on the polymer chains which act as a potential site for reaction with oxygen to form hydroperoxides.

4.1.2 Effect of Mixing Time on Concentration of Hydroperoxide Groups

The influence of mixing time on concentration is shown in Figure 8. Increasing the mixing time does seem to have an effect on increasing the concentration of hydroperoxides. This may be because, as the polymer is exposed to oxygen for longer period of time, formation of hydroperoxide groups also increases.

4.1.3 Effect of Rotor RPM on Concentration of Hydroperoxide Groups

The relationship between rotor RPM and concentration is shown in Figure 9. The plot indicates the increasing the rotor RPM has little effect on increasing the concentration. As the rotor RPM increases, the concentration seems to be slightly decreasing. It should be noted here that, from Table 2, a combination of high rotor RPM with high temperature, time, and air flow rate produces maximum concentration of hydroperoxide groups (1.1×10^{-2} mole/kg). However, the role played by the rotor speed may not be significant.

4.1.4 Effect of Air Flow Rate on Concentration of Hydroperoxide Groups

Figure 10 shows the effect of air flow rate on concentration. The slope of the curve in comparison with those in Figures 7, 8, and 9 indicates that air flow rate has a significant influence on the concentration of hydroperoxide functional groups. This may be because, as the supply of oxygen per minute increases, more polymer radicals react with oxygen , producing more OOH groups. However, increasing flow rate also results in breakdown of molecular chains thus decreasing the viscosity which is explained from the melt viscosity studies.

In general, it can be derived from the results that the concentration of hydroperoxide groups in polypropylene can be maximized by increasing the air flow rate, temperature and mixing time. The concentration of hydroperoxide groups obtained is in the range from 1.3×10^{-4} to 7.1×10^{-3} mole/kg of PP with an exception of a higher value of 1.1×10^{-2} mole/kg.

4.1.5 Melt Viscosity Studies

The test temperature at which viscosity studies were conducted was 230°C. Table 3 gives the melt viscosity at shear rates of 11, 54, 272, 1360 and 5441 sec^{-1}. Figure 11 shows the changes in melt viscosity with increasing shear rates, corresponding to pseudoplastic behavior. (Pseudoplastic behavior of polymers is advantageous from processing point of view). Figure 12 shows the melt viscosity values at a shear rate of 272 sec^{-1}. At a constant shear rate, for example 272 sec^{-1}, maximum reduction in viscosity is observed for sample 12, which was processed under extreme processing conditions. Sample 12 also gives the highest concentration of hydroperoxide groups. It is evident that hydroperoxidation is accompanied by breakup of molecular chains possibly due to β-scission resulting in viscosity changes.

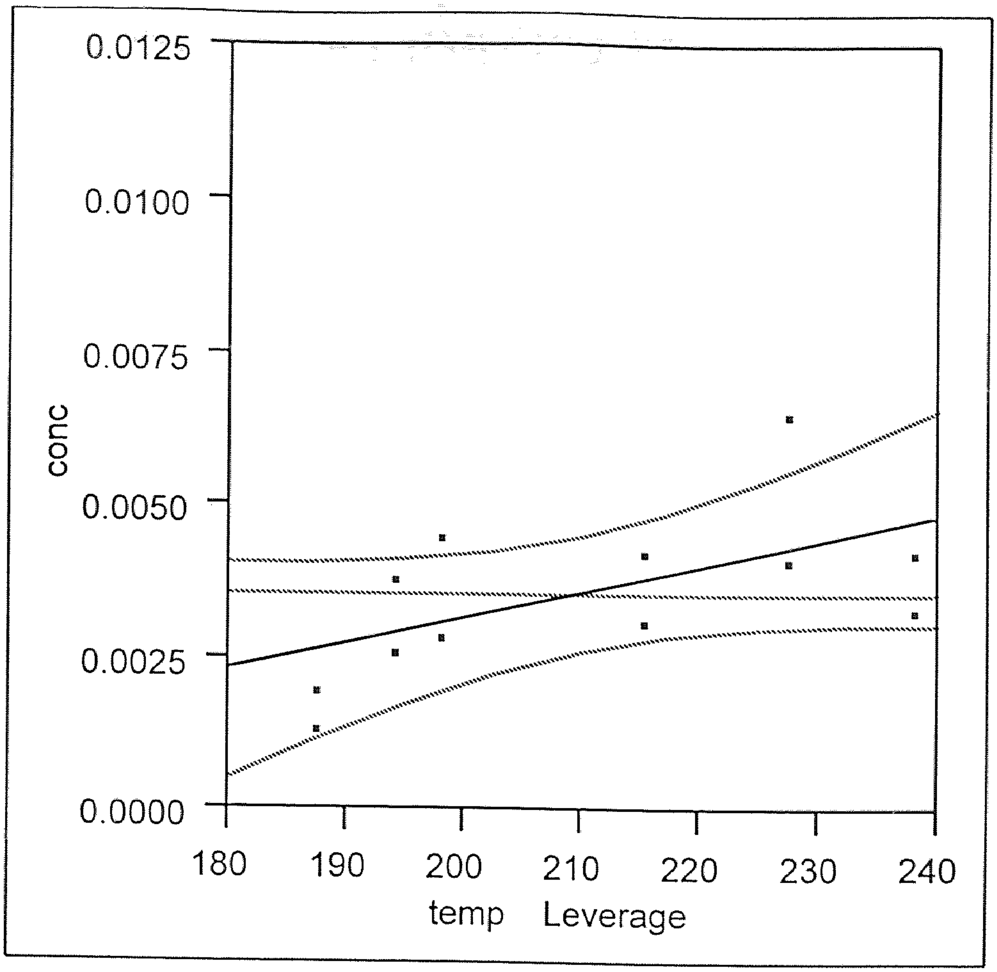
4.1.6 FTIR Analysis

Figure 13 shows the standard transmission infrared spectrum of unmodified polypropylene film sample. The spectrum shows bands at 809, 843, 898 and 1167 cm^{-1} that are characteristic of the helical structure of isotactic polypropylene chains. Figure 14 gives the subtracted spectra of experimental samples after reaction. Only few of the experimental sample spectra were combined in Figure 14, in order to minimize cluttering and also to highlight the differences in spectra of samples which have high and low concentrations of OOH. Figure 14a is of the same samples as that of Figure 14 except that it is taken in a narrow range of 4000 - 3000 cm^{-1}.

In order to bring out the details from the chemical changes on the polypropylene, each spectrum was transmission subtracted relative to the initial unreacted polymer. In Figure 14, the spectra of the reacted samples also show characteristic bands of the structure of polypropylene. These also show however, new bands between 1700 cm^{-1} and 1800 cm^{-1} and between 3400 - 3600 cm^{-1}. In the subtracted spectra, carbonyl peaks at 1715 - 1778 cm^{-1} as well as broad hydroperoxide peaks at 3400 - 3478 cm^{-1} are quite evident. The broad peak centered at 3478 cm^{-1} is prominent for sample 12 which also showed a high concentration of hydroperoxide groups by iodometric titration.

Table 2 Concentration of hydroperoxide groups from batch mixing experiments

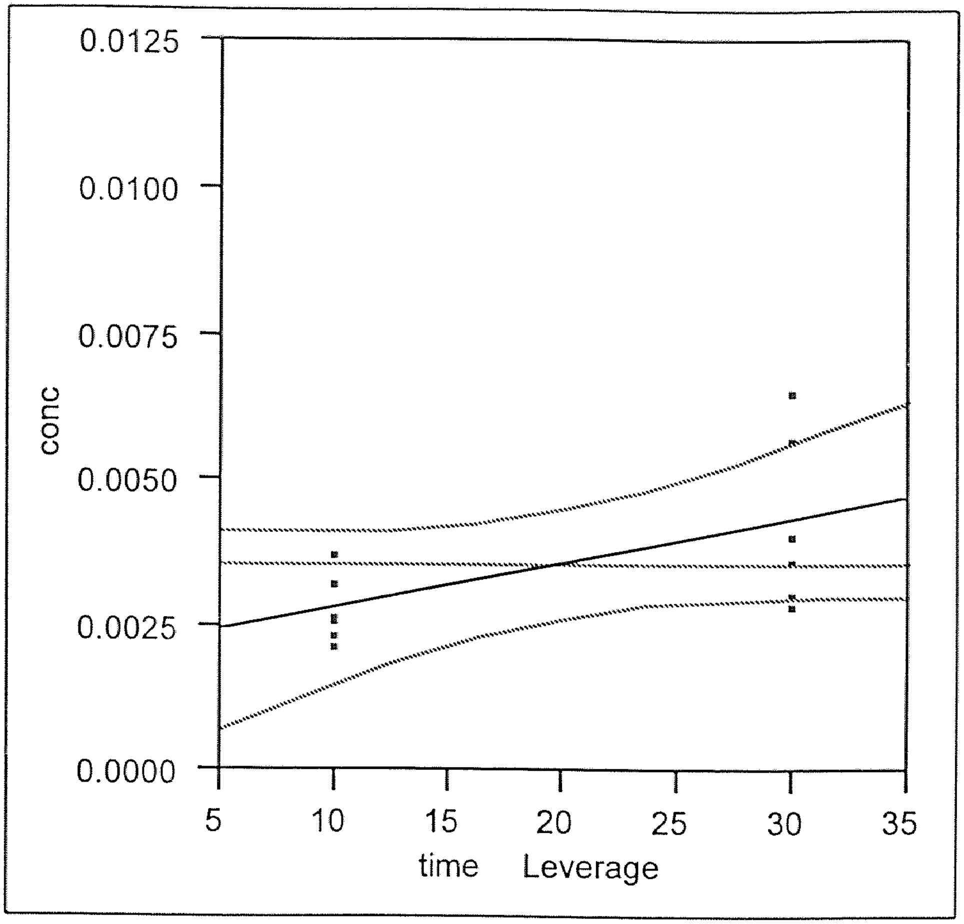
Experiment No.	Mixing Temp. (deg. C)	Mixing Time (mins)	Air Flow Rate (scc/min)	Rotor Speed (RPM)	Concentration of OOH (mole/kg)
PD 6501					nil
1	190	10	1000	40	$1.5 * 10^{-3}$
2	190	30	1000	40	$4.6 * 10^{-3}$
3	230	10	1000	40	$2.9 * 10^{-3}$
4	230	30	1000	40	$3.4 * 10^{-3}$
5	190	10	0	40	$1.3 * 10^{-4}$
6	190	30	0	40	$4.5 * 10^{-4}$
7	230	10	0	80	$2.8 * 10^{-4}$
8	230	30	0	80	$6.7 * 10^{-4}$
9	190	10	3000	80	$5.0 * 10^{-3}$
10	190	30	3000	80	$5.8 * 10^{-3}$
11	230	10	3000	80	$7.1 * 10^{-3}$
12	230	30	3000	80	$1.1 * 10^{-2}$



Effect Test

Sum of Squares	F Ratio	DF	Prob>F
0.00000705	3.7894	1	0.0926

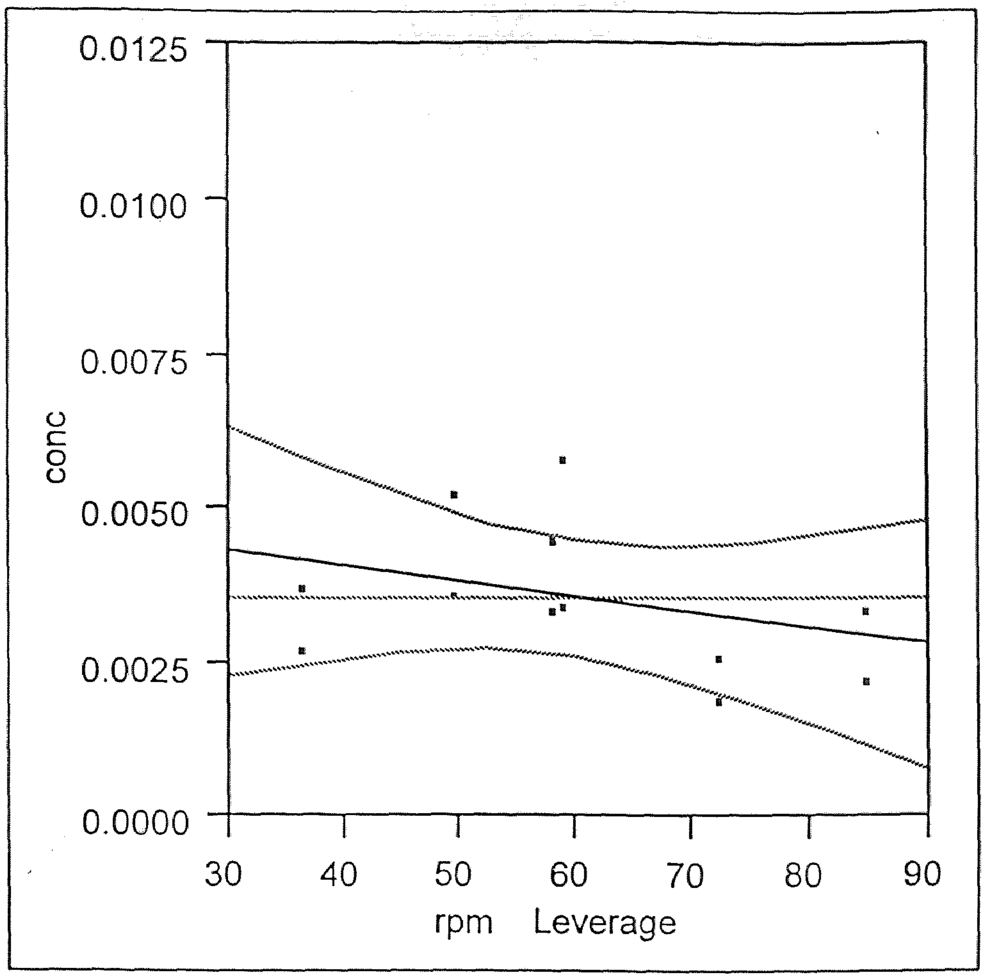
Figure 7 Effect of temperature on concentration of hydroperoxide groups (temperature vs. concentration in mole/kg)



Effect Test

Sum of Squares	F Ratio	DF	Prob>F
0.00000684	3.6775	1	0.0967

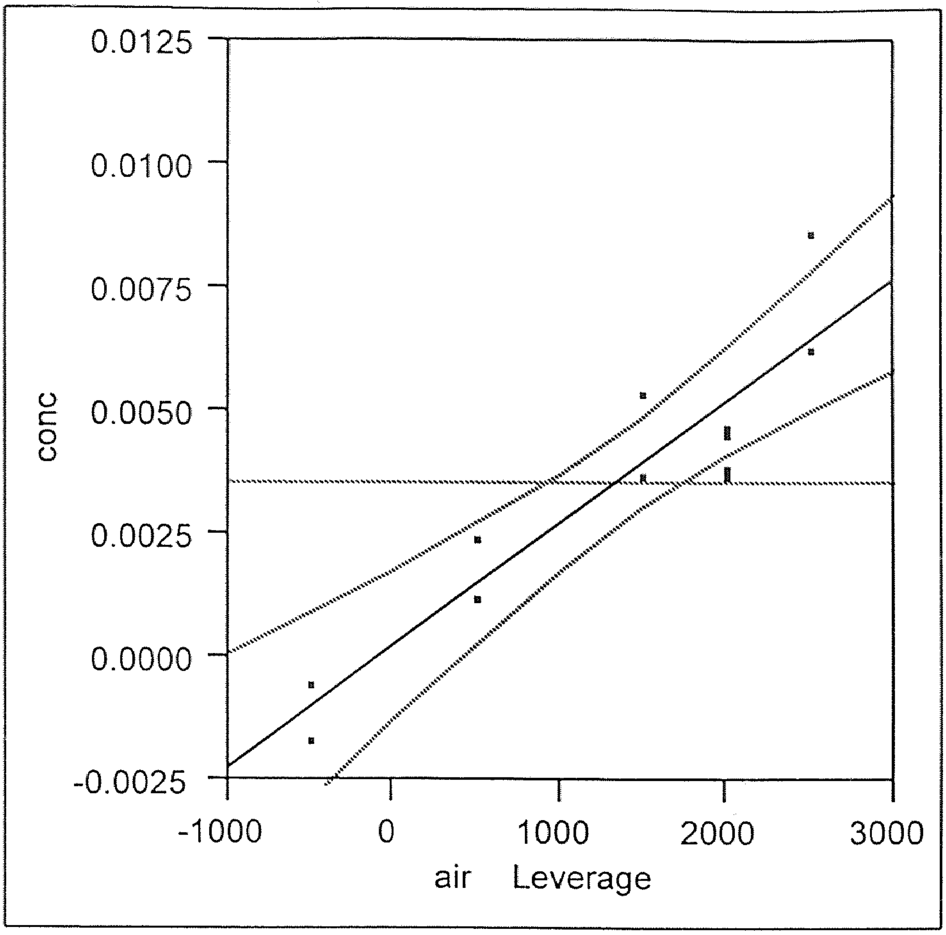
Figure 8 Effect of time on concentration of hydroperoxide groups (mixing time vs. concentration in mole/kg)



Effect Test

Sum of Squares	F Ratio	DF	Prob>F
0.00000193	1.0403	1	0.3417

Figure 9 Effect of rotor RPM on concentration of hydroperoxide groups (RPM vs. concentration in mole/kg)



Effect Test

Sum of Squares	F Ratio	DF	Prob>F
0.00007734	41.5815	1	0.0004

Figure 10 Effect of air flow rate on concentration of hydroperoxide groups
(air flow rate vs. concentration in mole/kg)

Table 3 Melt viscosity data of batch mixing experiments

					Melt viscosity (poise)				
Expt. No.	Mixing temp. (deg. C)	Mixing time (mins)	Air flow rate (scc/min)	Rotor speed (RPM)	Shear rate (sec^{-1})				
					11	54	272	1360	5441
PD 6501					11900	5742	2373	873	344
1	190	10	1000	40	7630	4320	1783	610	258
2	190	30	1000	40	1912	1438	1228	420	125
3	230	10	1000	40	5723	2919	1347	521	214
4	230	30	1000	40	2194	1297	709	333	148
5	190	10	0	40	4666	3074	1658	542	278
6	190	30	0	40	2141	1529	1345	480	210
7	230	10	0	80	1711	1267	991	398	148
8	230	30	0	80	1529	948	774	351	120
9	190	10	3000	80	2509	1210	998	482	207
10	190	30	3000	80	1882	887	765	455	156
11	230	10	3000	80	1606	1086	654	302	132
12	230	30	3000	80	1147	760	468	227	107

Test Temperature 230°C

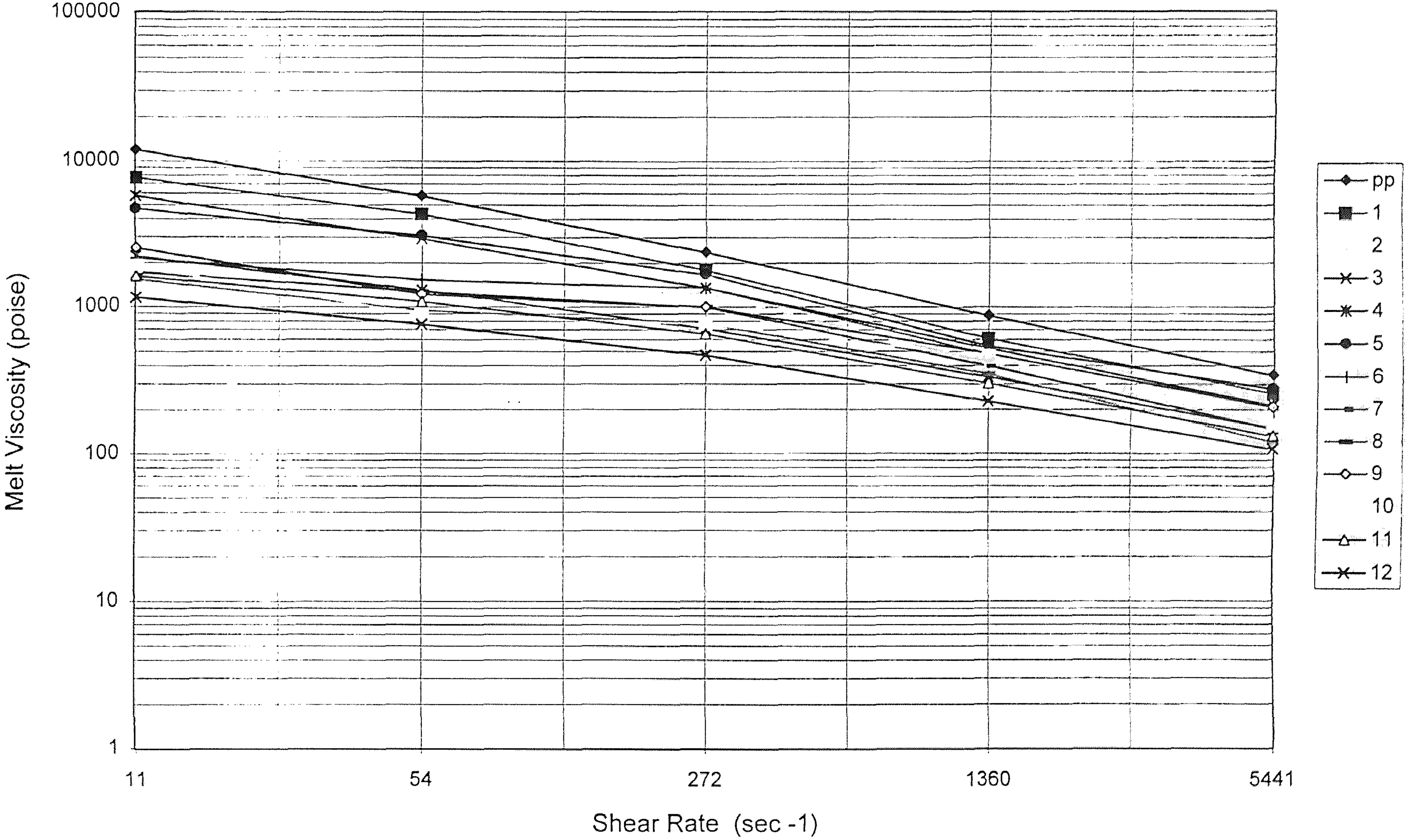
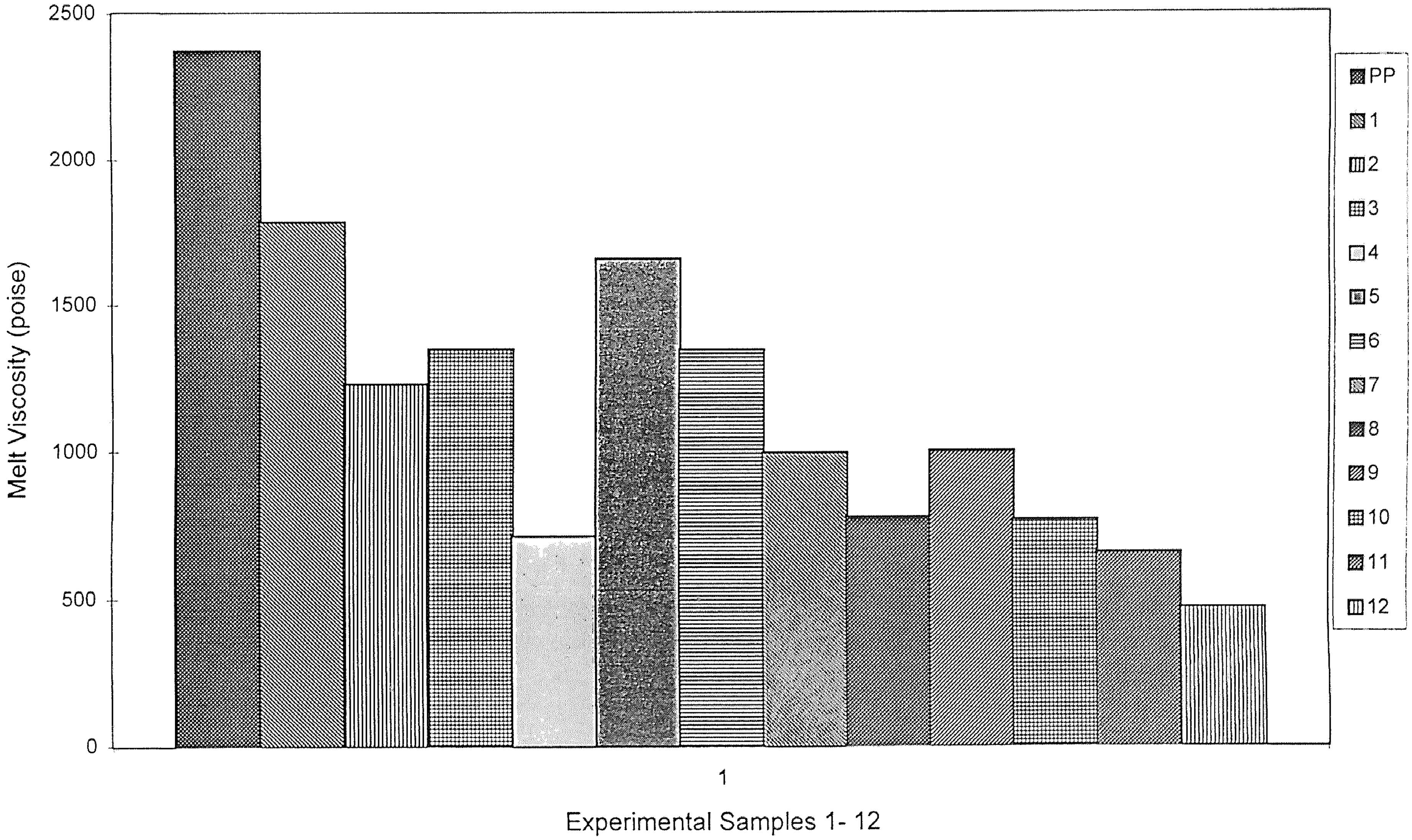


Figure 11 Melt viscosity vs shear rate



Test temperature : 230 °C

Shear Rate : 272 sec^{-1}

Figure 12 Melt viscosity at Constant shear rate

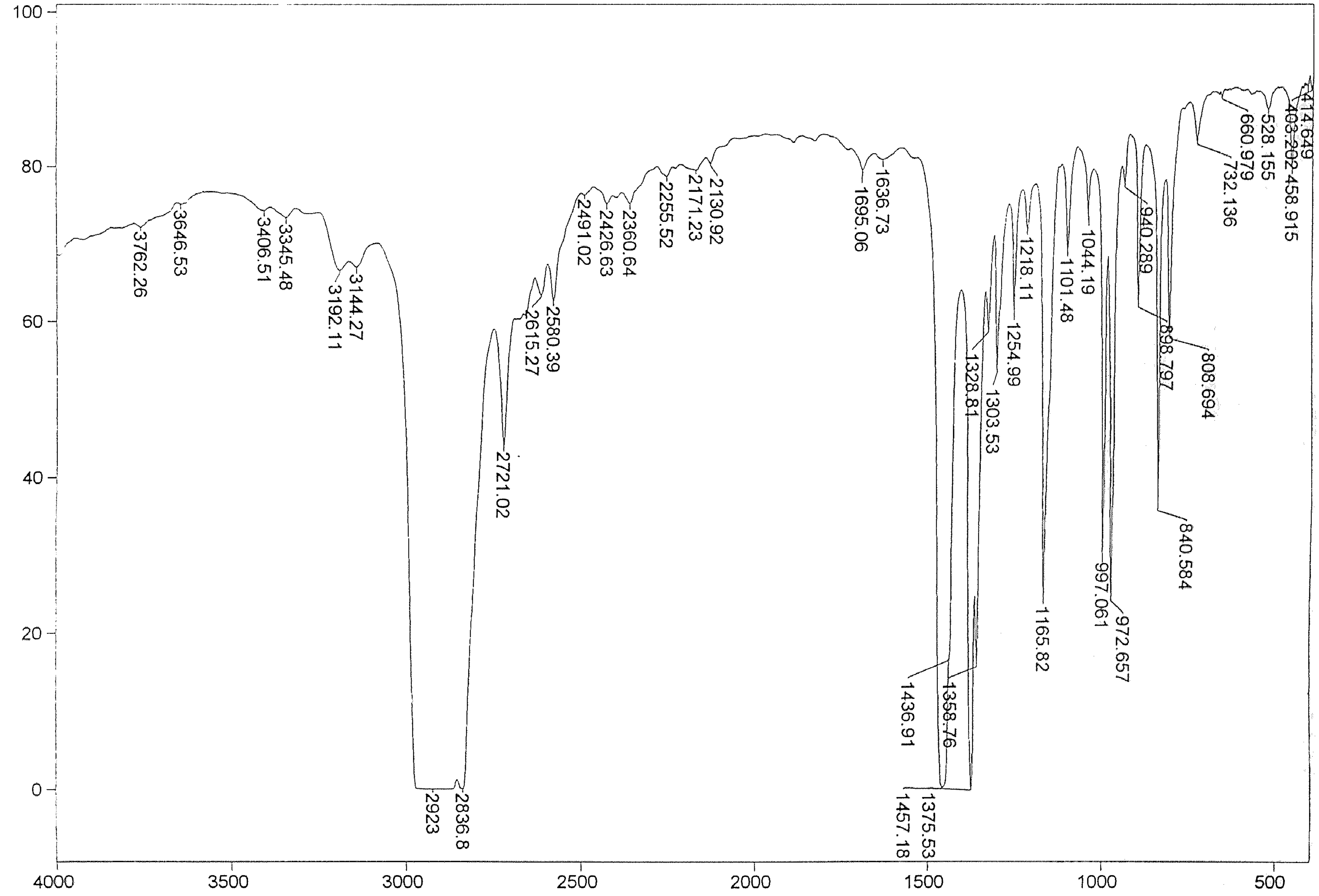


Figure 13 FTIR spectrum of unreacted polypropylene

nsmittance / Wavenumber (cm-1) Number of Scans= 25 Apodization:

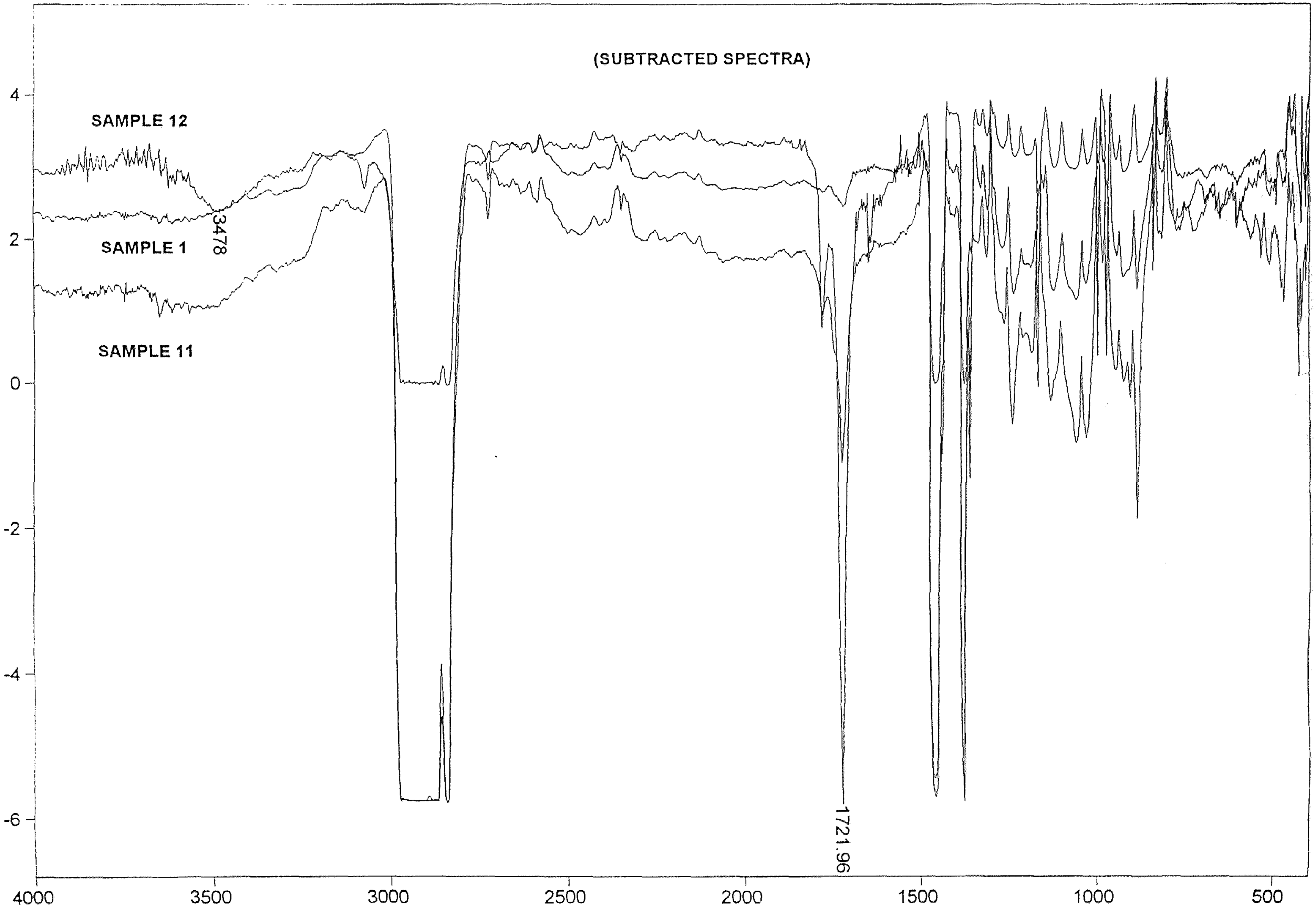


Figure 14 FTIR subtracted spectra of reacted samples from batch mixing

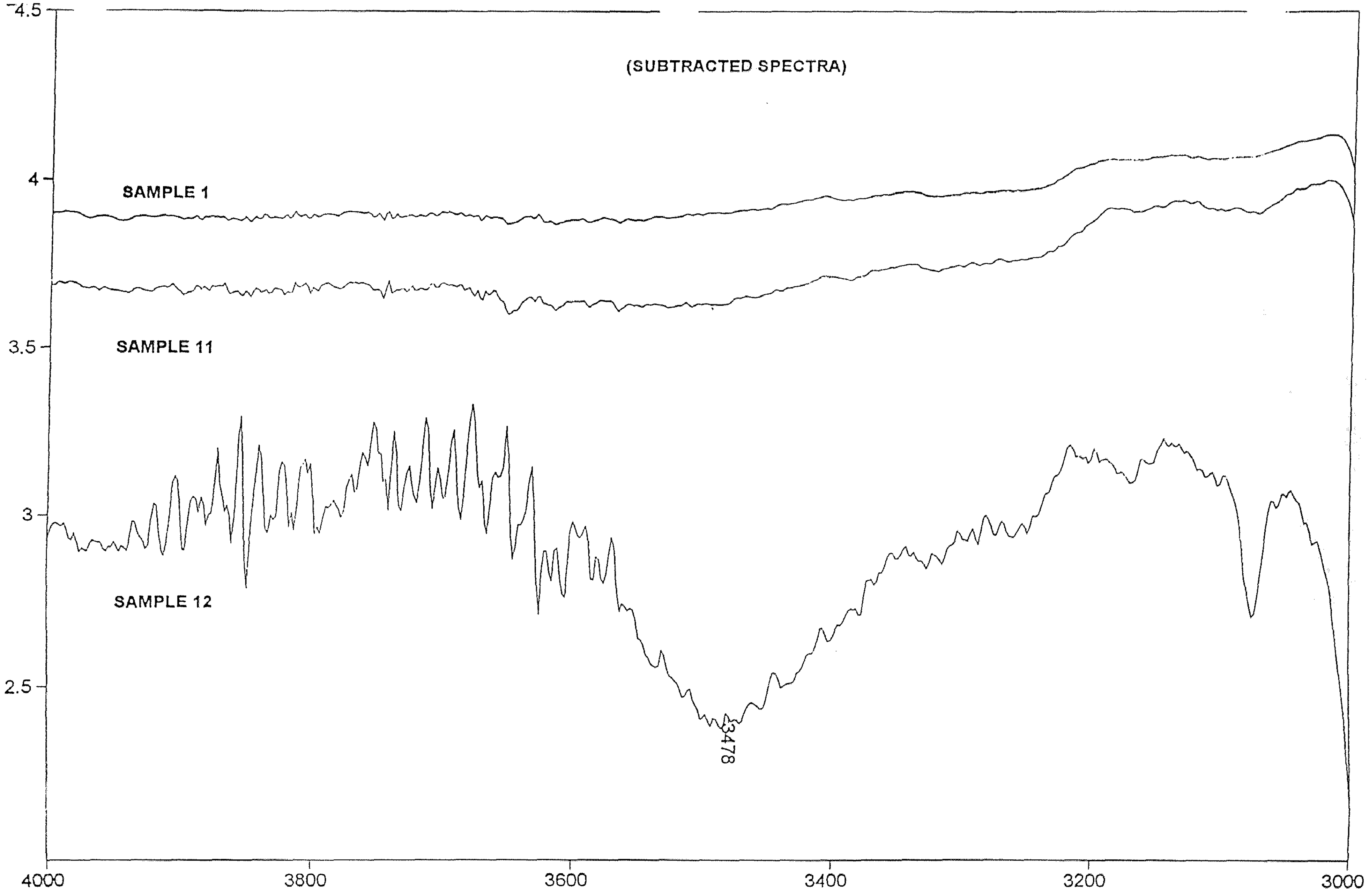


Figure 14a FTIR subtracted spectra (4000-3000cm^{-1}) of reacted samples

nittance / Wavenumber (cm-1)

Number of Scans= 25 Apodization=

4.2 Reactive Extrusion Studies

4.2.1 Effect of Processing Parameters on the Hydroperoxide Concentration

Table 4 gives the results on the concentration of hydroperoxide groups for each extrusion run. Figure 15 shows the influence of melt temperature on the concentration. The feed rate, screw speed and air pressure were kept constant. The results show that, under processing conditions, involving melt temperatures from 220-230°C, the concentration of hydroperoxide groups was highest, as high as 0.09 mole/kg at 225°C. This value is still lower than values (0.6 mole/kg) obtained through high energy intensive γ- irradiation (Ao, 1993).

Experiments were carried out by varying the air pressure while keeping melt temperature constant. The effect of air pressure on the concentration is shown in Table 4. As the air pressure is increased from 400 to 600 psi, the concentration tends to decrease. This could be due to breaking up of the polymer molecule into low molecular weight fractions, so much so that only a few reaction sites are available for hydroperoxidation. This can be further supported from data of Table 5, which give the melt viscosity of these samples tested at a temperature of 180°C and constant shear rate (lower test temperature of 180°C was chosen due to the expected low viscosity of the samples). Samples run at high air pressures, showed liquid like flow in the capillary rheometer, which made impossible to measure their melt visosity.

4.2.2 FTIR Analysis

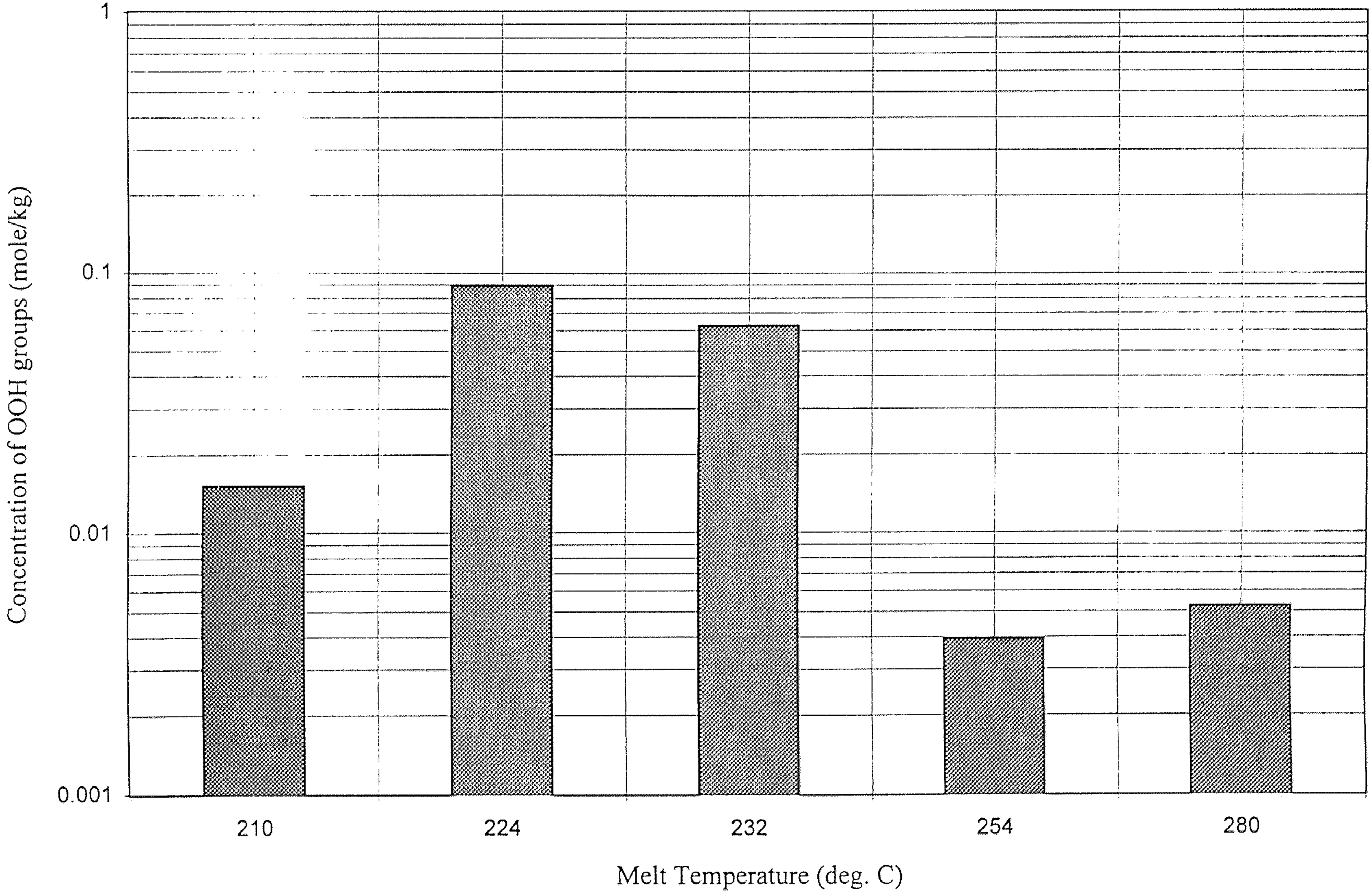
The oxidation of polypropylene during batch mixing and reactive extrusion causes a build-up of polypropylene hydroperoxides. This is observed from the iodometric results.

However, a satisfactory correlation between iodometric results and the FTIR analysis could not be achieved. This could be due to the offline measurement adopted for IR analysis. During compression molding, which involves high pressure and temperature, some of the hydroperoxide groups may decompose due to their poor stability at high temperature. However, additional peaks were observed in the region 3600-3690 cm^{-1} in Figure 18, which is the subtracted spectrum of Run 6, which may be associated to alcoholic OH groups, formed as the decomposition products of hydroperoxides. Figure 16 shows the spectrum of experimental sample from Run 2, which gave maximum concentration by iodometric analysis. The broad peak centered at 3478 cm^{-1} for hydroperoxide groups is quite evident. Figure 17 shows the combined subtracted spectra of certain reactive extrusion samples.

Regardless of the processing conditions, all spectra showed strong peaks at 1715 and 1778 cm^{-1} associated with the accumulation of carbonyl groups. This can be clearly seen in Figures 15 and 16. In general, hydroperoxides are unstable and may undergo thermal, photochemical, or catalytic decomposition to generate free radicals which propagate the oxidative process and ultimately lead to the formation of alcohol and /or carbonyl groups in the polymer . In one particular case, the decomposition of hydroperoxides in addition to the formation of OH groups, it also results in a scission leading to the formation of carbonyl groups.

Table 4 Concentration of hydroperoxide groups from reactive extrusion experiments

Run	zone	zone	zone	zone	zone	zone	zone	zone	zone	zone	Melt	Die	Screw	Air	Concentration
No.	1	2	3	4	5	6	7	8	9	10	Temp.	Temp.	RPM	Pressure	of OOH
											(^oC)	(^oC)		(psi)	mole/kg
1	149	160	188	188	193	193	188	182	185	188	210	210	13	400	$1.5 * 10^{-2}$
2	149	160	199	199	199	199	193	193	196	199	224	225	13	400	$8.9 * 10^{-2}$
3	149	210	210	210	199	199	199	210	204	204	232	235	13	400	$6.2 * 10^{-2}$
4	149	210	210	216	210	210	210	216	221	224	254	260	13	400	$3.9 * 10^{-3}$
5	149	210	210	216	210	210	210	221	238	246	280	280	13	400	$5.2 * 10^{-3}$
6	149	210	210	216	210	210	210	216	221	224	254	280	13	500	$1.3 * 10^{-3}$
7	149	210	210	216	210	210	210	216	221	224	254	280	13	600	$1.6 * 10^{-3}$



Air Pressure : 400 psi
Screw Speed : 13
Feed Rate : 28

Figure 15 Effect of melt temperature on concentration of hydroperoxides

Table 5 Melt Viscosity Results of Reactive Extrusion Experiments

Run No.	Melt temp (deg. C)	Screw speed	Air pressure (psi)	Melt viscosity at constant shear rate (poise)
PD 6501	_	_	_	3873
1	210	13	400	885
2	224	13	400	148
3	232	13	400	122
4	254	13	400	103
5	280	13	400	*
6	254	13	500	*
7	254	13	600	*

* Could not be measured due to very low viscosity

Test Temperature 180 ° C
Shear Rate 272 sec^{-1}

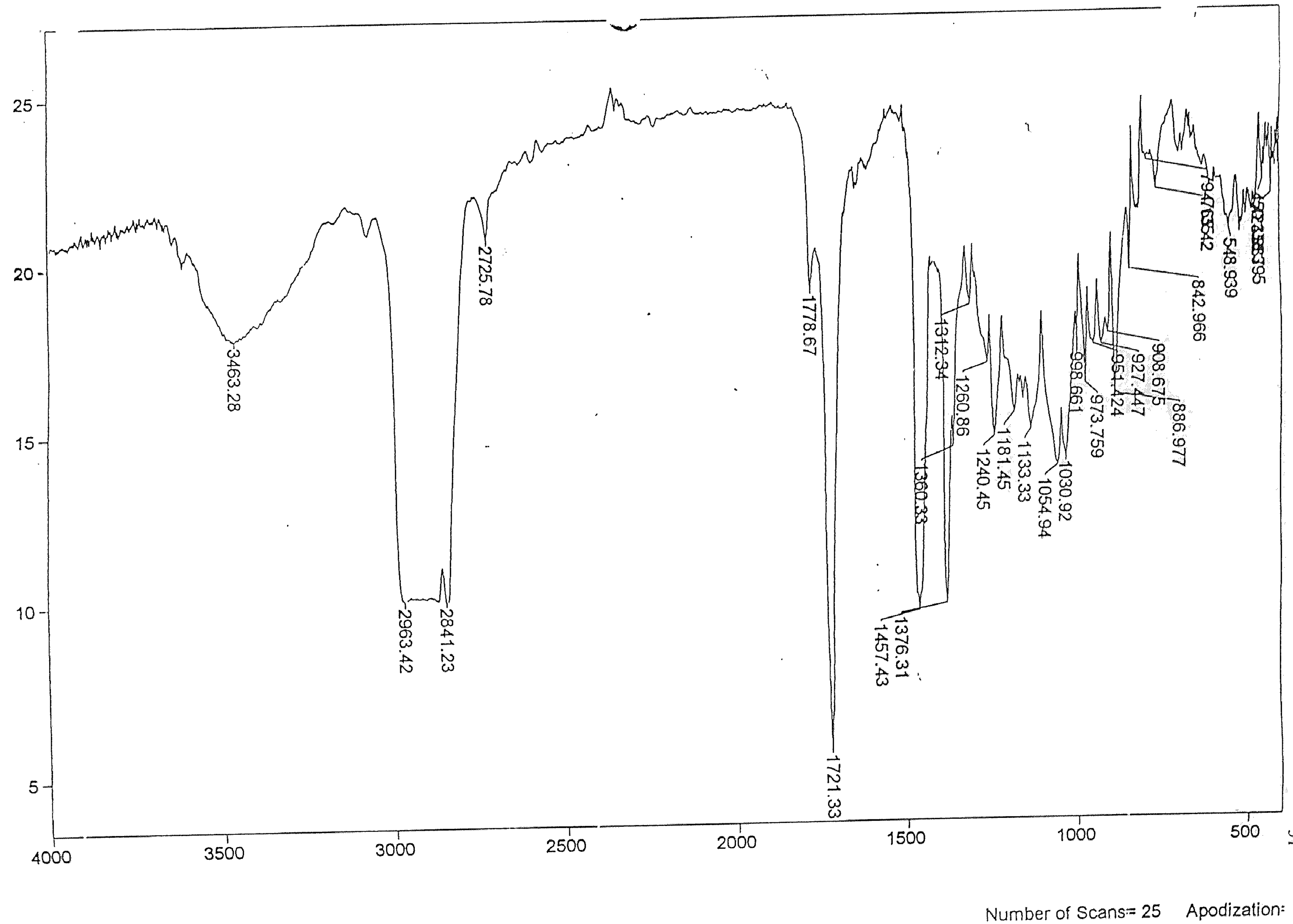


Figure 16 FTIR subtracted spectrum of run 2 sample from reactive extrusion

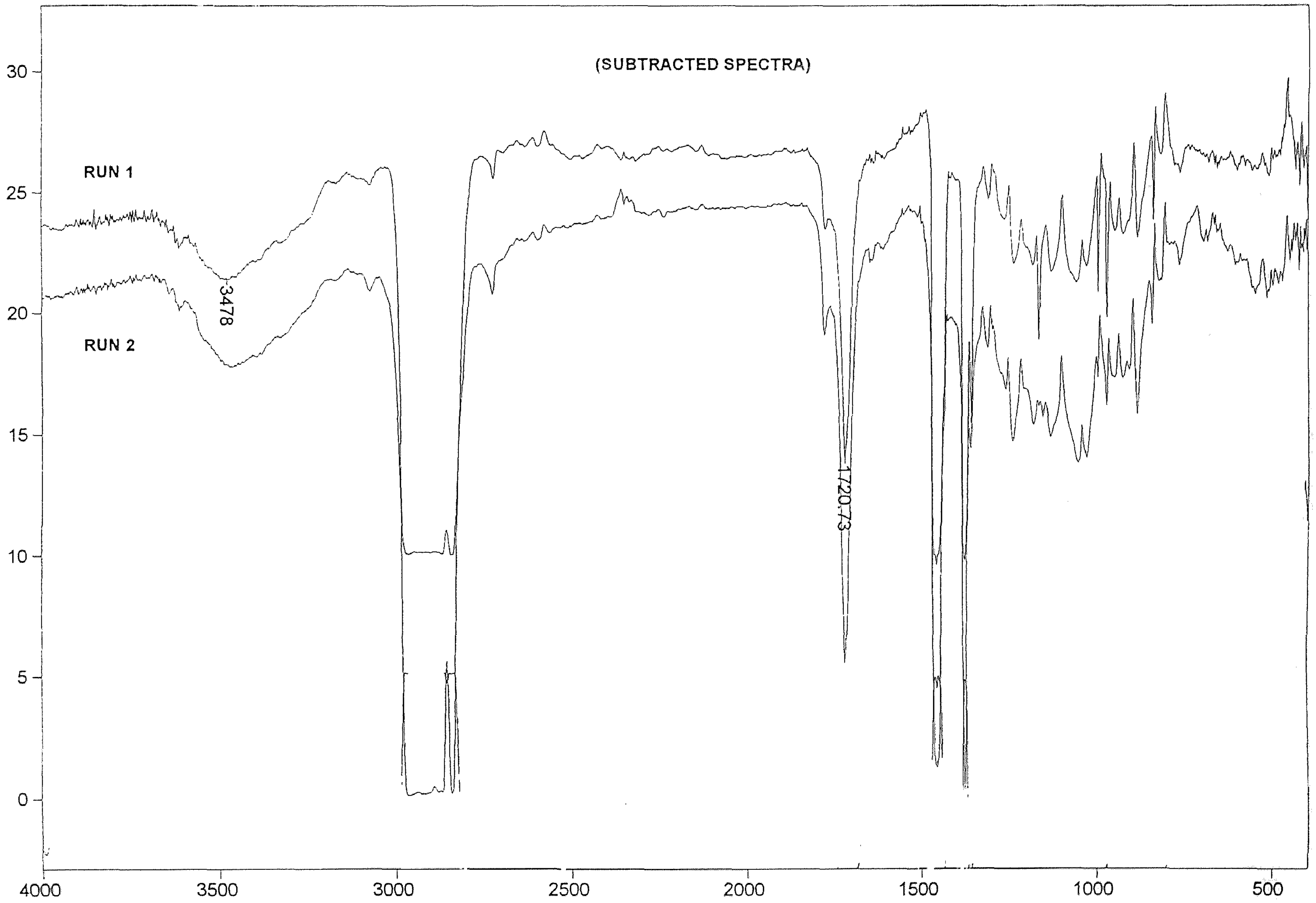


Figure 17 FTIR subtracted spectra of samples from reactive extrusion

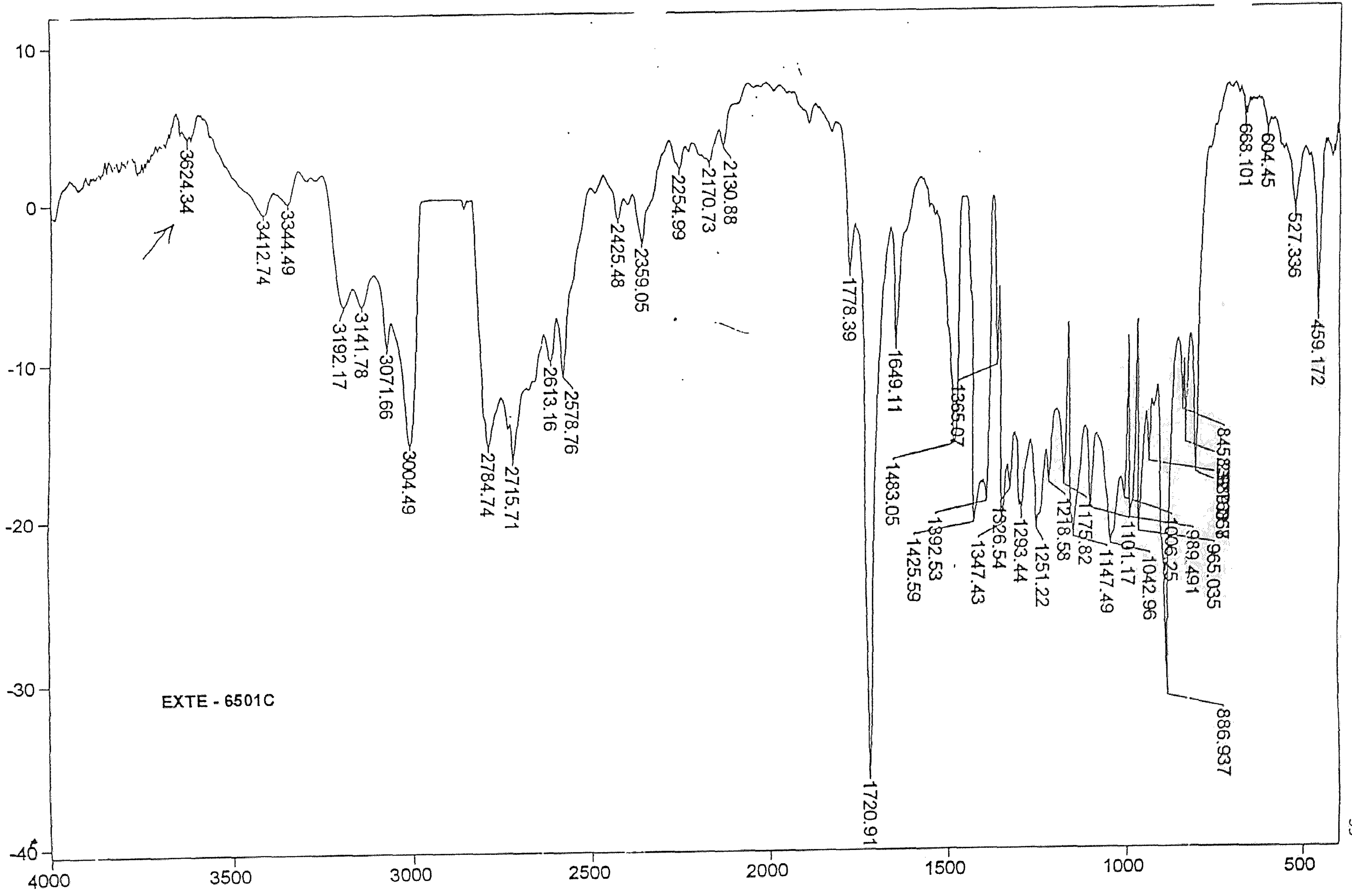


Figure 18 FTIR subtracted spectrum of run 6 from reactive extrusion

4.2.3 Preliminary Scrubbing Experiments

The polypropylene sample which had the highest concentration of hydroperoxide groups, produced through reactive extrusion was selected for preliminary scrubbing experiments, to study the oxidizing ability of hydroperoxidized polypropylene. From iodometric analysis, this sample has 0.089 mole of hydroperoxide groups per kg of polypropylene. The sample was in the form of a fabric with lot of soft fibers.

Preliminary attempts to study the scrubbing efficiency of this hydroperoxidized polymer sample were made. In one attempt, the sample was introduced to 60 cm length and 2.5 cm ID mild carbon steel tube . A schematic diagram of the apparatus is shown in Figure 19. The polymer sample was packed up to a length of 40 cm. The tube is then placed in a ATS series 3210 Furnace oven and heated to 120°C. A mixture of 1860 ppm of NO and N_2 was passed through the polymer at a rate of 1 liter/min. NO cylinder was supplied by Matheson gas Inc. NO was analyzed by a thermoelectron AR-10 chemoluminescent NO_x analyzer. The experiment was continued for one hour. The results showed no absorption of NO by the hydroperoxide groups of the polymer. However, Iodometric analysis of the sample taken after the experiment showed a 21% reduction in hydroperoxide groups from the original value.

A second attempt was made using a ACS glass model # 5820-107 chromatography column of length about 1.5 meters and 7.5 cm diameter. A schematic diagram of the scrubbing apparatus is shown in Figure 20. One liter of aqueous NaOH solution of 12. 7 pH was placed in the column. This was done to wet the sample in order to facilitate better diffusion of NO gas into the sample. A known weight of polymer sample was placed in a muslin bag and introduced into the column. The column has a heating coil and a thermocouple to raise and measure the temperature. The temperature was increased from ambient to 95°C. NO gas was bubbled into the column at a fixed flow rate of one liter per minute for 2 hours. No absorption of NO by hydroperoxide groups was observed. Iodometric analysis of sample taken out after this experiment showed very little presence of hydroperoxide (OOH) groups, which may have probably decomposed under continuous exposure to high temperature.

It is not clear as yet, if this apparent lack of reactivity was due to various parameters such as insufficient surface area that would affect the reaction rate, molecular orientation that would affect the penetration of NO, conversion of OOH to OH groups, excessive reaction of carbonyl groups or due to the inappropriate scrubbing experimental conditions. Furthermore, it is known (Perlmutter, et al., 1993), that the reaction between NO and -OOH is sensitive to variables such as sample mass, flow rate, temperature, time and level of hydroperoxides. These parameters were not investigated in the limited experiments that were carried out in this work.

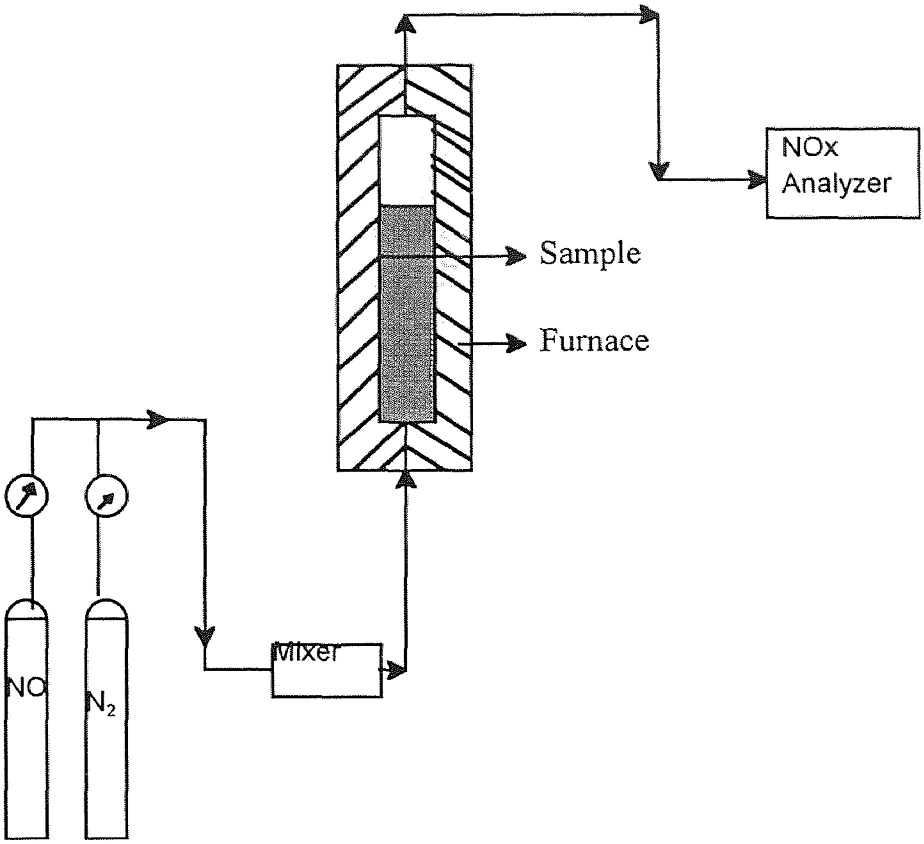


Figure 19 A Schematic diagram of gas scrubbing apparatus

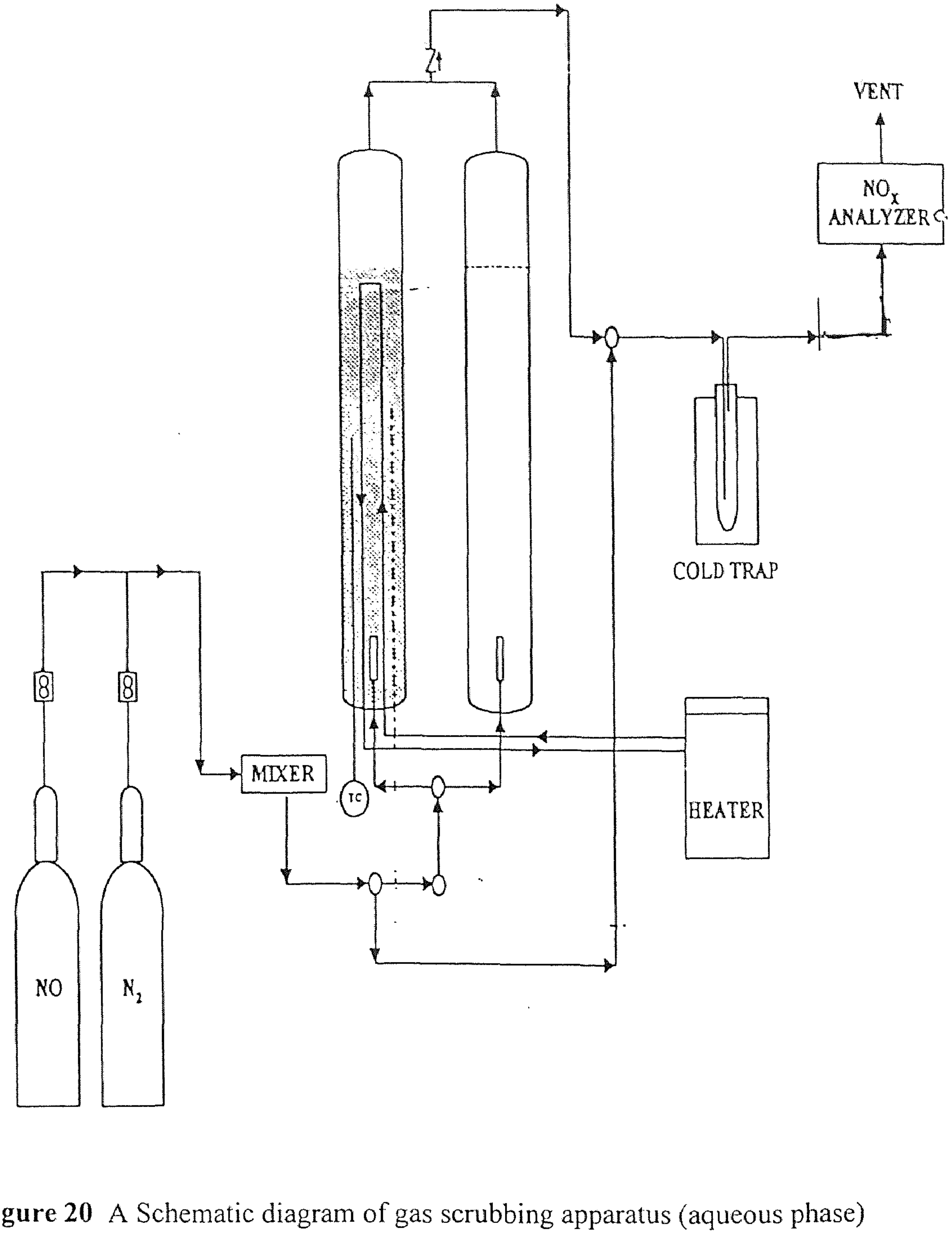


Figure 20 A Schematic diagram of gas scrubbing apparatus (aqueous phase)

CHAPTER 5

CONCLUSIONS AND RECOMMEDATIONS

The following are the main conclusions derived from the batch mixing studies:

1. The concentration of hydroperoxide groups can be maximized by increasing mixing temperature and mixing time. However, this may lead to molecular weight changes causing reduction in viscosity. This may affect the integrity of the polymer and its strength.
2. By increasing the air flow rate, the concentration of hydroperoxide groups increases. Also, the results obtained from this study indicate that air, which is readily available can be used in place of high energy intensive γ- irradiation method on solid films. However, the concentration of hydroperoxide groups may not be as high as that by γ- irradiation directly on polymer film or fibers.

The following are the main conclusions from the reactive extrusion studies.

1. It is possible in an extruder to produce polypropylene with hydroperoxide group concentration closer to that produced by irradiation. The highest concentration obtained is 0.089 mole/kg of PP, though, it is still lower than that achieved by irradiation (0.6 mole/kg). However, the maximum concentration which can be obtained from reactive extrusion still needs to be determined by conducting a larger number of experiments by varying process parameters.
2. Melt temperature does have an effect on the concentration of hydroperoxide groups. Concentration is maximum at an optimum melt temperature (220-230°C) below which

above which chances of producing higher concentration of hydroperoxides are minimum. Higher temperature may produce excess carbonyl groups through decomposition of hydroperoxides. Temperature lower than the optimum may not bring sufficient viscosity reduction of the polymer needed for thorough mixing of the air with the polymer melt.

3. Increasing the air pressure reduces the viscosity of the modified polymer drastically. Hence, a maximum air pressure of about 400 psi would be appropriate to increase the concentration of hydroperoxide groups without significant reduction in the molecular weight.

4. Offline FTIR analysis may not give a good correlation with the concentration of hydroperoxide groups as determined from iodometric method. Since the hydroperoxidized PP is again subjected to another heat history in the compression molding process, some of the hydroperoxide groups may decompose. This may lead to negligible absorption in the region 3400 to 3600 cm^{-1} in the IR spectrum. It is recommended to detect the formation of hydroperoxide groups through online IR spectrometer which is attached to the extruder.

5. A suitable scrubbing system needs to be developed to maximize the residence time of NO in the fabric sample obtained through reactive extrusion. It is recommended that the effect of variables such as sample mass, flow rate, temperature on NO conversion are studied by conducting a larger number of experiments and investigate the potential of the prepared material.

CHAPTER 6

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