

Surface Modification of Polyolefins for Hydrophilicity and Bondability: Ozonization and Grafting Hydrophilic Monomers on Ozonized Polyolefins

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Synopsis

Ozonization is a very efficient, economical, and potentially practical method to modify polypropylene (PP) as well as polyethylene (PE) surfaces. Carbonyl, carboxyl, and hydroperoxide groups can be very conveniently generated by reacting these polymers with ozone. In the case of fibers and powders, surface treatment with ozone in an aqueous medium offers advantages: water can be used as a carrier in commercial processes, and since water enhances generation of hydroperoxide it may be used for potential reaction purposes. The extent of reaction of polyolefins with ozone depends on the extent of agitation of the slurry, the slurry temperature, solid consistency, and ozone concentration in the gas. Within the limits of the present work, the ozone uptake of fibers increases linearly with time. The carbonyl (%) and carboxyl (meq/g) contents are approximately 0.08 and 0.04 times the ozone uptake (%) of the PP fibers. Hydroperoxide generation is found optimum at a slurry temperature of 60–80°C, and the amount of active oxygen (%) at 60°C is about 0.1 times the ozone uptake (%) of the PP pulp. Spurred polypropylene fibers show two different kinds of crystallinity in X-ray diffraction analysis, namely monoclinic and smectic. The type of fibers produced depends on the spurting conditions. The monoclinic fibers have a mostly rodlike structure while the smectic fibers have a ribbonlike appearance. The fiber types give different sheet properties in blends with cellulose, and show different grafting rate behavior. The smectic fibers provide relatively stronger sheets, and graft acrylamide monomers at a higher rate. Ozonization degrades the chain length of polyolefins as shown by intrinsic viscosity of treated material. It is possible to have an additive in the polymer to reduce degradation rate of the chain length. Further work in this area is needed, however, for better understanding of the reaction, and to achieve complete control over the degradation process to make the product commercially viable. Effects of some additives on ozone reaction to enhance the generation of functional groups also opens an area for further study. Handsheets were prepared with blends of 30% ozonized polypropylene pulp and 70% wood pulp. About 90% of the strength of a 100% wood pulp sheet can be achieved by either grafting acrylamide (25–30%) on the polypropylene pulp, or by disk refining with 5% of a bonding resin. Polypropylene pulp significantly raises the bulk, opacity, and brightness of the sheets. High levels of acrylamide grafted to pulp reduce opacity and caliper of sheets. Grafting with a redox system of hydrophilic monomers, such as acrylamide, to ozonized pulps containing a reasonable amount of hydroperoxide (0.1–0.5% active oxygen) also provides an effective method for surface modification. The surface of both ozonized and grafted pulps becomes highly hydrophilic. Polyethylene, in the limited results obtained in this work, behaves very similarly to polypropylene. The activation energy of ozone reaction with both polypropylene and polyethylene is approximately 7 kcal/mol.

INTRODUCTION

Polypropylene and polyethylene are basically nonpolar polymeric materials. They are chemically nonreactive, and have remarkable mechanical and thermal properties; but their surfaces are hydrophobic and not chemically bondable to

TABLE I
 Paper Sheet Properties^a

Crystallinity of pp-pulp	PP-pulp surface area (m ² /g)	Caliper (mil)	Bonding resin S2448 (% pp-pulp)	Mullen bust (% control)	Tensile (% control)	Brightness (%)	Opacity (%)
Predominantly monoclinic	19	9.6	6.5	48	57	87	83
Predominantly smectic	44	8.0	6.4	88	89	89	91
100% wood pulp (control)	—	5.8	none	33.8 (psi)	7814.8 (psi)	82	76

^a 70/30 wood pulp/ozonized polypropylene pulp in 40 lb basis wt hand sheet.

other materials. This limits their practical use. Extensive work to develop practical and economical methods for surface modification of polypropylene and polyethylene has been carried out by several workers.¹⁻⁸ For adhesion, bonding, and wettability, use of corona-discharge treatment of the surface of these polyolefins with activated gas plasma or glow discharge has been actively studied.⁴⁻⁸ Surface oxidation by treating with acids had also been attempted. None of these methods has yet attained desirable success because of either technical or economical problems.

Use of ozone in surface-treating polyolefins also has received some attention.⁹⁻¹³ However, not enough basic and fundamental information has been generated to understand the mechanism of ozone reaction and its control so that the process can receive adequate attention for a commercial success. It is hoped that the results presented in this work will contribute toward this objective.

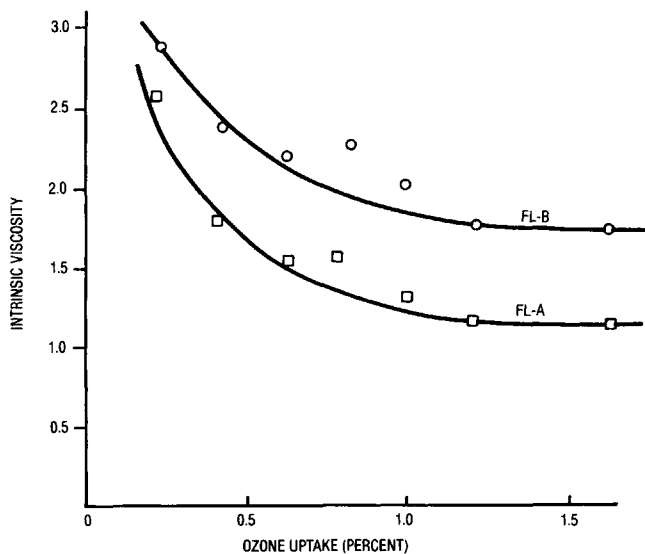


Fig. 1. Intrinsic viscosity of polypropylene flake at various levels of ozone treatment. Flake FL-A and FL-B, which is FL-A-treated with a phenolic antioxidant stabilizer, are Hercules products.

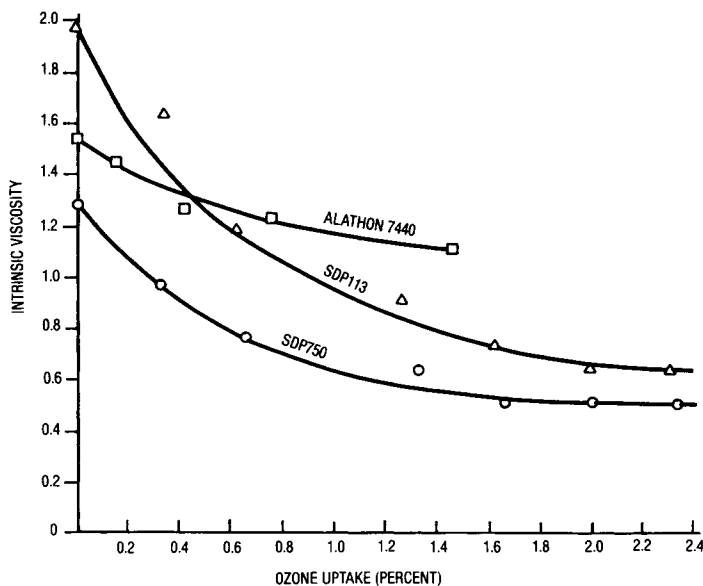


Fig. 2. Intrinsic viscosity of polyethylene flake at various levels of ozone treatment. Alathon 7440 (DuPont) SPD-113 and SPD-750 (ARCO) have different molecular weights represented by intrinsic viscosity values.

Possible Mechanism of Ozonization

There has been a substantial amount of discussion about the possible mechanism of ozone reaction with saturated hydrocarbons.¹⁴⁻¹⁶ Reaction capability of ozone has been suggested¹⁷⁻¹⁹ through possible thermal or photochemical decomposition products.

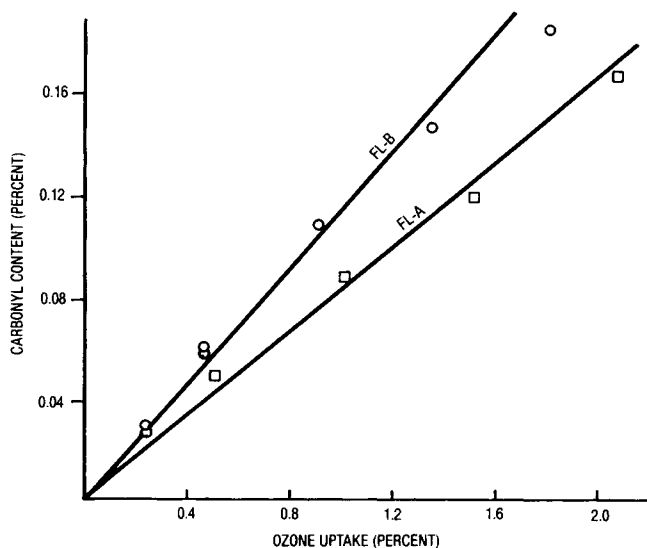


Fig. 3. Carbonyl contents of ozonized stabilized and unstabilized polypropylene flake, FL-B and FL-A respectively.

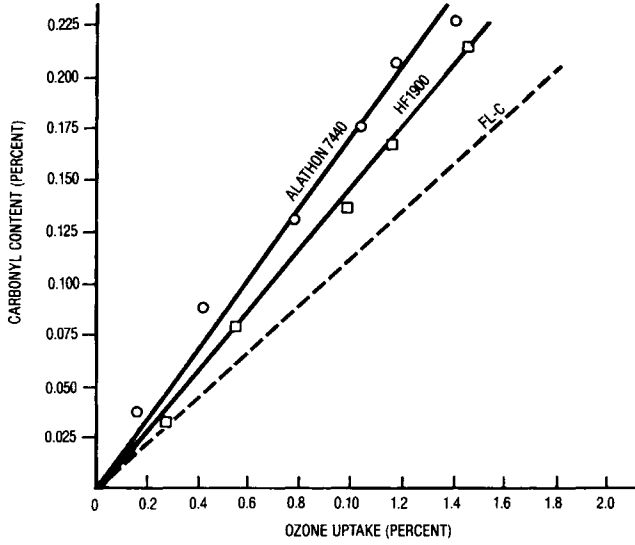
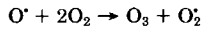
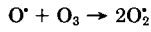
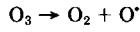


Fig. 4. Carbonyl contents of ozonized polyethylene flake. Similar data for FL-C, a polypropylene flake provide a reasonable comparison.



However, the following is considered to be a reasonable guideline in characterizing the reaction of ozone with a hydrocarbon material,

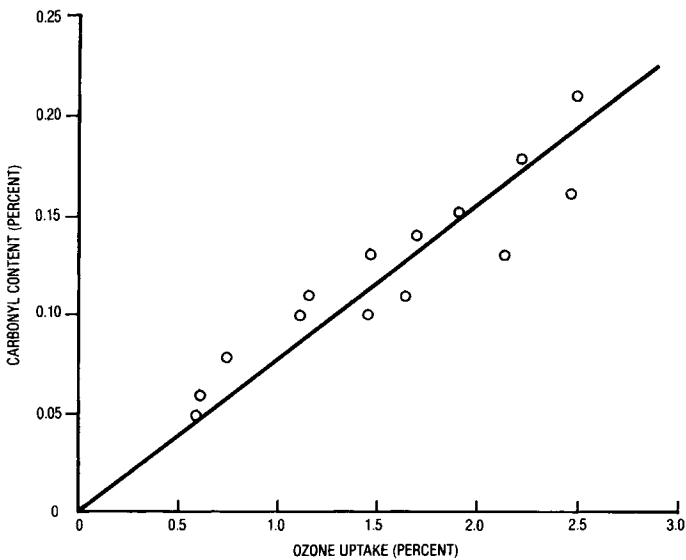


Fig. 5. Carbonyl contents of ozonized Pulpex polypropylene pulp at various levels of treatment.

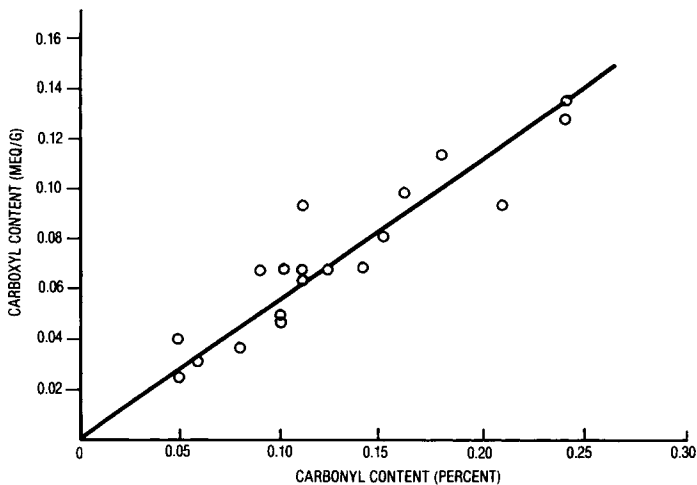
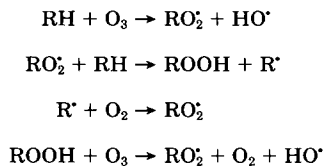


Fig. 6. Carboxyl contents of ozonized Pulpex polypropylene pulp at various levels of treatment.



The zwitterion-carbonyl scheme through the Criegee mechanism has been suggested to explain the reaction of ozone with alkenes.²⁰ Generation of carbonyl and hydroperoxide in the amounts observed in this work can be explained on

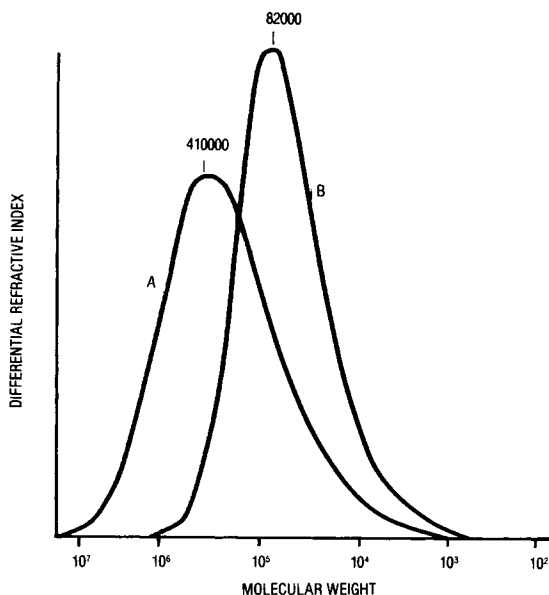


Fig. 7. GPC analysis of untreated (A) and ozone treated (B) polypropylene pulp.

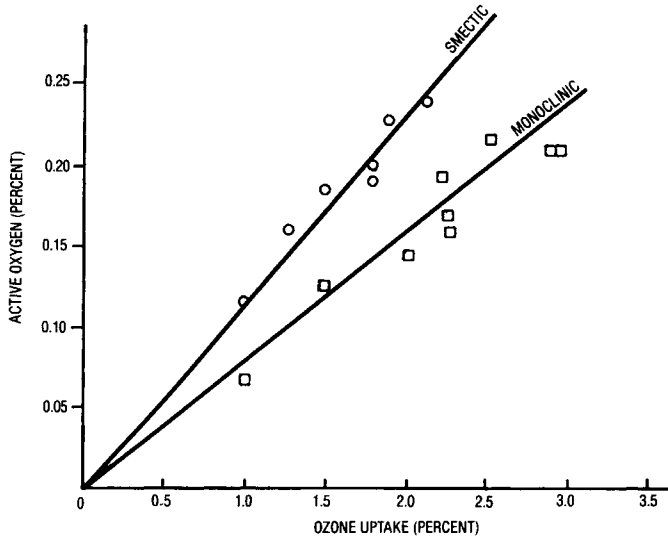


Fig. 8. Generation of active oxygen as a function of ozone uptake of polypropylene pulp.

the basis of the reaction steps above, but generation of the carboxyl groups in the amount observed is not easily understood. Kefeli et al.¹⁰ have suggested a method of carboxyl group formation.

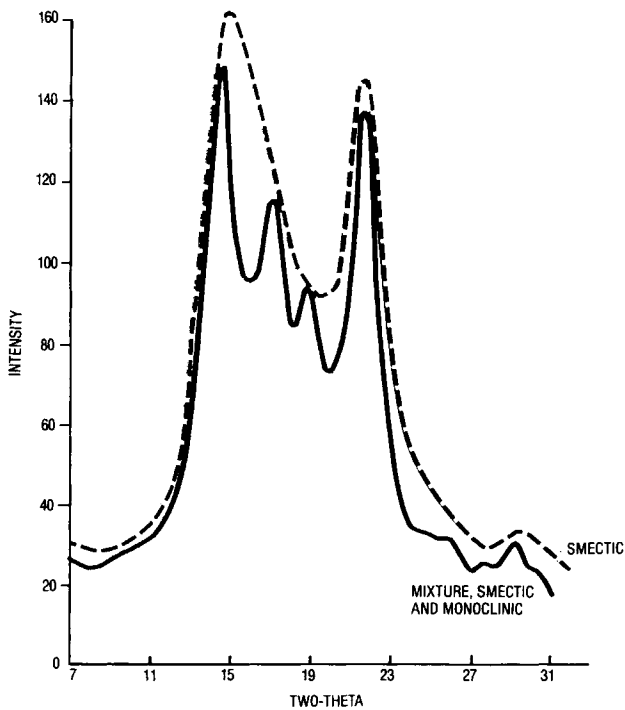


Fig. 9. X-ray diffraction pattern of polypropylene having predominantly smectic or mixture of smectic and monoclinic crystalline character.

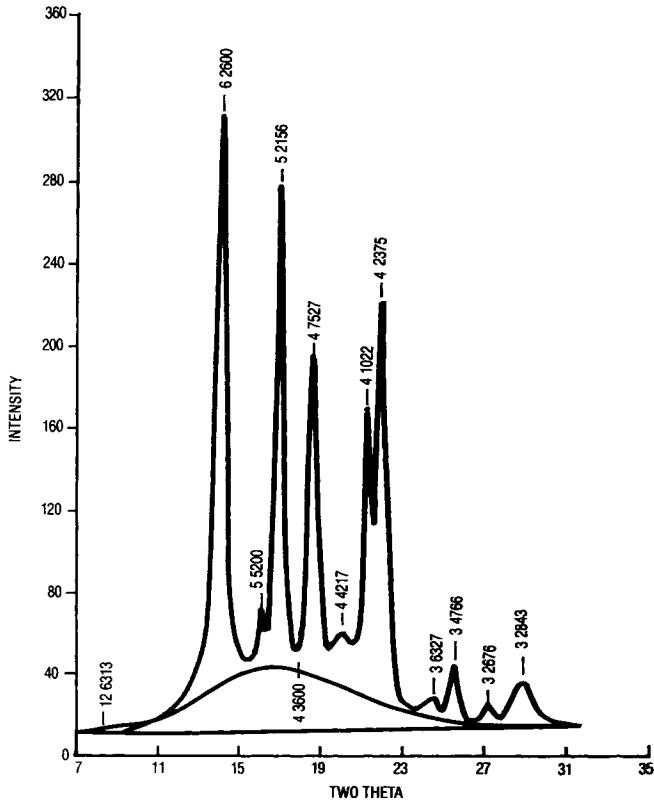
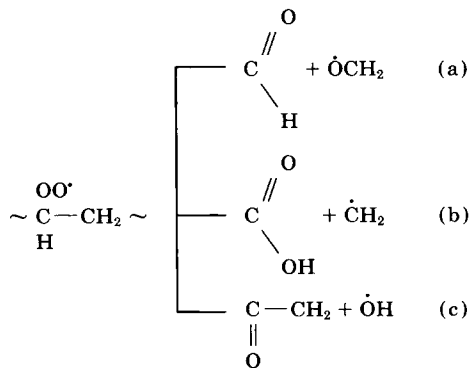


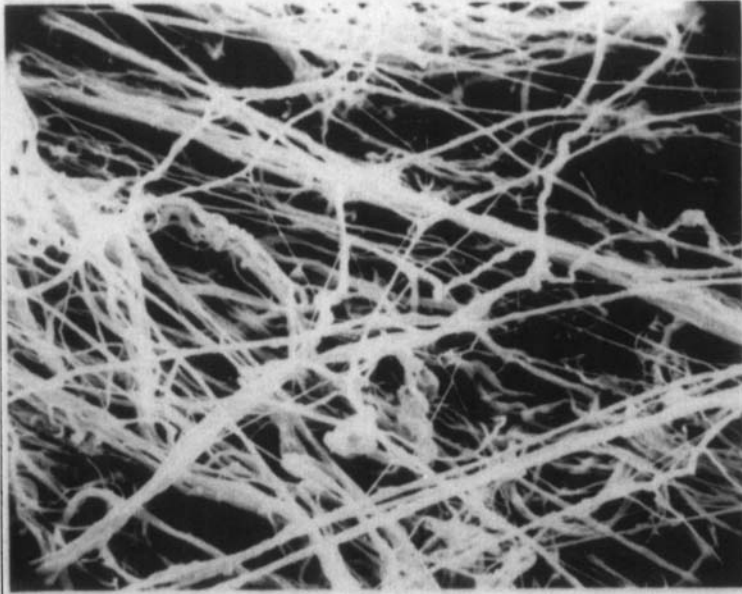
Fig. 10. X-ray diffraction pattern of polypropylene having predominantly monoclinic crystalline character.



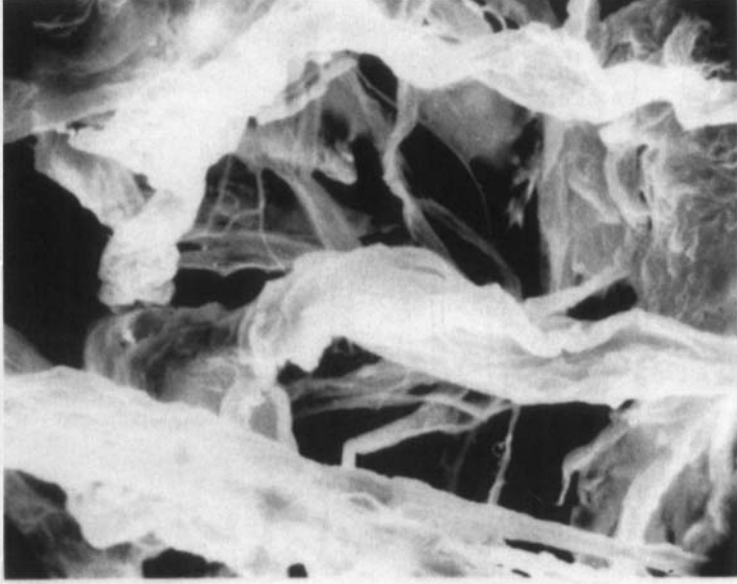
Reaction (a) is well recognized. Each ozone molecule absorbed generates a single peroxide radical and its decomposition leads to macromolecular degradation. A large RO₂ fraction is, however, decomposed by mechanism (c).

Pryor¹⁴ suggested that an electron transfer is one of the simplest radical-producing reactions. If O₂⁻ is produced, it might explain the enhancement of hydroperoxide generation by the presence of water through the reaction products of O₃ and water. In general, the triplets are expected to be efficient in extracting

SEM:
MAG: 240X



Surface Area - 4 m²/g
Crystallinity: Monocline



Surface Area - 19 m²/g
Crystallinity: Smectic

hydrogen from polyolefin and in introducing hydroperoxide in the presence of oxygen.

EXPERIMENTAL

Ozonization in Aqueous Medium: Laboratory Scale

The reaction was carried out in a 12-L glass flask fitted with stainless steel inlet and outlet tubes for gas flow, a stirrer, and a thermometer. The slurry containing 0.5–2.5% by weight solid in the case of polyolefin fibers and 10–20% in the case of flake powder, was well stirred during reaction while passing a regulated amount of ozone through the inlet tube placed at the bottom of the flask. A Welsbach laboratory ozonator, Model T-23, was used to generate ozone from oxygen. The flow rate of the gas was usually maintained at 0.06 CFM and ozone generation was controlled between 0.01 to 0.04 g/min by regulating the voltage applied. The temperature of the slurry was elevated when necessary by means of a heating mantle.

Ozone Uptake

The amount of ozone in the gas was determined by passing it through an excess of potassium iodide solution and then titrating the solution with about 0.1 *N* sodium thiosulfate solution under acid conditions. The reaction was run in a closed system and the outlet gas was passed through an excess amount of potassium iodide solution during the whole reaction time. Titration of an aliquot part of the solution provided the amount of ozone that escaped through the outlet gas during the reaction. The difference in the amounts of ozone in and out is considered as the ozone uptake of the fibers or flake.

Carbonyl Content

An infrared method was developed to measure the estimated weight percentage of carbonyl in ozonized fibers or flakes. The samples were pressed into 10 mil films with a 25-ton (Model M) Carver press at 190°C. The percent carbonyl was calculated from the height of the carbonyl band (1710–1720 cm^{-1}) using Beer's law. An average absorptivity for C=O was determined from a series of standards, such as stearic acid, in solution.

Carboxyl Content

For analysis of carboxyl content, a sample of treated flake or fiber weighed to the nearest 0.0001 g, was dissolved in picoline, heated to reflux and then titrated with sodium laurylate in *O*-dichlorobenzene using a potentiometric titrator.

Active Oxygen

The active oxygen content was determined by refluxing the treated material with isopropyl alcohol and acetic acid solution in the presence of a known amount of sodium iodide, then titrating with sodium thiosulfate of known normality.

Materials

Flake—Polyolefins are marketed as 200–400 μm size powder. The difference in molecular size is in general represented by the intrinsic viscosity (IV) value of the material. The IV values for polypropylene flake FL-A and FL-C are 5.3 and 2.8 dL/g. FL-B is actually FL-A stabilized with a phenolic type antioxidant; FL-C is also stabilized with the same antioxidant. Alathon 7440 (DuPont), SPD-113 and SPD-750 (ARCO) are polyethylene powder having IV values of 1.6, 2.0, and 1.3 dL/g respectively.

Pulpex Polypropylene Pulp—Polypropylene synthetic pulps are prepared by spurting with flake from solvents such as methylene chloride, pentane or heptane in an autoclave at various conditions of temperature, pressure, and solid concentrations. The spurting conditions control the physical properties of the pulps with BET surface area ranging from 5 to 45 m^2/g .

Production of Pulpex polypropylene pulps and their properties are extensively described in a review article by Rave.²¹

DISCUSSION OF RESULTS

Ozonization

Polypropylene. All the results presented in this work were obtained from ozone treatment of the polymer either in flake or in fiber form in an aqueous medium. The introduction of water in the treatment process was prompted by several practical reasons: for a large scale continuous commercial process, water would act as an economical and efficient carrier of the spurted synthetic pulp or flake; ozonization of dry polypropylene pulp was found to be hazardous without special care and the dry pulp was difficult to move. Using a water medium maintained uniform treatment over the bulk of the material and enhanced the generation of hydroperoxide needed for the grafting process.

(a) *Flake*: The effect of ozonization on the viscosity of polypropylene and polyethylene flake is presented in Figures 1 and 2. The results show a decrease in the molecular weight of the polymer in the initial stage of the ozone-uptake with no significant additional loss after about 1% of ozone-uptake based on the polymer weight. A phenolic antioxidant stabilizer system, about 0.55% based on polymer weight, significantly retards the process of molecular breakdown. Further, the stabilizer system also enhances the generation of the functional groups ($> \text{C}=\text{O}$) due to ozonization (Fig. 3). Figure 4 presents the carbonyl contents in ozonized polyethylene flake samples. In general PE generates higher levels of carbonyl groups than PP (FL-C). The generation of carbonyl groups in the polymer is reasonably linear with the ozone uptake within the level of treatment made ($< 3\%$ ozone uptake).

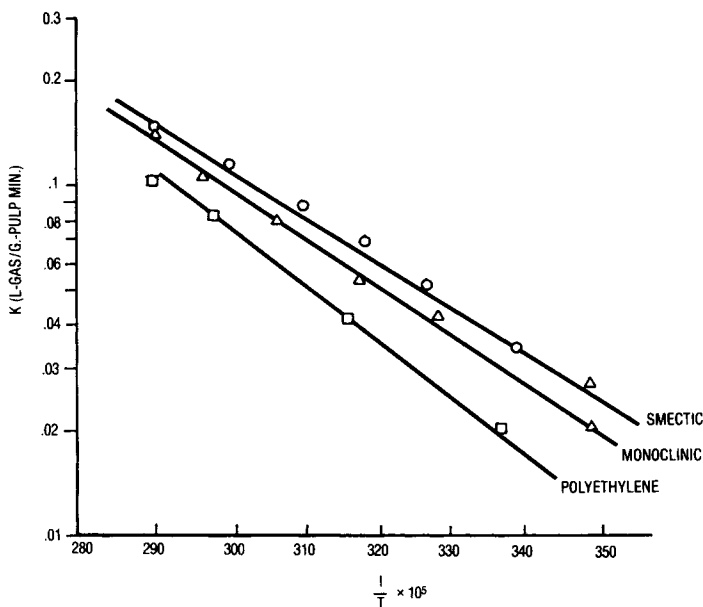


Fig. 12. Rate constants of various olefin pulps at different temperatures.

(b) *Polyolefin fibers*: Pulpex polypropylene pulp, a Hercules product, has been the major material in this investigation. A review article by Rave²¹ provides a description of production and properties of Pulpex. Extensive efforts are in progress to expand various end uses of these pulps in the market. An efficient, economical, and practical method to modify the surface of these polyolefin fibers for bondability and water wettability is needed to assure market expansion. Analytical results for carbonyl and carboxyl groups in Pulpex treated at various levels of ozone uptake of the pulp are presented in Figures 5 and 6. The results show a linear relationship between them. These results obtained in the laboratory with ozonization of Pulpex were very closely reproduced in a pilot plant operation. Results of gel permeation chromatographic analysis for ozonized and unozonized Pulpex showing the reduction in the average molecular weight and the narrowing of the distribution of molecular weight due to ozonization are presented in Figure 7.

Grafting of Hydrophilic Monomers onto Ozonized Pulps

Grafting vinyl chloride to ozonized polyethylene was studied previously.⁶ There are several routes one may follow to achieve this goal and the grafting steps may be carried out under various ambient conditions. The monomers may be used in the vapor phase, possibly with dry pulp, and the medium may be either organic, aqueous, or a mixture of the two. There are various monomers such as acrylamide, acrylic acid, maleic anhydride, or any combinations of them that may be grafted onto the pulp surface to modify pulp quality. In the present work, the results obtained by peroxidizing polypropylene pulps with ozone in an aqueous medium and by grafting acrylamide onto them are presented. A redox recipe was used to initiate grafting of acrylamide onto ozonized pulp.

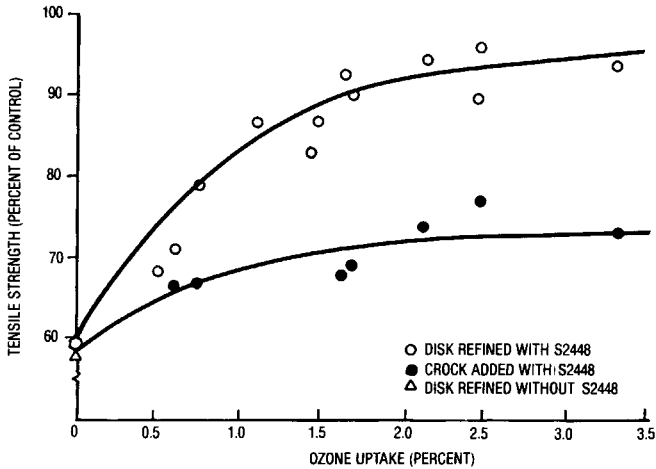


Fig. 13. Tensile strength of 30/70 polypropylene/wood pulps blend sheets with different levels of ozone uptake on polypropylene pulp. The ozonized polypropylene pulps were treated with 5% of bonding resin S2448 by two different methods.

Peroxidation of polypropylene pulp, which is determined by the amount of active oxygen, is enhanced by the temperature of the aqueous medium; the range between 60° and 80°C was found optimum. The presence of water is beneficial for generating active oxygen within the pulp. Generation of active oxygen is also dependent on the crystalline character of the polyolefin pulp as shown in Figure 8.

Crystalline Character of Fibers

When a polymeric material is cooled with a relatively fast rate from melt or solution at high temperature, the crystals are of small size (low crystallinity) and of low degree of perfection. In this case, we call this crystalline type smectic (Figs. 9 and 11). When the cooling rate is relatively slow, the crystal size is large and they have high degree of perfection. We call this type monoclinic

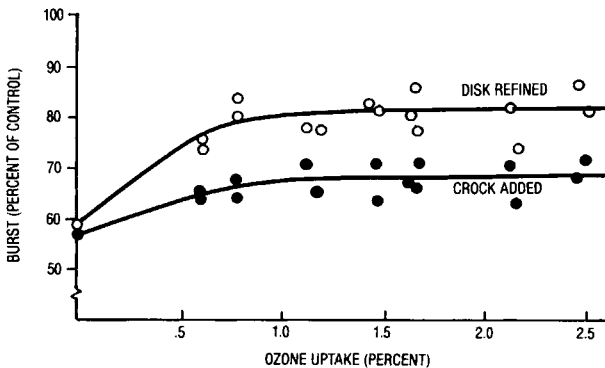


Fig. 14. Burst strength of 30/70 polypropylene/wood pulps blend sheets with ozone uptake on polypropylene pulp. The ozonized pulp was treated with S2448 bond resin by two different methods.

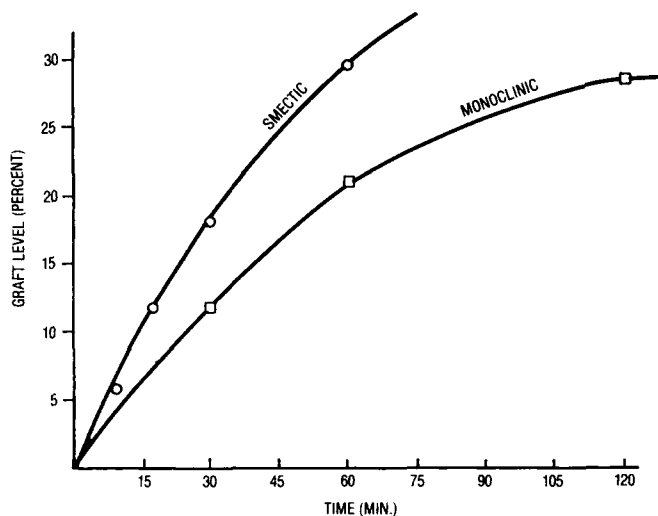


Fig. 15. Amounts of acrylamide grafted to ozonized polypropylene pulps with time. Grafted levels also depend on crystalline character, smectic or monoclinic, of the pulps (both pulps contain 0.2% active oxygen).

(Figs. 10 and 11). During spurling, fibers are produced that are predominantly either smectic or monoclinic, or a mixture of the two, depending on the spurling conditions and the rate of cooling during spurling. X-ray diffraction analysis is an excellent tool to determine the crystalline character of polypropylene fibers or pulps.

Reaction Rate

The rate equation for this well-stirred batch reactor model may be expressed as²²:

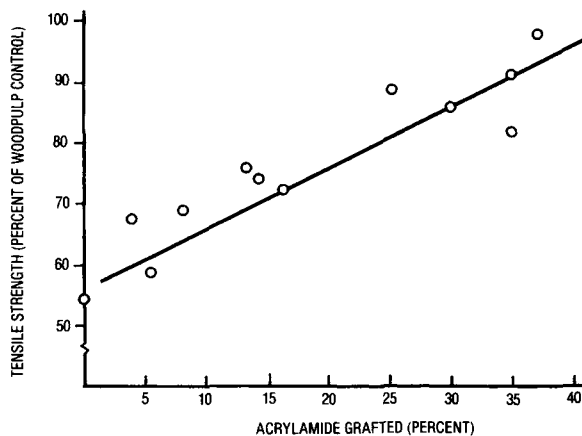


Fig. 16. Tensile strength of 30/70 polypropylene/wood pulps blend sheets with the graft level of acrylamide on predominantly smectic polypropylene pulp.

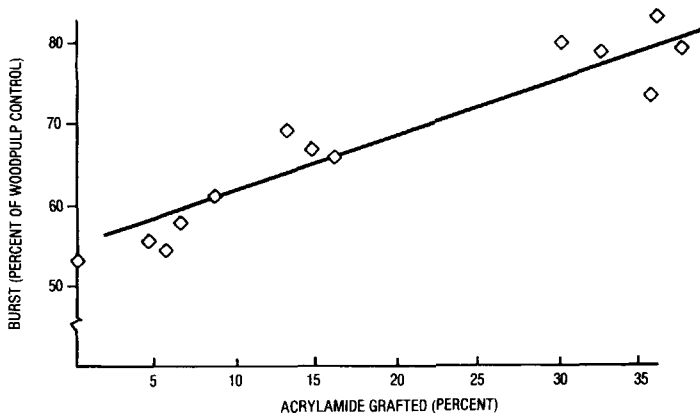


Fig. 17. Burst strength of 30/70 polypropylene/wood pulps blend sheets with the graft level of acrylamide on ozonized predominately smectic polypropylene pulp.

$$\frac{dX}{dt} = K(1 - E)[O] \tag{1}$$

where X = ozone uptake, g O_3 consumed/g pulp; t = time, min; K = rate constant, liter gas/g pulp min; E = efficiency, g O_3 consumed/g O_3 in feed; and $[O]$ = concentration of ozone in feed gas, g O_3 /L gas at reaction temperature. Thus $(1 - E) Co$ is the concentration of ozone in the gas leaving the reactor, which in the case of a well-stirred reactor model is assumed to be equal to the concentration of ozone in the gas phase throughout the reactor.

The rate constant was calculated from experimental data using an equation.

$$K = \frac{X}{t(1 - E)[O]} \tag{2}$$

Since the rate constant K is a function of $e^{E/kt}$, E , the activation energy was calculated from runs at several temperatures. Figure 12 presents the results of rate constant values calculation at different temperatures.

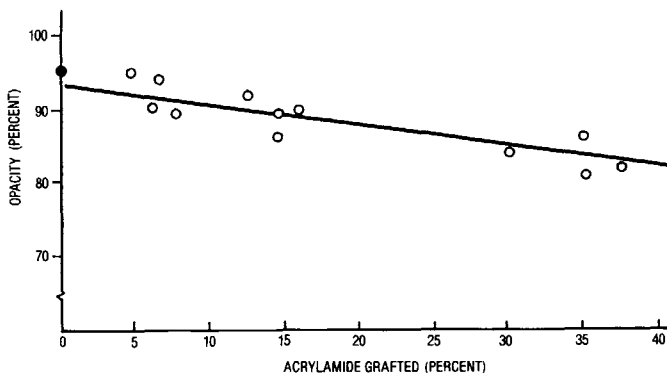


Fig. 18. Opacity of 30/70 polypropylene/wood pulps blend sheets with the graft level of acrylamide on ozonized predominately smectic polypropylene pulp.

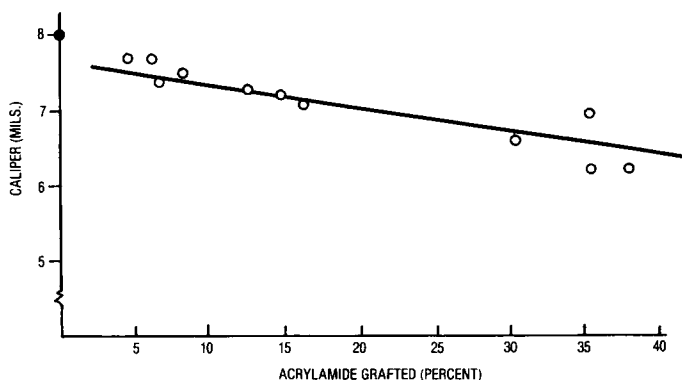


Fig. 19. Caliper of 30/70 polypropylene/wood pulps blend sheets with the level of grafted acrylamide on ozonized predominately smectic polypropylene pulp.

To determine the activation energy value, a pulp consistency of 0.25% was used so that the reaction rate would not be mass transfer limited. The value of activation energy in the case of both polypropylene and polyethylene is approximately 7.0 kcal/mol.

Blend Paper Sheets

Ozonized Fiber with a Dry Strength Resin

The cost to prepare paper sheets containing 100% polyolefin pulps, ozonized or grafted, with an acceptable strength is too high. Therefore all work in this area has been with blended 30% ozonized synthetic fiber and 70% wood pulp. Ozonized pulp without any bonding resin or grafted monomer produced only a low level of bonding with wood pulp. As a result, 1 to 5% of a special bonding resin²³ was incorporated to achieve a reasonable blend sheet strength. The results are presented in Figures 13 and 14. It was also demonstrated that higher than 5% of the strength resin based on synthetic fiber produced no extra sheet strength.

The following are the important features observed in the blend sheets study: 80 to 90% of the wood pulp sheet strength (tensile, burst) can be obtained in 30/70 ozonized polypropylene/wood pulps blend sheets. The maximum strength corresponds to the minimum of about 0.1% total carbonyl group on the pulp due to ozonization and 5% (based on pulp weight) of a bonding resin.²³ There was a significant increase in opacity, brightness, and bulk in the blend sheets over those of 100% wood pulp sheets (Table I). The blend sheet strength is higher with smectic pulp than with the monoclinic one, but the caliper is slightly lower with smectic pulp. The sheet strength depends on the technique of incorporating the bond resin to ozonized pulp. Just adding the resin in the crock is not as effective as treating the pulp in a disc refiner with the resin. Polyethylene pulps provide higher strength in blend sheets than polypropylene pulps, but the sheet caliper is slightly lower in the former case.

Polypropylene Pulp Grafted with Acrylamide

The properties of blend sheets prepared with ozonized polypropylene pulp grafted with acrylamide and wood pulp are presented in Figures 15 to 19. As

expected, the sheet strength increases with the amount of grafted monomer on the pulps; however, the caliper and opacity of sheets decrease with the amount of graft. This is possibly because the monomer grafted to the fibers make them soft, resulting in their laying closer during the process of sheet making. The decrease in opacity of the paper sheets may also be attributed, to a degree, to the denser polyacrylamide molecules formed on the polypropylene fiber surface during grafting.

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