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POLYPROPYLENE MODIFIED WITH SULPHUR DIOXIDE

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ABSTRACT

The bonding of sulphate and sulphonate groups to atactic and isotactic polypropylene (PP) by the reaction of sulphur dioxide and hydroperoxides (ROOH) have been investigated. The oxidized PP and the blends of PP and low molecular cumylhydroperoxide (CHP) and t-butylhydroperoxide (TBHP) were used. The oxidized PP were prepared by low temperature oxidation of polymer foils, powder, and PP fabric at 50°C using ozone-oxygen mixture. The sulphoxy groups concentration in the atactic PP treated by SO_2 exceeds a concentration of hydroperoxides from 4 to 23 times as a temperature increases from 30 to 70°C. The overall activation energy 40 kJ/mol was determined for this process. The increasing stoichiometry of SO_2/ROOH, with raising a temperature and determined temperature coefficient, show on an increasing importance of hydrogen transfer reactions of free radicals on the extent of PP reaction.

The modification of an atactic PP was less effective if the blend of polymer with low molecular hydroperoxide was treated by SO_2. The stoichiometry at 50°C of SO_2/ROOH is 1.6, with a slight increase to 1.9 at the lowest concentrations of peroxide in blends. The range from 0.033 to 0.66 mol/kg ROOH was used.

The treatment of isotactic PP by low molecular hydroperoxides and SO_2 at temperatures over 120°C leads to the attachment of observ-able concentrations of sulphoxy groups to PP. The isotactic PP acti-vated by the ozone-oxygen mixture does not differ markedly in sensibility to modification with SO_2 in comparison with oxidized atactic PP. When compared to the starting polymer, the modified isotactic PP foils and fabrics are suitable for a deep dyeing, and show better wettability by polar solvents.

INTRODUCTION

An interest in chemical modification of polypropylene (PP) continues with unceasing intensity from the early beginning of PP application. A principal problem in such chemistry is activation of polymer molecules by synthesis of an initiator site. The hydroperoxy groups serve as relatively suitable precursors for free radical reactions on PP macromolecules. These are easily generated by mild thermal oxidation [1-4] or by a variety of other treatments of PP, including radiation [4, 5] or low-temperature plasma procedures [6].

This paper describes an attachment of polar sulphate and sulphonate groups to both atactic and isotactic PP by the reaction of sulphur dioxide with oxidized PP macromolecules or low molecular hydroperoxides (ROOH).

Different aspects in studies of hydroperoxides decomposition by SO_2 were referred to in the literature. One of them, which interests polymer chemists, is the generation of free radicals suitable for initiation of polymerization of vinyl monomers. It was found that the reaction conditions influenced considerably the mechanism of hydroperoxide decomposition in the presence of SO_2. The aryl-alkyl hydroperoxides are quantitatively decomposed into phenols and ketones in an anhydrous non-nucleophilic medium by ionic process even using traces of SO_2 [7]. However, hydroperoxides with SO_2 also form a very active redox initiating system generating free radicals at temperatures well below 0°C [8-12] if the reaction is carried out in the presence of nucleophilic agents (alcohols, esters, ketones). The free radicals $HOSO_2$, $C_4H_9OSO_2$ were detected in solution of tert-butyl-hydroperoxide in methanol after addition of SO_2 [10] or radicals $HOSO_2M$ and $C_4H_9OSO_2M$ were observed if a small amount of vinyl monomer M was present during hydroperoxide decomposition. In an excess of monomers, analogical systems act as effective initiators of radical polymerization.

The reaction of sulphur dioxide with hydroperoxidic groups of polyethylene [13] or PP [14, 15] was applied to quantification of peroxidic and carbonyl species in oxidized polyolefins. The approach to kinetic and mechanistic analysis emphasizes the final state with no or little attention to free radical intermediates as initiating sites for polyolefin modifications.

Nevertheless, it can hardly be expected that oxidized PP reacts with SO_2 in exactly dry and non-polar medium. The carbonyls and other nucleophilic groups that accompanied the PP oxidation in concentrations comparable to hydroperoxides appear to be suitable coagents for generation of free radicals by the reaction of SO_2 with the oxidized PP. The consecutive recombination of various types of free radicals and propagation of the reaction by hydrogen transfer may be used in PP modification. This is the basis of the work reported herein. The PP macromolecules with pendant sulfate and sulphonate groups were prepared using treatment of oxidized PP by SO_2. The activated decomposition of low molecular hydroperoxides blended with PP was also used for PP modification in the presence of SO_2. The extent of reaction in the systems containing hydroperoxy groups bonded to PP macromolecules has been compared with experiments when low molecular hydroperoxides reacted with SO_2. The hydrophility of reaction products were evaluated by measuring the wettability of PP surface with water and by sensitivity to deep dyebility.

EXPERIMENTAL

Materials

The atactic PP for the present study was purified by separation of diethyl ether-insoluble fractions and of low molecular acetone-soluble fractions. The average molecular weight 4.1×10^4 g/mol was determined by viscosimetry of polymer solutions in toluene at 30°C [16]. The isotactic PP powder, without additives, had the free flowing weight 0.430 g/cm^3 and the melt flow index 10.4 g/10 min. (ISO 1133). The PP fabric was extracted in boiling acetone for 1 hour to remove process antioxidants. The polymers used are commercial products (Tatren-HPF, SLOVNAFT Company, Slovak Republic).

The foils of atactic PP, both pure or blended with cumylhydroperoxide (CHP) or t-butylhydroperoxide (TBHP), were prepared from cyclohexane solutions inside the round glass frames of 90 mm diameter. Foils of pure atactic PP were cast on the water surface, those of blends with low molecular peroxide were laid on a mercury surface.

Sulphur dioxide was synthesized by heating the copper wires with concentrated sulphuric acid. The SO_2 gas was dried over the anhydrous sodium sulphate and stored in a liquid state at -40°C.

Methylene blue was purified using an extraction of aqueous solution at pH 10 with chloroform [17].

Cumylhydroperoxide (CHP) and t-butylhydroperoxide (TBHP) were purchased from FLUKA, Switzerland.

All other chemicals in analytical grade purity were supplied from LACHEMA, Czech Republic.

Activation of PP

The peroxidized atactic PP was prepared by low temperature oxidation. The 100 ± 10 μm foils sustained in glass frames were exposed 5 hours at 50°C to the atmosphere of oxygene containing ozone 1.2 mg/l [1]. The gas flow was 270 ml/min. The total concentration of peroxides $(9.39 \pm 0.03) \times 10^{-2}$ mol/kg was determined by iodometry. The same conditions were used also for the activation of PP powder and fabric which were oxidized to 3.52×10^{-2} mol/kg of peroxides.

As the components for reaction with sulphur dioxide, the blends of isotactic PP with CHP and TBHP were prepared using a diffusion of the hydroperoxide in to PP grains from cyclohexane solution during free evaporation of solvent at room temperature.

Apparatus

A glass 1 L desiccator, thermostated in a water bath, was used as a reactor for PP modification by pure sulphur dioxide. The molar concentration of gaseous SO_2 exceeded by two decimal orders that of peroxides in oxidized PP and by one decimal order a maximum molar concentration of the low molecular hydroperoxides blended with PP. The exposure time to SO_2 was 30 minutes at various temperatures. The samples were degassed before analysis in vacuum.

Analysis

The dye partition technique [18] was used to determination a concentration of sulphoxy groups bonded to PP. This method is based on interaction between the ionic groups in polymer and suitable ionic dye. The principle of analysis is the transfer of methylene blue (selected here) from water phase to the chloroform phase with dissolved modified PP. The intensity of coloration of the polymer solution is proportional to concentration of sulphoxy groups in PP.

The concentration of peroxides in oxidized polymer was determined using the iodometry adapted to PP [2].

The contact angles of water on modified PP surfaces were measured with an optical goniometer Amphval POLD, Germany.

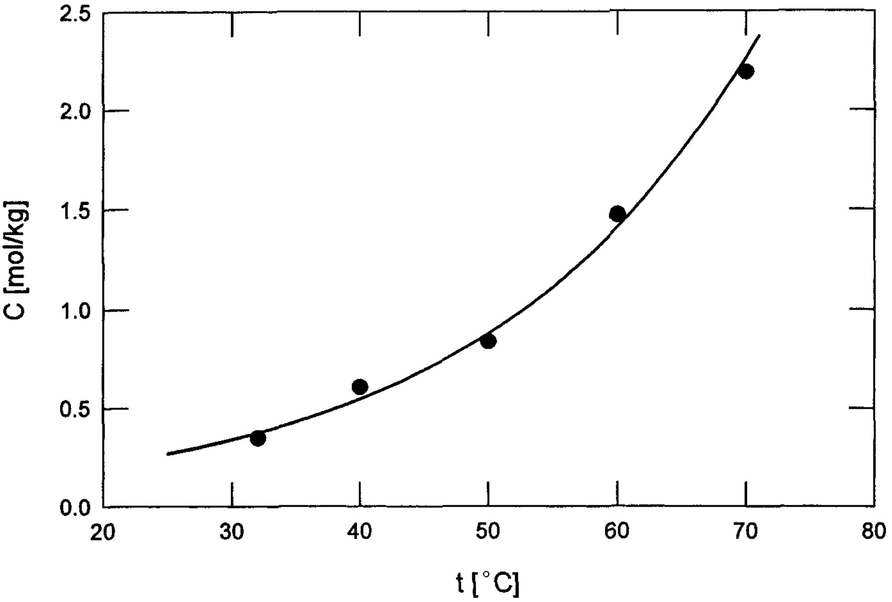

Figure 1. The concentration C of sulphoxy groups bound to oxidized atactic PP foils (0.0939 mol/kg of -OOH) in dependence on temperature of the reaction with the pure gaseous SO_2 (101.3 kPa) during 30 minutes. The 50 fold molar excess of SO_2 over -OOH was used.

The IR spectra of isotactic PP foils were obtained with SPECORD 71/IR, Germany. The polymer foils of 100 μm thickness were press molded at 180°C from isotactic PP powders.

RESULTS AND DISCUSSION

The rubbery PP foils were held inside the glass frames to provide access of reactants to both surfaces of the polymer foils. An amorphous state of the atactic PP enables the diffusion of gases into the foils, and makes the reactions with oxygen, and subsequently with sulphur dioxide, more homogeneous. The oxidized atactic PP foils 100 ± 10 μm thick were exposed to pure SO_2 in the temperature range from 30 to 70°C. The dye partition procedure recommended for sulphate ($-OSO_3H$) and sulphonate ($-SO_3H$) groups determination was applied to an analysis of the modified PP. The results obtained are in Figure 1. The concentration of the sulphoxy groups exceeds that of the hydroperoxides in atactic PP (0.0939 mol/kg) by 4 to as much as 23 times the temperature of the reaction increases from 30 to 70°C. The excess of bound sulphoxy groups over the hydroperoxides conforms to an idea that the chain free radical mechanism operates in the reaction of oxidized atactic PP with SO_2. Ghosh and Billmayer [11] depicted the scheme for the reaction of low molecular hydroperoxide ROOH and SO_2. The set of parallel reactions includes among others complexes, SO_2 with hydroperoxide, solvent and monomer, and transfer reactions of the free radical centrum to double bond of a vinyl monomer and a hydrogen atom abstraction from the solvent molecule XH.

$$\begin{array}{lllllll}
[ROOH \ldots\ldots\ldots SO_2] & + & M & \rightarrow & RO^{o} & + & HSO_3M^{o} \\
 & & & & RO_2^{o} & + & HSO_2M^{o} \\
 & & & & ROH & + & SO_3M^{o} \\
 & & & & RSO_3^{o} & + & HOM^{o} \\
 & & & & RO^{-} & + & HSO_3M^{+} \\
[XH \ldots\ldots\ldots SO_2] & + & ROOH & \rightarrow & ROH & + & HSO_3^{o} + X^{o} \\
[M \ldots\ldots\ldots SO_2] & + & ROOH & \rightarrow & ROH & + & SO_3M^{o} \\
[ROOH \ldots\ldots\ldots XH] & + & SO_2 & \rightarrow & ROH & + & HSO_3^{o} + X^{o}
\end{array}$$

In our system, XH denotes PP basic units, hydroxyls and carbonyls in oxidized PP chain, and ROOH stands for hydroperoxidic groups bonded to PP macromolecules (PPOOH).

The sulphoxy radicals produced in a hydroperoxide decomposition by SO_2 were proved by ESR spectroscopy [10]. The radical polymerization of vinyl monomers using the hydroperoxide - SO_2 initiating system and an analysis of end groups of synthesized polymer [11] also supported a presence of free radicals in this reaction. From this standpoint, the predominance of sulphoxy groups over the concentration of starting peroxides (Figure 1) can be explained using a similar mech-anism in ROOH decomposition by SO_2 which implicates the free radicals. The process of addition sulphoxy groups to an oxidized PP should involve a short reaction chain before the free radicals are bimoleculary terminated. The free radicals X^o on the PP backbone are the reactive sites where the extension of modification is

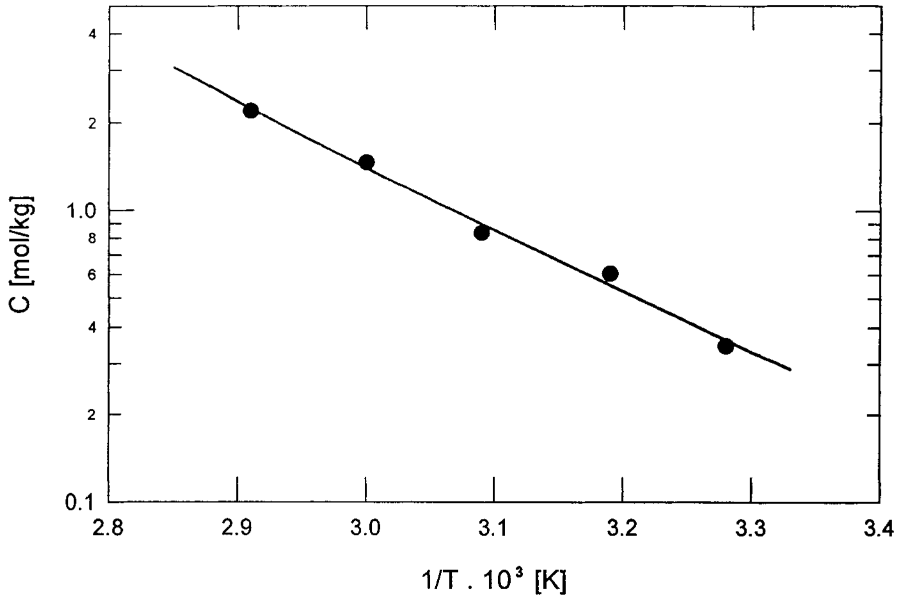

Figure 2. The influence of temperature on bonding the sulphoxy groups to oxidized atactic PP foils (0.0939 mol/kg of -OOH) by treatment the foils with pure SO_2 gas (101.3 kPa) during 30 minutes expressed in the Arrhenius coordinates.

initiated, probably by the chain addition of SO_2 in accordance with reactions [19]:

$$X^{o} + SO_2 \rightarrow XSO_2^{o}$$

$$XSO^{o}_2 + XH \rightarrow XSO_2H + X^{o}$$

The same data from Figure 1 transformed in Arrhenius coordinates (Figure 2) allows us to estimate the activation energy of the reaction. The temperature effect on the addition of sulphoxy groups to atactic PP is expressed by the activation energy about 40 kJ/mol. This is a substantially lower value compared to that of the thermal scission of peroxide oxygen bonds (125 kJ/mol). The SO_2 functions in reaction with hydroperoxides as a redox agent that considerably lowers the activation energy of the oxygen bond scission. This value becomes comparable to that of the temperature coefficient of hydrogen transfer reaction to free radicals in the range 40 to 80 kJ/mol in dependence on C-H bond reactivity. With respect to stoichiometry SO_2/PPOOH in the modification reaction the determined activation energy 40

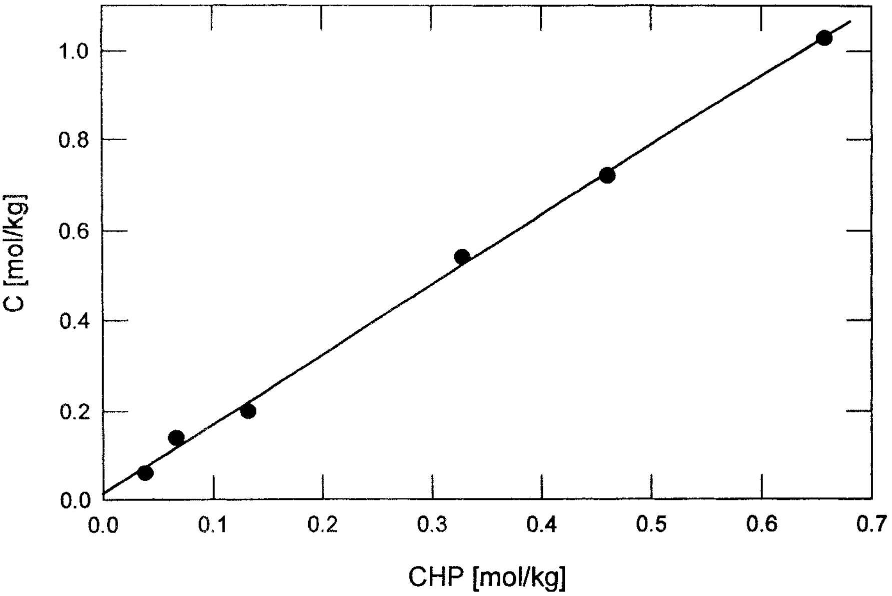

Figure 3. The sulphoxy groups concentration determined in atactic PP foils blended with CHP after their treatment in pure SO_2 gas (101.3 kPa) at 50 °C during 30 minutes.

kJ/mol can be held for the chain hydrogen transfer to free radicals. Thus, an increasing temperature is the important factor which intensify the modification process of PP with sulphoxy groups.

The participation of free radicals in the reaction of an attachment of sulphoxy groups to PP is also evidenced by curing experiments of the CHP-atactic PP blends in SO_2. The amount of sulphoxy groups determined in the reaction product in dependence on CHP concentration is presented on Figure 3. The stoichiometry SO_2/ROOH at 50°C is 1.6, and slightly increases to 1.9 at the lowest concentrations of CHP in blends. This value is almost 6 times lower compared with that found for SO_2/PPOOH at the same temperature. Besides the 45% of sulphoxy groups determined in the reaction products are the low molecular compounds. These were removed from SO_2 cured PP-CHP blend by dissolving the reaction product in chloroform and by precipitation the modified PP with methanol. Thus, it appears that a low molecular hydroperoxide -SO_2 system has the lower efficiency of PP modification. Nevertheless, the fact that half of all originated sulphoxy groups are bound to the polymer leads to a conclusion that PP macromolecules are activated by the reaction of hydrogen atom abstraction by free radicals.

An alternative to the participation of free radicals in bonding sulphoxy groups to the PP during SO_2-ROOH reactions [10, 11, 19], is carbocationic mechanism proposed by Carlsson [15]. The organo and ionic hydrogensulphates dominate among reaction products if an excess of SO_2 over the hydroperoxy groups is used. In an inverse ratio of reactants, the hydrogensulphate groups react further with an excess of hydroperoxide to give dialkyl peroxides and sulphuric acid.

$$\text{PPOOH} + \text{SO}_2 \rightarrow \text{PPOSO}_3\text{H} \qquad (\text{excess SO}_2)$$

$$\text{PPOSO}_3\text{H} \rightarrow [\text{PP}^+ \ldots\ldots {}^-\text{OSO}_3\text{H}]$$

$$[\text{PP}^+ \ldots\ldots {}^-\text{OSO}_3\text{H}] + \text{PPOOH} \rightarrow \text{PPOOPP} + \text{H}_2\text{SO}_4 \qquad (\text{excess PPOOH})$$

Admittedly, the reaction of SO_2 with oxidized PP may never be simple and stoichiometric. The adjacent -OOH groups cause an excess of hydroperoxides in the reaction domain and favor the reaction at SO_2 starved conditions. The authors [15] note the fact that peroxide bands in FTIR were not clearly distinguished because of masking by intense hydrosulphate and sulphuric acid bands.

The presence of cyclic peroxides was expected [15] but the intermolecular peroxides were not assumed. Nevertheless, the oxidized PP represents the multifunctional macromolecules and the decomposition of -OOH groups by SO_2, according to the mechanism leading to dialkyl peroxides, should cause the crosslinking of PP. Contrary to belief, neither the experiments with oxidized isotactic PP [15], nor the reactions of oxidized atactic PP with SO_2 presented in this work, result in a polymer network.

The different temperature dependence of parallel reactions of numerous intermediates also contributes to the complexity of SO_2-ROOH reaction. Among these reactions, the hydrogen atom abstraction by free radicals is the most accelerated by raising the temperature, and consequently, also increases an extent of PP modification. The application of the SO_2-ROOH reaction to the PP modification with sulphoxy groups was extended to isotactic PP. Two sets of samples of isotactic PP impregnated with 0.5-10 wt% of CHP or TBHP were exposed to gaseous SO_2 for 30 minutes at 60°C. Polymer samples with 5 wt% of CHP and TBHP were treated 30 minutes by SO_2 at temperatures from -20°C to 120°C.

The insolubility of isotactic PP, at moderate temperatures, is an obstacle in using the dye partition technic in evaluation of an extent of modification. Instead, the IR analysis was applied. The sulphoxy groups bound to isotactic PP, as it was found for atactic PP, was not proven in PP reprecipitated from a boiling toluene.

TABLE 1. The Contact Angles Θ and Work of Adhesion was Determined for H_2O on PP Films Press Molded from PP Powders Modified with Sulphoxy Groups. The Isotactic PP impregnated with Various Concentrations of CHP was Treated by Pure SO_2 Gas During 30 Minutes at 60°C. 20 Fold Excess of SO_2 over Hydro-peroxide was used

CHP [wt%]	$< \Theta^o$	SD *	W_A [Nm^{-1}]
starting polymer	71.6	1.10	0.965
0.5	62.4	1.28	1.065
1.0	61.0	1.60	1.075
2.0	59.2	1.44	1.100
5.0	54.4	1.12	1.120
10.0	55.8	1.04	1.140

*Standard Deviation

The absorption bands in IR spectrum of the polymer foils, which were press molded from reprecipitated modified PP powders, did not differ from the original PP. The only exception was the PP sample prepared at 120°C, showing new absorption bands at 690 and 760 cm^{-1} before and after purification. It is worth noting that the IR spectroscopy is less sensitive when compared with the dye partition analytical method. We believe that the bonding of sulphoxy groups, even to the isotactic PP, cannot be completely excluded. The indirect support gives the contact angle of water on PP films prepared from modified and purified PP (Tables 1 and 2). The increasing concentration of hydroperoxide in reactants, and an increase of temperature of the reaction results in a polymer with a surface better wetted with water. An additional 12 hours extraction of modified PP films by water (20 and 100 °C) and heptane (20 and 50°C), did not change the hydrophility of polymer surface. The increase of contact angle 3° was observed in films immersed in trichlor-ethylene during 12 hours at 50°C.

The data in Table 1 show the sharp decrease of the contact angle at the low CHP concentrations. An addition of more than 2 wt% of CHP to PP powder had only a little effect on wettability of polymer foils prepared from modified PP. The depth of impregnation of a PP powder with low molecular hydroperoxide is probably limited. CHP molecules over the saturation equilibrium remain on the surface of PP grains and react with SO_2 and thus are ineffective in reaction with PP. With a

TABLE 2. The Contact Angles Θ and Work of Adhesion W_A Determined for H_2O on PP films Press Molded from PP Powders Modified with Sulphoxy Groups. The Isotactic PP Impregnated with 5 wt% of TBH or CHP was Treated by Pure SO_2 Gas During 30 Minutes at Various Temperatures. 20 Fold Excess of SO_2 over Hydroperoxide was used.

T°C	tBHP < Θ°	tBHP SD*	tBHP W_A [Nm^{-1}]	CHP < Θ°	CHP SD*	CHP W_A [Nm^{-1}]
starting polym.	71.6	1.10	0.965	71.6	1.10	0.965
-10	55.2	0.96	1.143	63.2	0.64	1.056
20	48.4	4.32	1.210	59.8	1.36	1.093
60	46.8	2.84	1.226	55.0	1.20	1.145
80	-	-	-	51.8	2.24	1.177
120	46.0	1.40	1.233	-	-	-

*Standard Deviation

constant content of hydroperoxide in PP powder, the increasing temperature of the reaction with SO_2 contributes to better wettability of a product. This result agrees with the reaction mechanism that includes an activation of PP by hydrogen atoms transfer from PP to free radical intermediates generated in the SO_2-ROOH reaction. The increasing participation of these reactions in attachment of sulphoxy groups to PP is more convincing from data obtained in modification of an amorphous atactic PP in a preceding part of this work. Nevertheless, a practical absence of sulphoxy groups in isotactic PP treated with low molecular CHP or TBHP and SO_2 contrasts with analogous experiments using atactic PP.

An entirely different result was obtained in bonding the sulphoxy groups to oxidized isotactic PP. The hydroperoxy groups attached directly to PP make the polymer more suitable to modification by an interaction with SO_2. The sulphoxy groups were found in a treated isotactic PP before, as well as after, a reprecipitation from boiling toluene. This result shows, that oxidized PP in reaction with SO_2 behaves similarly as amorphous atactic PP. Irrespective of the fact that the quantitative kinetic study with isotactic PP was not performed, it is concluded that the hydroperoxy groups bound to PP macromolecules favor their modification with sulphoxy groups.

The surface modification by sulphoxy groups was applied to improve the dyeability of PP fibers. The hydroperoxy initiation sites of an oxidized PP fabric at a concentration 0.035 mol/kg reacted with pure SO_2 at normal pressure and 60°C for 30 minutes. The modified fabric was dyed by the standard procedure using Rhodamin B, Ostacetate blue ERL and Suminol Milling Orange QN. The original and modified PP fabrics were immersed to 0.5 wt% water solution of a dye in the dyeing bath with a modulus 1:100 and the temperature 100°C. A nonbound dye was washed out by repeated extraction by pure water. The modified PP fabrics were dyed to the substantially deeper colors compared to an original fabric.

CONCLUSION

The hydroperoxides decomposed by sulphur dioxide in the presence of PP can provide a proper process for binding sulphoxy groups to PP backbone. The hydroperoxy groups that were produced by mild oxidation directly on the PP macromolecules make the PP more suitable to modification compared to low molecular hydroperoxides. The important factor in increasing the extent of reaction is the reaction temperature. The results presented in this study support an idea that the hydrogen atoms abstraction by free radical intermediates at elevated temperatures activates the PP for binding more sulphoxy groups. The increasing efficiency of modification is reflected also in better wettability and dyeability of PP surface. The system used is quite susceptible to introduction of reactive sites to PP chains while the reaction mechanism is rather of free radical [11, 19] than the ionic mechanism considered in [15].

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