RADIATION INDUCED GRAFT COPOLYMERIZATION OF VINYL ACETATE AND ISOPROPENYL ACETATE ONTO ISOTACTIC POLYPROPYLENE

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Radiation-induced graft copolymerization of vinyl acetate (VAC) and isopropenyl acetate (PAC) onto isotactic polypropylene (IPP) has been studied. The percentage of grafting was calculated for various reaction parameters, and the optimum conditions for attaining the maximum percentage of grafting were determined. Maximal achieved extents of grafting are 39% and 29% for VAC and PAC, respectively. The reactivity of the two monomers with respect to grafting is discussed.

Key words: Graft copolymerization; Vinyl and isopropenyl acetates; Polypropylene, isotactic.

The grafting of a wide variety of monomers onto polypropylene using gamma rays as initiator has been studied by Wu et al.[1]. The dyeing and heat resistance properties of polypropylene-*graft*-poly(styrene-*alt*-maleic anhydride) have been found superior to those of unmodified isotactic polypropylene[2] (IPP). Odian and coworkers[3] observed that the radiation induced grafting of styrene and methyl methacrylate to polypropylene is accelerated by methanol. Solvent effects during the graft copolymerization of methyl methacrylate onto an IPP film by the mutual gamma radiation method were studied by Pruzinec et al.[5]. Grafting frequently resulted in an increased absorption of moisture and improved the dyeability of the grafted sample. Misra et al. successfully grafted acrylonitrile[6] and 4-vinylpyridine[7] onto isotactic polypropylene by using the preirradiation method. Alcohols of higher chain lengths were found to promote the grafting of acrylonitrile onto IPP (ref.[8]). In the present article we report on the graft copolymerization of vinyl acetate (VAC) and isopropenyl acetate (PAC), respectively, onto IPP using the preirradiation method. Little information is available on the use of PAC as the monomer in graft copolymerization. Decomposed thermally in air, preirradiated IPP readily undergoes grafting in the presence of vinyl acetate, with little degradation of the backbone[9]. Oshika[10] reported on the grafting of methyl methacrylate onto chlorinated PP using dibenzoyl peroxide as the initiator. UV-induced grafting of VAC onto PP gives a graft copolymer with an improved impact strength[11]. Mikulasova and Berek[12] reported on the graft copolymerization of VAC onto isotactic polypropylene and atactic polypropylene using γ rays and UV rays as initiators. The present study is concerned with the effect of methyl groups in vinyl acetate during grafting; the reactivity of vinyl acetate with respect to the grafting onto IPP is also compared with that of isopropenyl acetate.

EXPERIMENTAL

Materials and Method

Isotactic polypropylene in the fibrous form was received from National Rayon Corporation, Bombay, India. Vinyl acetate and isopropenyl acetate were freshly distilled before use. Distilled water served as the reaction medium in all the experiments. Irradiation of polypropylene was carried out in a Gamma Chamber-900 containing a Co^{60} source ($7\,770 \, . \, 10^{10}$ s^{-1}) in air at a dose rate of 10.4 kJ kg^{-1} h^{-1} for different time periods.

Graft Copolymerization

Irradiated IPP (100 mg) was suspended in a known amount of water in a round-bottom flask attached to a long water-cooled condenser. A chosen amount of the monomer was added and the reaction flask was placed in an oil bath held at a preselected temperature. The reaction was allowed to proceed for a time period, after which the flask was removed and the contents were filtered. The grafted polypropylene was separated from the homopolymer by extraction with benzene and acetone.

The percentage of grafting (p_g) was calculated as

$$p_g = 100\,(W_1 - W_0)/W_0,$$

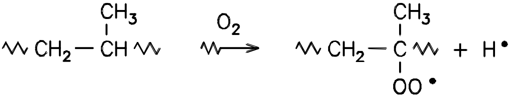
where W_0 and W_1 are the weights of the original IPP fiber and the graft copolymer, respectively.

IR Spectra

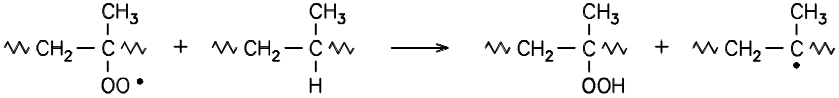
Both IPP-*graft*-poly(VAC) and IPP-*graft*-poly(PAC) showed absorption at 1 730 cm^{-1} assigned to the ester carbonyl of the grafted poly(VAC) and poly(PAC) chains. No such bands were present either in the IPP or in the preirradiated IPP.

RESULTS AND DISCUSSION

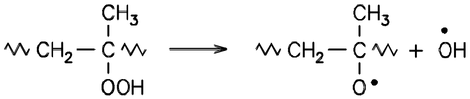
Irradiation of polypropylene in air leads to the formation of hydroperoxide groups owing to the presence of a large number of labile hydrogen atoms at the tertiary carbon atoms[13]. The hydroperoxide groups decompose upon heating, leading to the formation of macropolypropylene oxide radical ($PP{-}\dot{O}^{\bullet}$) and the hydroxyl radicals ($^{\bullet}\dot{O}H$). The OH radical may initiate polymerization of the vinyl monomer and the growing polymeric chain may be grafted onto IPP. Alternatively, vinyl monomers may directly polymerize on the active site of the polypropylene backbone. The following mechanism is suggested for the grafting of VAC and PAC onto polypropylene.



$$\sim CH_2-\overset{CH_3}{CH}\sim \xrightarrow{O_2} \sim CH_2-\underset{OO^{\bullet}}{\overset{CH_3}{C}}\sim + H^{\bullet} \qquad (A)$$

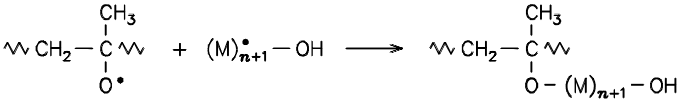


$$\sim CH_2-\underset{OO^{\bullet}}{\overset{CH_3}{C}}\sim + \sim CH_2-\underset{H}{\overset{CH_3}{C}}\sim \longrightarrow \sim CH_2-\underset{OOH}{\overset{CH_3}{C}}\sim + \sim CH_2-\underset{\bullet}{\overset{CH_3}{C}}\sim \qquad (B)$$

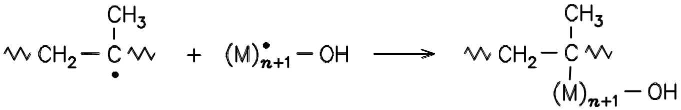


$$\sim CH_2-\underset{OOH}{\overset{CH_3}{C}}\sim \longrightarrow \sim CH_2-\underset{O^{\bullet}}{\overset{CH_3}{C}}\sim + \overset{\bullet}{O}H \qquad (C)$$

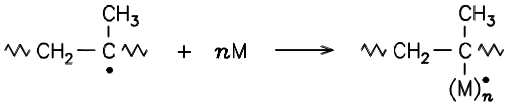
$$M + \overset{\bullet}{O}H \longrightarrow \overset{\bullet}{M}-OH \xrightarrow{nM} (M)^{\bullet}_{n+1}-OH \qquad (D)$$



$$\sim CH_2-\underset{O^{\bullet}}{\overset{CH_3}{C}}\sim + (M)^{\bullet}_{n+1}-OH \longrightarrow \sim CH_2-\underset{O-(M)_{n+1}-OH}{\overset{CH_3}{C}}\sim \qquad (E)$$



$$\sim CH_2=\underset{\bullet}{\overset{CH_3}{C}}\sim + (M)^{\bullet}_{n+1}=OH \longrightarrow \sim CH_2-\underset{(M)_{n+1}-OH}{\overset{CH_3}{C}}\sim \qquad (F)$$

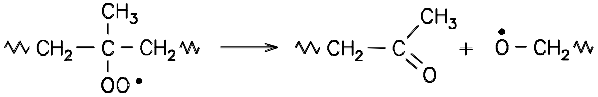


$$\sim CH_2-\underset{\bullet}{\overset{CH_3}{C}}\sim + nM \longrightarrow \sim CH_2-\underset{(M)^{\bullet}_{n}}{\overset{CH_3}{C}}\sim \qquad (G)$$

The effect of various parameters on the grafting of VAC and PAC is discussed in the light of the above proposed mechanism.

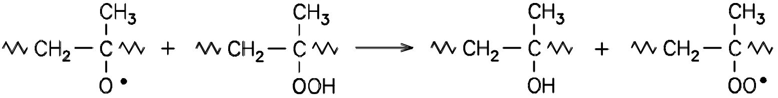
Effect of Total Radiation

The percentage of grafting (p_g) of VAC and PAC was studied as a function of the total radiation dose (Fig. 1*a*). The percentage of grafting of vinyl acetate is nearly constant at low total doses, but it increases sharply after exeeding the value of 346 kJ kg^{-1} to reach its maximum (11%) at a total dose of 576 kJ kg^{-1}, after which it decreases. The percentage of grafting of PAC, on the other hand, increases slowly to attain its maximum of 9% at a total dose of 568 kJ kg^{-1}, beyond which it decreases. The decrease in the percentage of grafting beyond the optimum dose with both of the monomers may be due to chain degradation.



$$\sim CH_2-\overset{CH_3}{\underset{OO^\bullet}{C}}-CH_2\sim \longrightarrow \sim CH_2-C\overset{\diagup CH_3}{\underset{\diagdown O}{}} + \overset{\bullet}{O}-CH_2\sim \qquad (H)$$

Alternatively, the active sites on the polymer backbone may be killed by induced decomposition of the hydroperoxidized polypropylene by the polypropylene macroradical in the following manner.



$$\sim CH_2-\overset{CH_3}{\underset{O^\bullet}{C}}\sim + \sim CH_2-\overset{CH_3}{\underset{OOH}{C}}\sim \longrightarrow \sim CH_2-\overset{CH_3}{\underset{OH}{C}}\sim + \sim CH_2-\overset{CH_3}{\underset{OO^\bullet}{C}}\sim \qquad (I)$$

Both these types of reactions are expected to reduce the percentage of grafting.

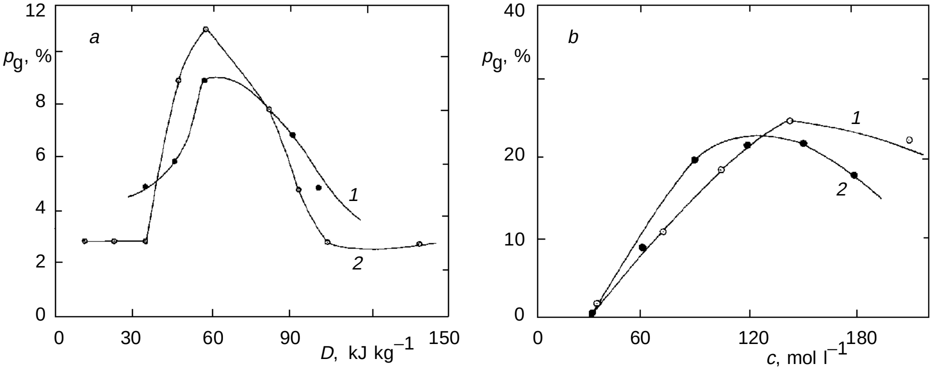
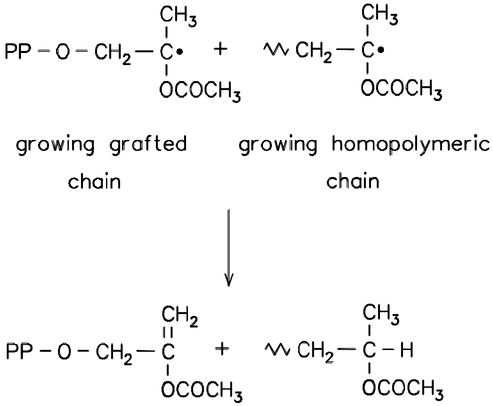


FIG. 1

Dependence of the extent of grafting on *a* the total radiation dose (*D*) and *b* the monomer concentration; *1* poly(IPP)-*graft*-poly(VAC), *2* poly(IPP)-*graft*-poly(PAC). Reaction conditions: 100 mg of IPP, 15 ml of water, 100 °C, 120 min; *a* [VAC] = 72.0 . 10^{-2} mol l^{-1}, [PAC]= 61.0 . 10^{-2} mol l^{-1}; *b* *D* = 57.60 and 56.80 kJ kg^{-1} for VAC and PAC, respectively

Effect of Monomer Concentration

The results are presented in Fig. 1*b*. The percentage of grafting of the two monomers increases with increase in their concentration giving the maximum grafting (25% and 22%) at [VAC] = 1.44 . 10^{-4} mol l^{-1} and [PAC] = 1.50 . 10^{-4} mol l^{-1}, respectively, after which it decreases. The decrease in grafting is sharper for VAC than for PAC. For the former, the decrease in the percetage of grafting beyond the optimum may be due to the fact that at higher monomer concentrations homopolymer formation may become the preferred process. Also, at higher monomer concentrations, the growing grafted chains may be involved in the monomer transfer reaction (monomer transfer constant 2.4 . 10^{-4} for VAC at 70 °C, ref.[14]) leading to a reduced extent of grafting. Furthermore, the growing grafted chains may take off hydrogen atoms from the poly(VAC) already formed by the polymer transfer reactions (polymer transfer constant 4 . 10^{-4} for VAC at 70 °C, ref.[14]). For isopropenyl acetate the extent of grafting is lower because the growing grafted chains can be terminated by a disproportionation reaction.



(*J*)

Effect of Time of Reaction

Figure 2*a* demonstrates that grafting of VAC and PAC starts after an induction period of 9 and 27 min, respectively, and increases sharply up to 60 min, after which the percentage of grafting changes only slightly; later the grafting increases again. The increase in the percentage of grafting with increasing reaction time may be due to the fact that as the time is extended, the two homopolymers, poly(VAC) and poly(PAC), become soluble in the unreacted monomer and the viscosity of the reaction medium decreses, whereupon the mobility of the growing grafted chains increases and the percentage of grafting rises.

Effect of Temperature

The temperature of the bath was held constant within the range of 100–130 °C during the reaction. The effect of temperature is shown in Fig. 2*b*. In the case of VAC, the percentage of grafting increases when the temperature is increased from 100 to 120 °C; a further increase in temperature, however, induces a sharp decrease in the percentage of grafting. The increase can again be explained on the basis of decreasing viscosity of the medium, promoting the grafting process, whereas the decrease in grafting of VAC after attaining a maximum (39% at 120 °C) may be due to the progress of various chain transfer reactions. For PAC, the percentage of grafting increases first slightly to reach a maximum of 29% at 110 °C, beyond which it decreases sharply. This decrease may again be due to the progress of various chain transfer reactions.

Effect of Amount of Water

The grafting is easier if water is used as the reaction medium (Fig. 3), the percentage of grafting growing with increasing amount of this solvent. This may be due to the fact that the two monomers are slightly soluble in water at the reaction temperature and so their access to the active sites is facilitated by the presence of water, whereupon the percentage of grafting increses. With 15 ml of water per 200 ml of the monomer, the percentage of grafting under the optimum conditions is 39% and 29% for VAC and PAC, respectively.

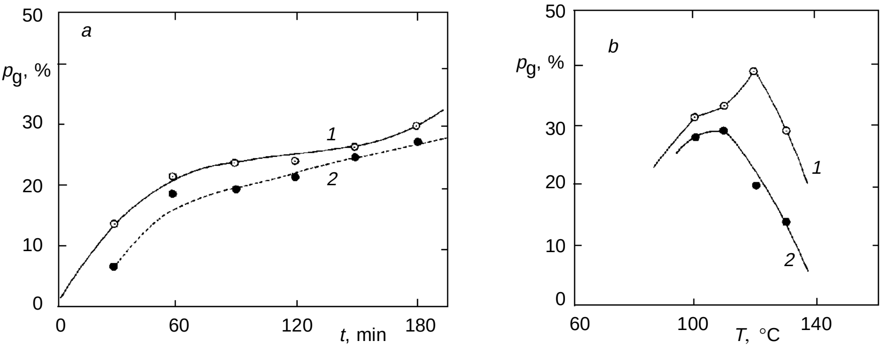


FIG. 2

Dependence of the extent of grafting on *a* the reaction time and *b* temperature; *1* poly(IPP)-*graft*-poly(VAC), *2* poly(IPP)-*graft*-poly(PAC). Reaction conditions: 100 mg of IPP, 15 ml of water, [VAC] = $144 . 10^{-2}$ mol l^{-1}, [PAC] = $120 . 10^{-2}$ mol l^{-1}, D = 57.60 and 56.80 kJ kg^{-1} for VAC and PAC, respectively; *a* temperature 100 °C, *b* reaction time 120 min

Effect of Solvent

The extent of grafting of VAC and PAC was also studied using different solvents. The results are presented in Table I. From among polar solvents, viz. water, methanol, ethanol and tetrahydrofuran, the maximum percentage of grafting of VAC (39%) was obtained in water, followed by methanol (28%), ethanol (22%) and THF (20%).

TABLE I
Effect of solvent upon the extent of grafting of VAC (2 ml) and PAC (2 ml) onto IPP (100 mg). The symbols p_5, p_{10}, and p_{15} denote the percentage of grafting in 5, 10, and 15 ml of solvent, respectively

Solvent	Monomer	p_5, %	p_{10}, %	p_{15}, %
H_2O	VAC	22	27	39
	PAC	16	22	29
MeOH	VAC	21	25	28
	PAC	16	18	21
EtOH	VAC	19	21	22
	PAC	15	14	17
THF	VAC	20	20	20
	PAC	15	17	23
1,4-Dioxane	VAC	25	23	22
	PAC	10	13	18
Cyclohexane	VAC	15	22	27
	PAC	16	11	9
Benzene	VAC	30	24	19
	PAC	18	14	13

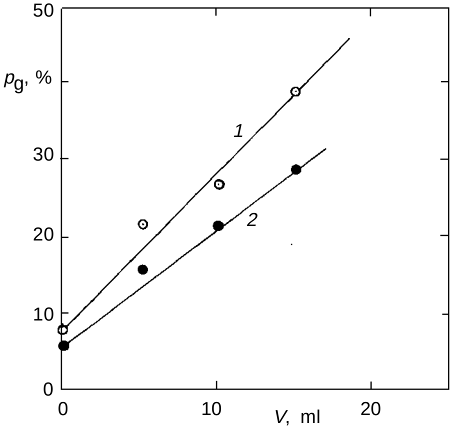
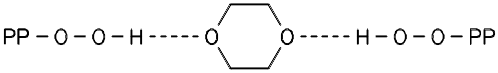


FIG. 3
Extent of grafting as a function of amount of water as the reaction medium: *1* poly(IPP)-*graft*-poly(VAC), *2* poly(IPP)-*graft*-poly(PAC). Reaction conditions: 100 mg of IPP, 2 ml of monomer, total radiation doses 57.60 kJ kg^{-1} (for VAC) and 56.80 kJ kg^{-1} (for PAC), 100 °C (VAC) or 110 °C (PAC), 180 min

Change in the fraction of THF had no effect on the percentage of grafting of VAC. The low percentage of grafting with methanol and ethanol is due to the fact that these solvents promote various chain transfer reactions, while water has a zero chain transfer constant. The chain transfer constants of VAC to methanol and ethanol at 70 °C are $5.5 \cdot 10^{-4}$ and $26.3 \cdot 10^{-4}$, respectively; so, ethanol with a higher chain transfer constant promotes the grafting to a lower extent than methanol.

In non-polar solvents, the extent of grafting is lower than in water or other polar solvents; the backbone polymer does not swell and the access of the monomer to the active sites is not facilitated by non-polar solvents. The solvent transfer constant of VAC is $3.6 \cdot 10^{-4}$ in benzene[15], $7.0 \cdot 10^{-4}$ in cyclohexane[16] and $49.1 \cdot 10^{-4}$ in 1,4-dioxane[17]. Although 1,4-dioxane has a higher chain transfer constant than benzene and cyclohexane, grafting is more extensive in it. This may be explained in terms of the fact that 1,4-dioxane, like water, is capable of forming hydrogen bonds with the hydroperoxide groups of polypropylene, thereby facilitating access of the monomer to the active sites owing to the swelling of the backbone polymer.



At higher concentrations of 1,4-dioxane, however, p_g decreases, since the growing grafted radicals participate in the chain transfer reaction with 1,4-dioxane.

The percentages of grafting of VAC in methanol (28%) and cyclohexane (27%) are almost the same, although methanol has a lower chain transfer constant than cyclohexane and so should promote the grafting to a higher extent. The same percentage of grafting in methanol, a polar solvent, and in cyclohexane, a non-polar solvent, is explained by the fact that poly(VAC), the homopolymer formed during grafting, is soluble in methanol; this increases the viscosity of the medium and hinders the mobility of the growing polymeric chains, thereby reducing the percentage of grafting. No such restriction in the mobility of the growing chains occurs in cyclohexane, which fact makes up for the non-polar nature of this solvent.

Isopropenyl acetate shows similar behaviour in water, methanol, ethanol, and benzene during grafting.

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