Grafting of Polypropylene Fibers. III. Electrical Conductivity of Grafted Fibers Polypropylene Grafted with Various Vinyl Monomers

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Synopsis

Electrical conductivity of polypropylene fibers grafted with methacrylic acid, vinyl acetate, and acrylonitrile for the samples conditioned at various relative humidities is reported. Electrical conductivity increases with the increase in graft in all three grafted polymers. The increase in conductivity of polypropylene fibers grafted with methacrylic acid is two orders of magnitude higher than control, while the increase in other cases is small. The results are explained on the basis of chemical structure of the grafted fibers. Increase in electrical conductivity with respect to methacrylic acid graft could be due to charge migration and electronic conductivity. In the case of the other two monomer-grafted PPs, increase could be predominantly due to electronic conduction.

INTRODUCTION

The electrical conductivity of cotton fibers was studied by Slater[1] as a function of relative humidity, and the studies were extended by various investigators.[2,3] Polycaprolactum mouldings were made electrically and thermally conductive by incorporating metals like Cu, Al, or Fe.[4] Brecial et al.[5] reported a decrease in resistivity of nylon by γ-irradiation. Kwarski and Buchenska[6] studied the electrical conductivity of nylon- and acrylic acid-grafted nylon fibers with different moisture uptake and swelling. The grafted fibers showed an increase in electrical conductivity. The conductivity of copolymers has been studied as a function of acrylic acid content in a copolymer of acrylic acid and acrylamide.[7] Conductivity of films of polypropylene and polyester was found to have increased on grafting with vinyl triethoxy silane.[8] Results obtained on the electical conductivity of polypropylene fibers grafted with methacrylic acid, vinyl acetate, and acrylonitrile are presented here and discussed.

EXPERIMENTAL

Materials

Polypropylene fibers grafted with methacrylic acid, vinyl acetate, and acrylonitrile, prepared as described earlier,[9] are used for measurement of electrical conductivity.

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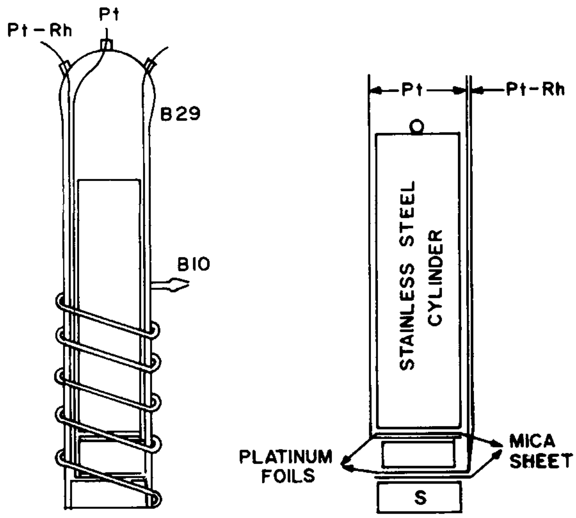

Fig. 1. Conductivity cell.

Apparatus

The conductivity cell is shown in Figure 1. The vacuum in the glass vacuum system was of the order of 10^{-4} mm obtained by means of a mercury diffusion pump and a rotary pump. The pressure was measured by a standard Mcleod gauge.

The conductivity cell was made of pyrex glass and was cylindrical in shape (l, 13.5 cm, d, 3 cm) closed at the bottom and fitted with a high vacuum standard joint at the top. For the evacuation of the cell, a glass spiral tube was connected at the bottom. Platinum electrodes (d, 2 cm, t, 0.1 cm) were used along with platinum lead wires. A platinum-rhodium thermocouple was welded to one disc, while the other disc was connected with platinum wire. The sample pallet (d, 1.4 cm and t, 0.15 cm) was placed in between the electrodes which were kept pressed against the sample with the help of stainless steel cylinder sealed in glass.

Measurement of Electrical Resistance

About 100 mg fibers were cut and palletized under a pressure of 12 to 15 tons in a press. The pallet was placed in between the electrodes in the conductivity cell. The cell was then evacuated for 6 h. The terminals of the two platinum wires were connected through a standard cell having a constant voltage (1.0018 V) to the electrometer amplifier type EA 814, made by Electronic Corporation of India Ltd. The conductivity cell, standard voltage source, and the wires were shielded from external signals by enclosing them in an aluminum box. The electrometer amplifier was switched on and the reading was recorded after equilibration. The input resistance was from a standard resistance box and the voltage across was read directly from the electrometer. The resistance was thus determined after calculating the current flowing. The

TABLE I
Relation Between Amount of Graft and Electrical Conductivity of Polypropylene Fibers Grafted with Different Vinyl Monomers

Vinyl acetate graft		Methacrylic acid graft		Acrylonitrile graft	
Graft %	Electrical conductivity $ohm^{-1} cm^{-1} 10^{-15}$	Graft %	Electrical conductivity $10^{-15} ohm^{-1} cm^{-1}$	Graft %	Electrical conductivity $10^{-15} ohm^{-1} cm^{-1}$
0	5.85	0	5.85	0	5.85
1.2	8.95	2.0	9.26	5.17	6.84
4.54	9.75	5.47	10.75	8.82	7.04
8.91	10.03	9.2	13.16	17.30	7.46
18.9	10.71	17.3	31.44	20.62	7.57

resistivity was calculated using the formula

$$\sigma = \frac{R \times A}{L}$$

where

σ = Resistivity, ohm cm

R = Resistance, ohm

A = Cross sectional area of the pallet cm^2

L = Thickness of the pallet, cm

The fibers were conditioned at different relative humidities (64-91%) first, and then after making their pallets, the measurements were performed for different moisture contents.

RESULTS AND DISCUSSION

The electrical conductivities of polypropylene fibers as a result of grafting with vinyl acetate, methacrylic acid, and acrylonitrile at various levels of graft in the fibers were determined and the results are given in Table I.

Figure 2 gives the logarithmic plot of electrical conductivity against the amount of methacrylic acid graft in polypropylene fibers. In general, the variation of electrical conductivity with the percentage of graft is similar for all three monomers studied. The electrical conductivity goes on increasing with the increase in the amount of graft, and if it is plotted on a log-log scale, a linear plot is obtained as is shown in Figure 3 for vinyl acetate-grafted polypropylene.

Figure 4 shows a log-log plot of the percentage relative humidity vs. electrical conductivity of polypropylene fibers grafted with these monomers at the same level of graft (9% approx.). For a given relative humidity value, the electrical conductivity is highest for methacrylic acid-grafted fibers and the least for acrylonitrile-grafted ones, possibly due to the high hydrophilic nature

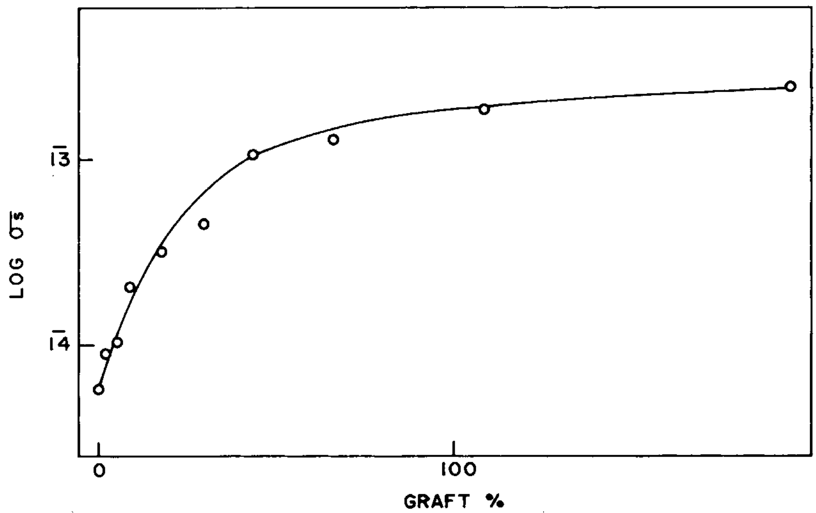

Fig. 2. Relation between graft percent and electrical conductivity of methacrylic acid-grafted polypropylene fibers.

of the grafted fibers. These results show deviation from those reported earlier in that the vinyl acetate-grafted polypropylene fibers were exhibiting lowest moisture regain compared to acrylonitrile-grafted polypropylene.[9]

Figure 5 gives the relationship between electrical conductivity and moisture content on log-log scale of the polypropylene fibers grafted with acrylonitrile, which is similar to methacrylic acid-grafted fibers. However, with vinyl acetate-grafted fibers there is a break in the linear plot at moisture content of 0.59% (Fig. 6). It is apparent that at lower moisture content values the rise in conductivity is not as sharp as at higher moisture values. This could be due to the decrease in the amount of the medium (moisture) for the electrical

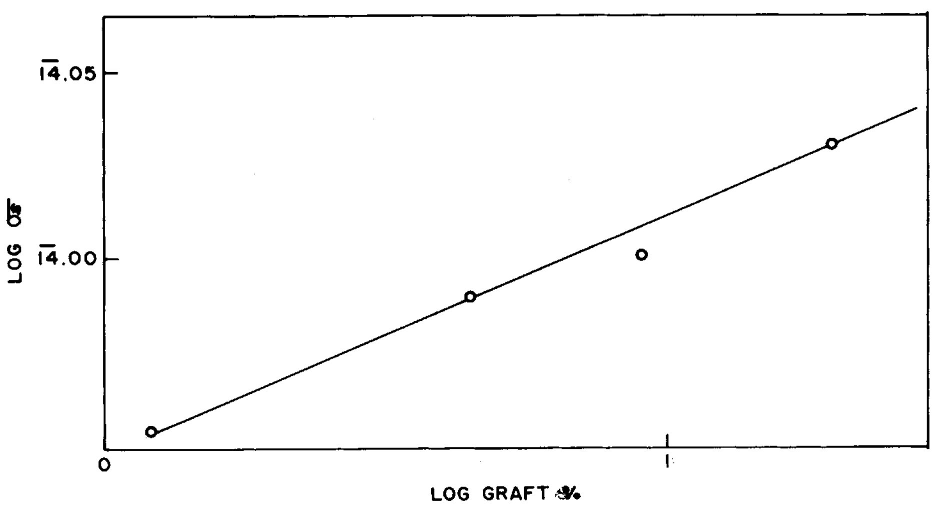

Fig. 3. Relation between graft percent and electrical conductivity of vinyl acetate-grafted polypropylene fibers.

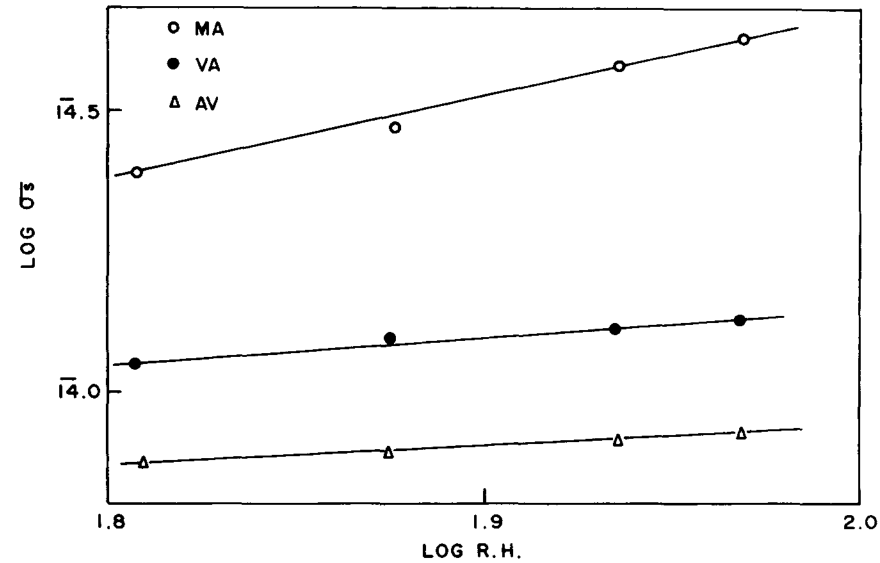

Fig. 4. Relation between relative humidity and electrical conductivity of polypropylene fibers grafted with VA, MA, and AN at the same level of graft (9%).

transport. It appears that a minimum threshold of moisture content is always needed.

The parameters which determine the electrical conductivity are the number of charge carriers and their movement through the bulk of the polymer. These parameters can be related to the chemical composition and morphology of the polymer. The origin of the charge carriers may be electrons or positive holes. The mobility of the charge carrier is determined from the polymer matrix,

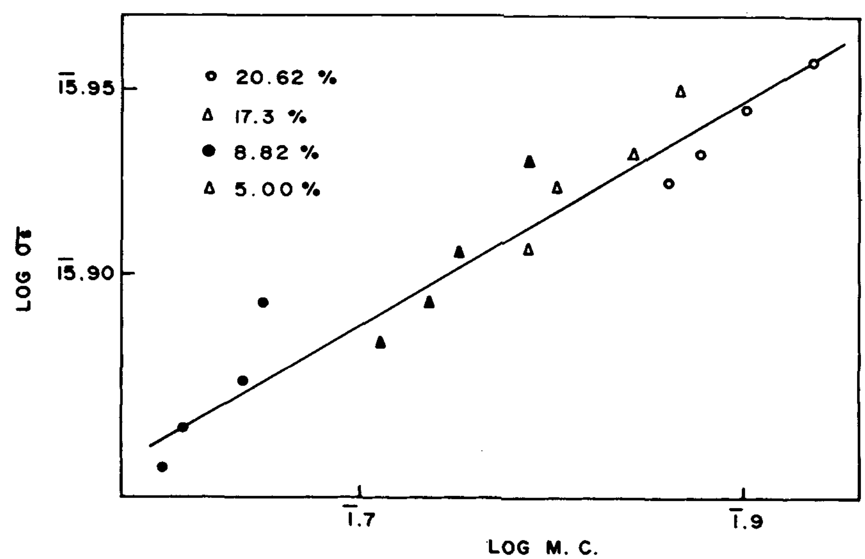

Fig. 5. Relation between moisture content and electrical conductivity of acrylonitrile-grafted polypropylene fibers.

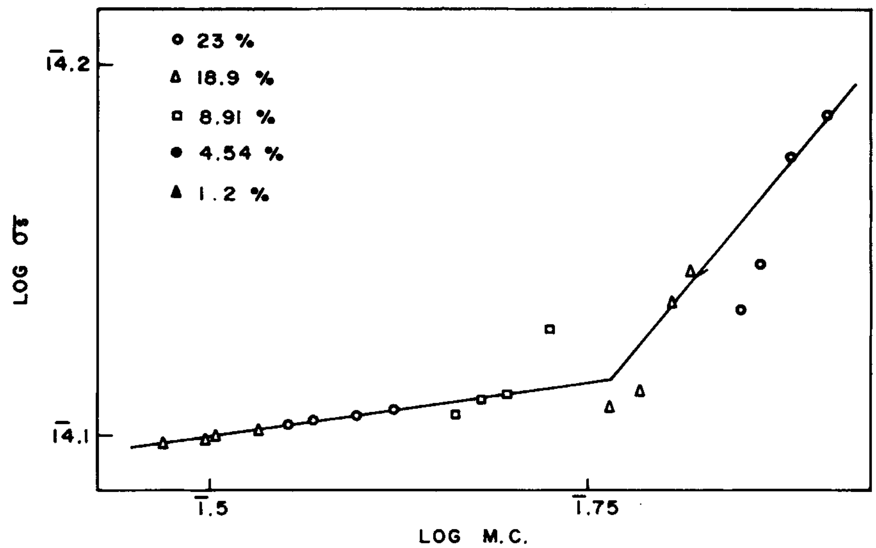

Fig. 6. Relation between moisture content and electrical conductivity of vinyl acetate-grafted polypropylene fibers.

which is modified by grafting. In polymers, the conductivity is due to the migration of charge carriers (i.e., protons or electrons).

Bercial et al.[5] reported increased conductivity with Nylon-6 after γ-irradiation, and found that after annealing the samples at 70°C the original conductivity was restored. This showed that the conductivity was perhaps due to the mobility of trapped electrons. They proposed that both protonic and electronic conduction might be responsible for the increase in electrical conductivity. Ikeda and Matuda[11] have suggested that at low temperatures the conductivity could be electronic in nature and at higher temperatures the ions could be participating. The difference in the electrical conductivity observed with vinyl acetate when compared to methacrylic acid and acrylonitrile could be explained on the basis of the chemical modification of the grafted chains. As suggested earlier the increase in electrical conductivity could be due to the migration of the protons as well as electrons. In the case of methacrylic acid graft, for each monomer molecule grafted on to the backbone polymer one proton is available for charge migration. The increase in conductivity should be greater for methacrylic acid-grafted material which, in fact, is observed. The contribution from ionic migration could be more than the contribution from the electronic migration. In case of vinyl acetate and acrylonitrile, since the magnitude of increase in the conductivity is quite low, the electronic conduction might be the primary source. The observed difference between the acrylonitrile- and vinyl acetate grafted-materials could be accounted for by their different chemical structures. The repeat unit in acrylonitrile-grafted material contains a triple bond in —C≡N, which might develop into a three-dimensional network structure through —C=N— linkage.[9] The same type of behavior was observed earlier with nylon irradiated for higher dose whose decrease in electrical conductivity was explained as being due to crosslinking. Perhaps this could also be due to the effect of radiation.

CONCLUSION

The electrical conductivity observed with grafted polypropylene fibers with methacrylic acid is two orders of magnitude higher than control. This is explained as being due to the mobility of both the charge carriers and electrons. In case of acrylonitrile- and vinyl acetate-grafted materials, the conductivity increase is marginal and it is explained solely due to the mobility of electrons.

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