

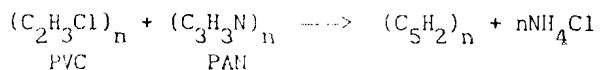
SUMMARY

INTRODUCTION

Polyvinylchloride (PVC) and polyacrylonitrile (PAN) are the two base polymers which in the form of their blends constitutes the materials of investigation in the study embodied in this dissertation. Theoretically, PVC-PAN blends may offer several interesting possibilities.

First, it will be interesting to see if NH_3 , evolved from PAN could influence the degradation (deHCl process) of PVC, and on the otherhand, if HCl produced from the degradation of PVC would influence the polymerization of nitrile groups in PAN.

Second, in case of any mutual interaction between the two homopolymers, whether thermal degradation of PVC and PAN in their blends would render an effective removal of nitrogen to a structure which will be steps ahead to the formation of carbon fibers according to the following reaction



Beyond these possibilities, the third interesting aspect is the study of the electrical conductance behavior of suitably degraded PVC-PAN blends at various compositions. It is envisaged that PVC on complete dehydrochlorination would offer a polyene skeleton very similar to that of polyacetylene. PAN, under the condition of the same thermal treatment would offer conjugated polyimine

structure.

It is expected that the lone pair of nitrogen may effectively make the polyimine sequence in degraded PAN an electron rich conjugated system and would act as donor to extended polyene conjugation in degraded PVC. It will be interesting to see if an intimate blend of thermally polymerized PAN and dehydrochlorinated PVC would mutually dope each other and thereby exhibit synergized electrical conductivity. This possibility of mutual doping by the degraded PVC and PAN constitutes the primary aspect of investigation which is embodied in this thesis.

PROGRAM OF INVESTIGATION

With these primary objectives, the present investigation has been divided into several parts.

In the first part, a detail analysis of thermal degradation of PVC covering a wide range of temperature and all the possible mechanistic aspects of its degradation has been made. The major objectives of this study were to ascertain the right condition of temperature and environment to effect complete dehydrochlorination of PVC to conjugated polyene sequence which has not undergone any significant structural changes due to secondary reactions like crosslinking, isomerization, aromatization, Diels-Alder type of reaction etc.

A rational interpretation of the thermal degradation characteristics of polyacrylonitrile (PAN) by combined differential thermal analysis and thermogravimetric analysis in inert atmosphere constitutes the second part of the investigation. The primary objective was to ascertain the optimum conditions of

(iii)

temperature and environment to effect the intramolecular polymerization of nitrile groups of PAN to a conjugated polyimine structure with little structural degradation.

The third part of the investigation is concerned with preparation of PVC-PAN blends and their thermoanalytical characteristics by DTA-DSC-TGA techniques. The basic aim has been to see if the individual homopolymers interfere with each other in their thermal degradation and lead to removal of nitrogen in the form of NH_4Cl . The other objectives have been to see if the homopolymers are compatible to each other, and to ascertain the conditions of thermal degradation, that would ensure formation of polyconjugated structures from the individual homopolymers.

The fourth and the concluding part of the investigation relates to the spectroscopic and electrical conductivity characterization of the degraded blends of PVC and PAN. The primary objectives were to see if there could be any electronic interaction between the thermally degraded phases of the two homopolymers, and whether any synergized electrical conductivity could be observed in the degraded blends.

RESULTS AND CONCLUSIONS

Thermal Degradation of PVC

Four distinct stages have been observed in the thermal degradation of PVC. The first stage, spanning upto a temperature of 185°C is essentially eventless with no net thermicity or mass loss.

The second stage of degradation spans upto $\sim 375^\circ\text{C}$ and is primarily an almost quantitative endothermic dehydrochlorination to some polyene residue.

(iv)

The endothermic dehydrochlorination in the second stage is preceded by a weakly exothermic decomposition of hydroperoxide group possibly to carbonylallyl group which starts at about 190°C. Tertiary chlorine and allylic chlorine sites together with carbonylallyl sites appear to initiate zip-like dehydrochlorination of PVC.

The third stage degradation starts after 375°C and involves structural reorganization, represented by such processes as crystallization, isomerization, crosslinking and aromatization, which accompany elimination of certain moieties with a steady weight loss. Both crosslinking and aromatization are most likely to be preceded by Diels-Alder type of addition involving polyene sequences.

The fourth stage of degradation, which generally occurs beyond 500°C, is only poorly understood, and perhaps involves structural breakdown of an organized carbonaceous residue from the third stage.

Retention of eliminated HCl in the second stage of degradation is greatly enhanced by bigger particle size or higher film thickness of PVC. Besides a possible catalysis offered to the actual dehydrochlorination process, the role of liberated HCl is perhaps best appreciated in terms of its catalyzing a set of secondary reactions in the second stage itself which normally should have occurred in the third stage. The thermal analytical behavior of a base catalyzed dehydrochlorinated PVC at low temperature and a very finely powdered PVC precipitated from its solution in DMF lends support to the proposed role of the liberated HCl.

(v)

The study shows that a very fine particulate form and a temperature lower than 280°C are necessary for isothermal degradation of PVC that would offer a conjugated polyene residue which is very close to polyacetylenes in structure.

Thermal Degradation of PAN

Studies on the thermal degradation of PAN have provided more insight into the role of microstructure in the thermal degradation of PAN. It has been inferred from the studies that (a) the low temperature anaerobic polymerization of PAN is confined primarily to the amorphous zone, (b) polymerization in the crystalline zones takes place only after melting of crystallites, (c) HCN is predominantly given off from the chain segments at the amorphous-crystalline interface at the onset of crystalline melting, and (d) NH_3 is liberated at the end of the melting process. The equilibrium melting temperature of PAN has also been estimated from the thermal analytical data.

Thermal Degradation of PVC-PAN Blends

The DSC studies of the PVC-PAN blends at various compositions suggest that the two individual polymers are basically incompatible to each other mainly due to large difference in their solubility parameters. But there might be some compatibility window at compositions around 80 PVC/20 PAN and 80 PAN/20 PVC. The thermal degradation pattern of the blends at different proportions of PAN and PVC show that the homopolymer components of the blends degrade individually with little mutual interference. The results also suggest that the degraded phases from PVC and PAN form separate domains in the degraded blends. The study also discounts the possibility of a chemical interaction leading to complete removal of nitrogen and chlorine in the form of NH_4Cl .

Characterization of Thermally Degraded Blends

Thermal degradation of PVC, PAN and their blends indicates that a temperature of 275°C or less and a time of 24h would ensure complete and desired degradation of the homopolymers with little or no mutual chemical interference between the degraded phases of PVC and PAN, nor any thermally aided secondary chemical transformation within the degraded phases.

The UV-Vis spectra of the degraded blends showed no difference in their features and offered no positive or negative indication about any electronic interaction between the two phases. In the X-ray diffractograms of the degraded blends some peaks characteristic of trans- and cis- polyacetylene have been observed. But the intensities were very low. Some characteristic lines due to crystalline PAN are, however, observed in the degraded blends, particularly those containing higher proportion of PAN.

Electrical conductivity of the degraded blends show distinct synergistic effects. For the degraded blend of 100% PVC, the observed electrical conductivity at room temperature was $-\log\sigma = 13.1$ with the increase in the PAN content, the conductivity increased and reached a maximum value of $-\log\sigma = 5.31$ at an original composition of 60% PAN. Beyond this, the conductivity again steadily declined till it reached a value of $-\log\sigma = 7.5$ for 100% PAN.

The results show that the mutual doping between the degraded phases of PVC and PAN is quite possible, although the nature of this interaction and experimental evidence in support of the same could not be established by UV-Vis and solid state NMR spectroscopy.