

Studies on Interfacial Adhesion, Tensile and Thermal Characteristics in Blends of Polystyrene/Novolac Resin

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ABSTRACT: Specific interactions generate stability of the component parts in blends. Present work aims to elucidate intermolecular interactions in polystyrene/novolac blends by means of Infrared spectroscopic studies. It was found that strong interactions were observed at band 3095 cm^{-1} assigned to aromatic C–H stretching vibrations, at band 2980 cm^{-1} assigned to aliphatic C–H stretching vibration and at band 1635 cm^{-1} assigned to C=C stretch vibration of aromatic ring system. Maximum interaction was observed in blend consisting polystyrene/novolac (80:20 by parts, in this study it is blend B). Mechanical and thermal properties of the blends were also studied. Tensile strength data was found maximum in blend B. Nonisothermal method of Freeman

and Carrol was used to investigate the kinetics of thermal degradation. The reactions were studied by thermogravimetry in nitrogen atmosphere. Decomposition of the blends was found in consecutive stages. The activation energies were determined for each stage of reactions. From thermal studies, blend B was found to be most stable. A degradation mechanism was suggested by compiling the reports of previous authors. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4630–4636, 2006

Key words: polystyrene/novolac blend; infrared spectroscopy; mechanical properties; thermogravimetry; activation energy

INTRODUCTION

Interfacial adhesion in polymer blends refers to the bonding between its phases. Truly miscible polymer blends are rare, particularly in commercial use. In practice, two or more polymers are blended together to form a wide variety of structured morphologies, to obtain products that potentially offer desirable combinations of characteristics. In immiscible blend, there exists an interfacial layer of about 4 nm thickness containing about 60% of one polymer.¹ This layer is termed as interfacial region or simply an interphase, a third phase in the immiscible blends with its own characteristic properties. Interfacial failure under low stress is customarily said to be due to poor adhesion of the polymers in the blend. There is little mixing of the two polymers at the interface resulting in high interfacial tension. Interfacial tension also imposes a limit on the phase size, which can be attained under a suitable condition of shear mixing. When the interfacial tension is lower, phase size will be smaller and adhesion at the interface of the blend will be more. Interfacial energy, structure, and adhesion between polymers are related to the tensile and thermal properties of the polymer blends. Van der Waal forces and diffusion of polymer chains across the interface is necessary for a strong

bond. Van der Waal attraction is 2.5 kcal/mol, whereas chemical bond energy is about 80 kcal/mol. Thus, interfacial chemical bonds could be utilized effectively to promote adhesion. Reactive functional groups like hydroxyl, carboxyl, etc., have been found to promote adhesion at the interface in polymer blends. Generally, hydrogen bonding groups, acid/base groups, charge transfer complexes, ionic groups, etc., have been found to be very effective adhesion promoters.

Polystyrene (PS) is a noncrystalline commodity resin.^{2–4} It contains π orbitals in the aromatic rings and active hydrogen of the CH group.⁵ These may cause specific interactions with other polymers. The styrenic part may impart the properties like toughening, flame resistance, and solvent resistance. Polystyrene has many deficiencies in several technological properties,⁶ and from a commercial point of view, it requires modifications by multiphase polymer systems. As a modifying polymer, novolac resin^{7,8} was used in the present work. The objective of the present work is to elucidate specific interactions between the two polymers in blends⁹ and the thermal degradation characteristics⁷ along with the mechanical properties.

EXPERIMENTAL

Materials were used in their normal commercial forms without preparatory treatment.

Polystyrene, a radically initiated linear atactic polymer, was obtained from L.G. Polymer, Vishakapatnam,

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TABLE I
Composition of the Blends

| Name of the blend | Styrene (wt %) | Novolac (wt %) |
|-------------------|----------------|----------------|
| Blend A | 90 | 10 |
| Blend B | 80 | 20 |
| Blend C | 70 | 30 |
| Blend D | 60 | 40 |
| Blend E | 50 | 50 |

AP. Novolac, a soluble and fusible polymer, was obtained from Allied Resin and Chemical (West Bengal).

Blend preparation

Finely powdered polystyrene and novolac were taken by varying their weight ratio as shown in Table I. These were separately mixed in a blender (solid phase mixing). Then, the premix material was passed through a laboratory size extruder (1½ inch size) at 100°C (melt mixing). The extruded material was chopped into pieces, cooled, and grounded to a fine powder in a high power blender. This powdered blend was then characterized by the following methods.

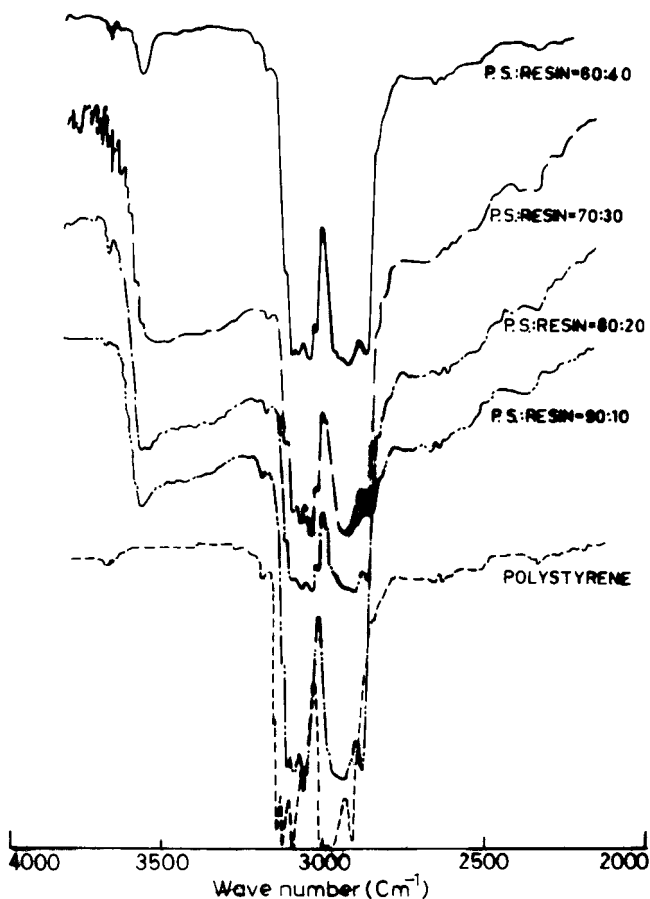


Figure 1 Portion of IR of polystyrene/novolac resin blend.

Spectroscopy

Very thin transparent films were prepared both by compression molding and by solution-casting over mercury. Spectra were recorded on a PerkinElmer 1330 Infrared Spectrophotometer at a resolution of 2 cm^{-1} and 16 scans.

Physical testing

Sheets were prepared in a laboratory compression type press (460 mm × 460 mm platens) in a flat mold of 220 mm × 300 mm. Temperature was set at 220°C and pressure was maintained at 15 N/m^2 for 5 min. Sheet formed after cooling under pressure was used for physical testing. Bar samples (4 mm width) were prepared using electric cutter. Samples were tested in an Instron Universal Tensile tester machine (model

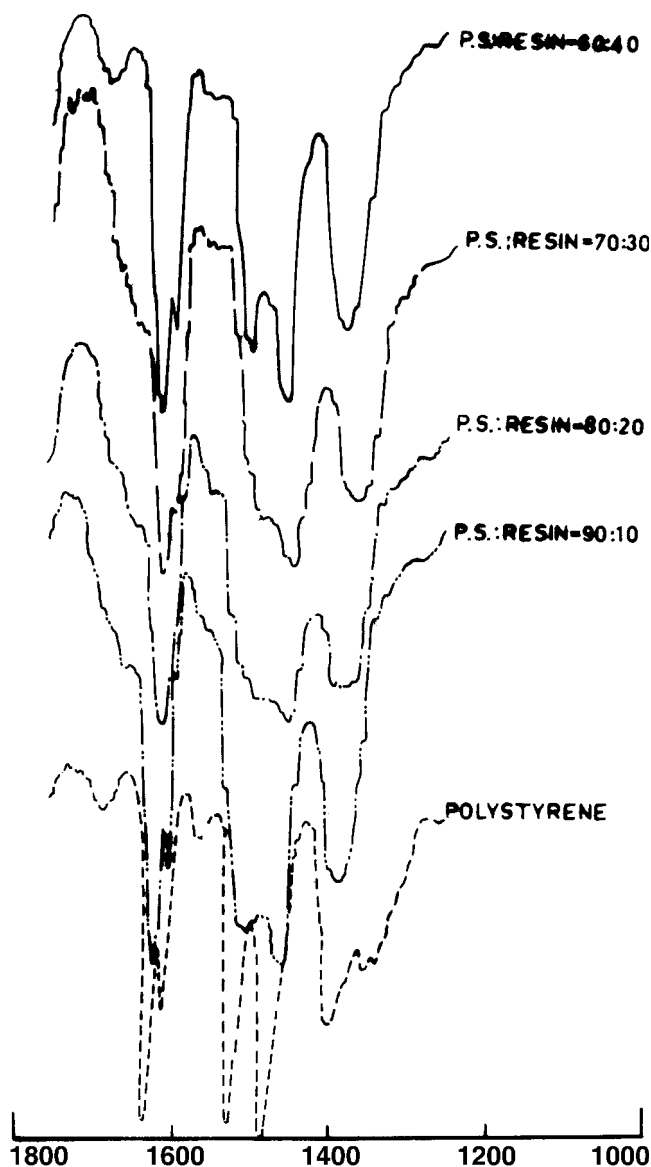


Figure 2 Portion of IR of polystyrene/novolac resin blends.

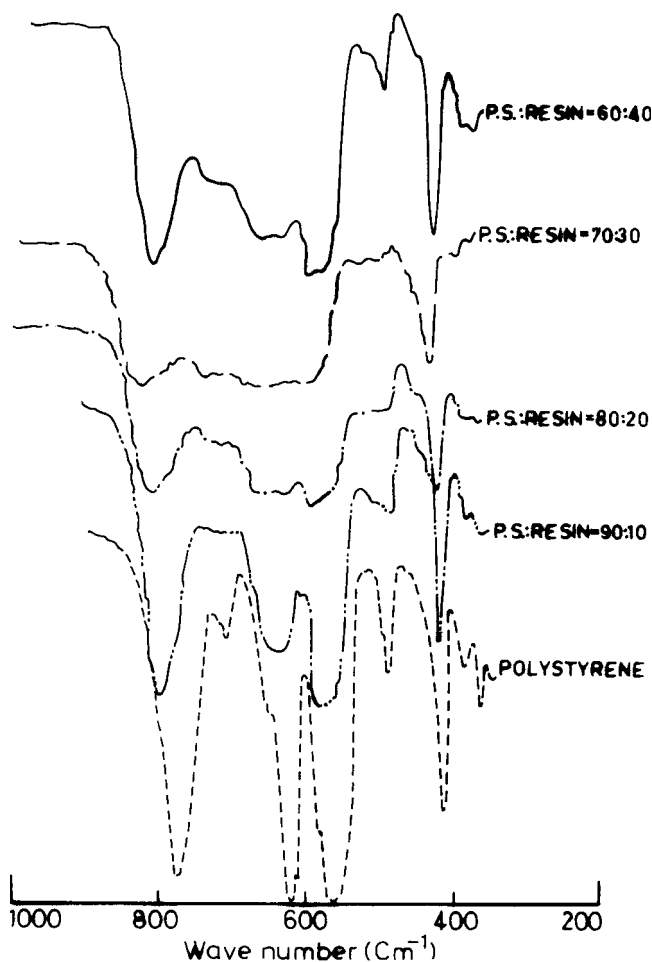


Figure 3 Portion of IR spectra of polystyrene/novolac resin blends.

4301) at a pulling rate of 5 mm per minute at room temperature (30°C), according to ASTM Standard D 412-87. Hardness was measured according to ASTM D 2240-86.

Thermal

Pyrolysis was done in a PerkinElmer TA C7/3 Thermogravimetric Analysis (TGA) instrument in nitrogen atmosphere at a scanning rate of 20°C/min over the temperature range of 40 to 500°C.

RESULTS AND DISCUSSION

Spectroscopy

Infrared spectroscopy (IR)¹⁰ was used in characterization of bonding of polystyrene and novolac resin blends. The spectra of the blends are shown in Figures 1-3. The results obtained from the figures are given in Table II. It is clearly observed from Table II that the peaks due to pure polystyrene are shifted in the blends. The characteristic peak 3095, 2980, and 2910 cm⁻¹

of pure polystyrene are shifted to 3030, 2920, and 2860 cm⁻¹ in blend-D. The strong band near 3095 cm⁻¹ in polystyrene occurs due to aromatic C-H stretching vibrations. This band is shifted to lower wave number with increasing amount of novolac in the blends, and this shift is maximum (65 cm⁻¹) in Blend-D with 40 wt % novolac. It clearly indicates strong intermolecular interaction between polystyrene and novolac in the blend. It is also interesting to note that in pure novolac band at 3620-3590 cm⁻¹ due to the O-H stretching vibration is little affected in the blends (3600 to 3500 cm⁻¹), signifying no macromolecular conformation of hydrogen bonding in the blend. Similarly, the change of the peak at 2980 cm⁻¹ is due to aliphatic C-H stretching vibrations, and the change at 2910 cm⁻¹ is due to CH₂ stretching absorption in polystyrene-novolac blends. Apart from these, results from Figure 2 also indicate two shifts (1635 to 1610 cm⁻¹ and 1485 to 1450 cm⁻¹). The bands are responsible for C=C stretch vibration due to aromatic ring system. There is a rhythmical movement along bond axis and peaks are considered as important peaks. Results also show shift towards lower wave number in blends, indicating the presence of intermolecular interaction due to aromatic rings of polystyrene and novolac.

Results obtained from Figure 3 are also shown in Table II. It is the fingerprint region and contains particularly large number of unassigned vibrations. Two important peaks are at 775 and 560 cm⁻¹. Both the peaks have a shifting tendency towards higher wave number (775 to 820 cm⁻¹ and 560 to 605 cm⁻¹). It is opposite to previous shifts. This is due to the functional group interactions, either intermolecular or intramolecular. Peak at 775 cm⁻¹, C-H bending vibration connected to aromatic ring (out of plane bending) and at 560 cm⁻¹ inplane bending of functional group "ethylbenzene" (-CH₂CH₂-)



i.e., =C-C-C- group.

These results are important as the bending vibration may consist of a change in bond angle between bonds with common atoms or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with

TABLE II
Spectral Data of Polystyrene-Novolac Resin Blends
(Vibration Wave No., cm⁻¹)

| Polystyrene | Blend A | Blend B | Blend C | Blend D | Novolac resin |
|-------------|---------|---------|---------|---------|---------------|
| 3,095 | 3,050 | 3,040 | 3,040 | 3,030 | 3,020 |
| 2,980 | 2,950 | 2,920 | 2,930 | 2,920 | 2,920 |
| 2,910 | 2,880 | 2,850 | 2,860 | 2,860 | 2,850 |
| 1,635 | 1,610 | 1,605 | 1,605 | 1,610 | 1,610 |
| 1,485 | 1,470 | 1,450 | 1,445 | 1,450 | 1,450 |
| 775 | 800 | 810 | 820 | 820 | 820 |
| 560 | 585 | 600 | 605 | 605 | 605 |

TABLE III
Mechanical Properties of Polystyrene–Novolac Blends

| | Tensile strength (MPa) | Difference from P.S. (MPa) | Hardness Shore D (at 30°C) | Difference from P.S. Shore D |
|-------------|------------------------|----------------------------|----------------------------|------------------------------|
| Polystyrene | 40 | – | 75 | – |
| Blend A | 56 | +16 | 77 | +2 |
| Blend B | 130 | +90 | 78 | +3 |
| Blend C | 60 | +20 | 82 | +7 |
| Blend D | 50 | +10 | 84 | +9 |
| Blend E | 49 | +9 | 84 | +9 |
| Novolac | 55 | – | 84 | – |

respect to one another. However, since the upper critical solution temperature (UCST) for this system is well known,¹¹ and steric restrictions¹² were detected; there is no reason to expect strong interactions of this type. But the most sensitive vibrations to change intermolecular environment may be out-of-plane CH (775 cm^{-1}) in polystyrene and in plane bending (560 cm^{-1}) in novolac, respectively. The present work reports on the peak shift in blends due to intermolecular interactions between components of the blends. This is not due to hydrogen bonding as evidenced by the peaks, i.e., —OH absorption region ($3500\text{ to }3600\text{ cm}^{-1}$),¹³ —C=O stretching (1737 cm^{-1})¹⁴ and —CH₂— symmetric stretching (2886 cm^{-1}),¹⁵ which are not affected in the blend. Interactions regulate compatibility among the component polymer molecules and could be used to elucidate molecular mechanism, if any, involved in mechanical and thermal properties.

Mechanical properties

Blend properties are shown in Table III. Highest tensile strength was found for the experimented blend "B" (polystyrene:novolac = 80:20). Upon further increase of resin (novolac) concentration, there is a decrease in tensile strength. The maximum tensile strength of blend B may be due to the optimum interaction between the two polymers in this blend as also evidenced by maximum shift in the characteristic peaks of polystyrene in this blend discussed above under Spectroscopy. Spectroscopic analysis also indicates that peaks 2910 , 1635 , and 1485 cm^{-1} change

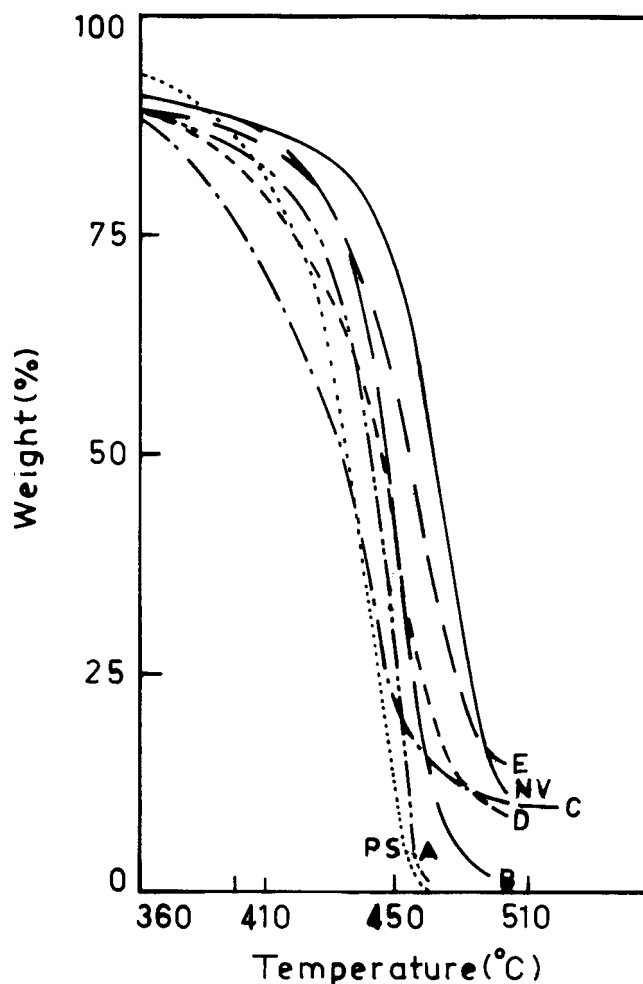


Figure 4 Thermogravimetric analysis. Pyrograms of polystyrene (PS)/novolac(NV) resin blends, PS : NV = A 90 : 10, B 80 : 20, C 70 : 30, D 60 : 40, E 50 : 50.

upto "blend B" and then remain unaltered, i.e., after blend "B," C—H stretch and C—C stretch vibration is not affected further. Decrease in tensile strength in blend C or D may be ascribed to increase in flaws between the layers of blend molecules with high resin concentration.¹⁶ Property such as hardness is less dependent on such flaws and continues to improve with increase in concentration of novolac.

TABLE IV
Thermogravimetry Analysis of Polystyrene–Novolac Resin Blends

| | Initial decomposition temperature | Temperature of maximum weight loss (very rapid rate temp.) (°C) | Weight loss at the end in sample weight up to 500°C (%) |
|-------------|-----------------------------------|---|---|
| Polystyrene | 417 | 455 | 100 |
| Blend A | 437 | 469 | 97.9 |
| Blend B | 437 | 467 | 98.3 |
| Blend C | 407 | 455 | 89.6 |
| Blend D | 430 | 469 | 90.3 |
| Blend E | 439 | 471 | 84.1 |
| Novolac | 431 | 482 | 87.6 |

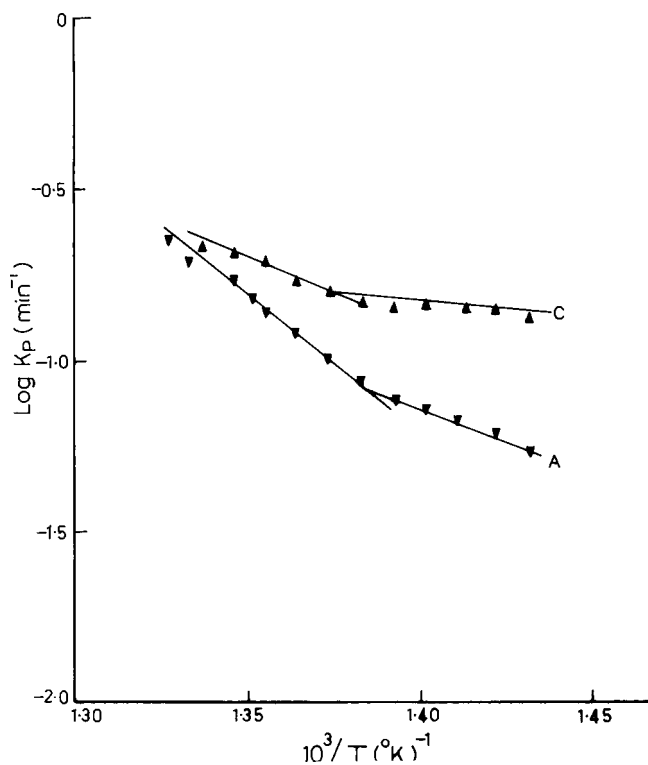


Figure 5 Arrhenius plots for the decomposition of polystyrene/novolac resin blend (A and C).

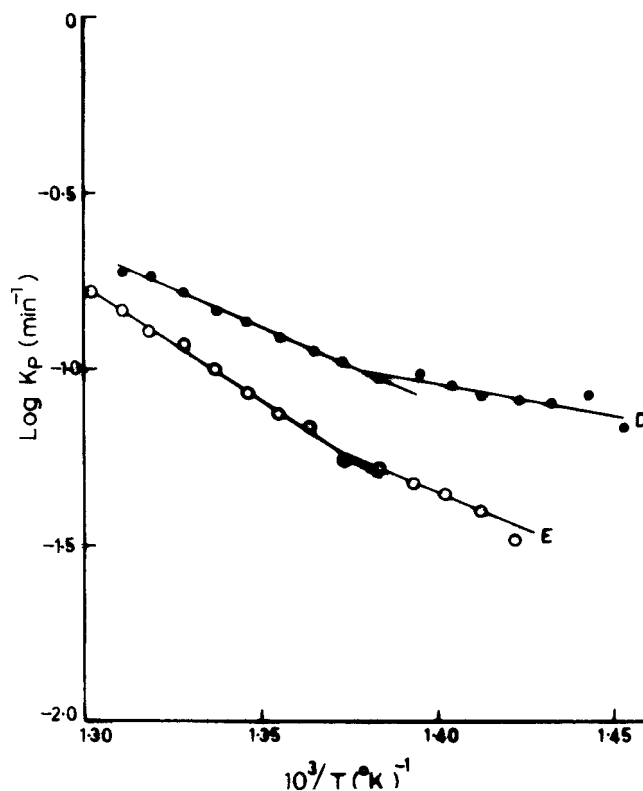


Figure 7 Arrhenius plots for the decomposition of polystyrene/novolac resin blend (D and E).

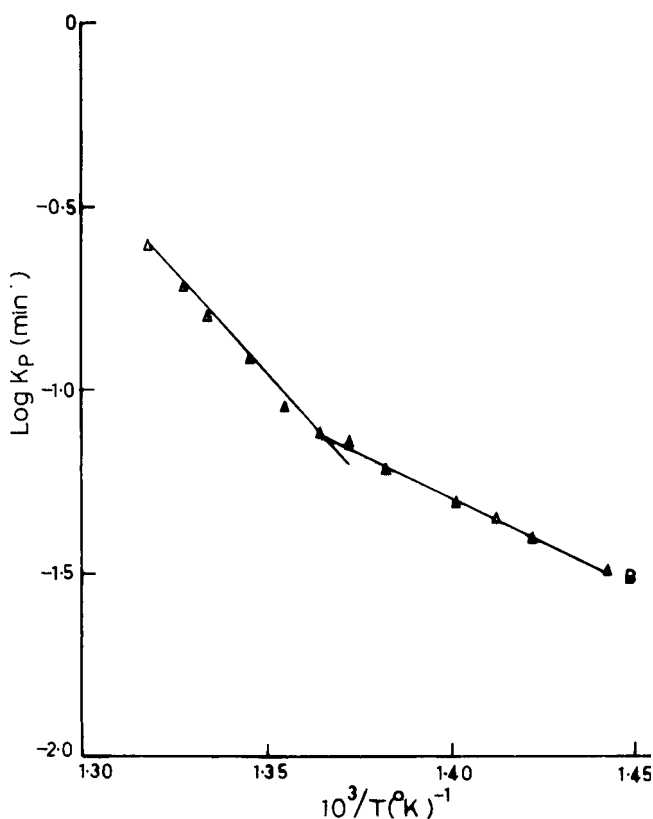


Figure 6 Arrhenius Plots for the decomposition of polystyrene/Novolac resin blend B.

Thermal stability characteristics

It has been found from many observations that energies of the formation and deformation of molecules are dependent on the type of primary bonds.¹⁷ Thermal stability of polymers is mainly influenced by primary bond. But secondary bonds (intermolecular bonds) also affect it. It has been noted that blending may change shear or thermal degradation of polymer.¹⁸ Pyrolytic stability indicates bond strength (both primary and secondary). For useful application knowledge of bond strength is essential for blend selection. In polystyrene–novolac blend systems, important purpose of observation is to study the stability at elevated temperatures in the absence of oxygen (to avoid oxidative degradation) for longer period of heating at typical processing temperature. In nitrogen atmosphere (i.e., in presence of an inert gas), thermogravimetric analysis (integral curves of pyrolysis under nonisothermal condition) represented by residual weight (%) versus temperature curves ranging 360–510°C are shown in Figure 4. The onset of decomposition temperature of all the blends are shown in the Table IV. No systematic results for the onset of decomposition temperature (T_p) of the blends were observed.

All decomposition reactions begin slowly and become very rapid at temperatures (derivative peak value) shown in Table IV. Decomposition results in

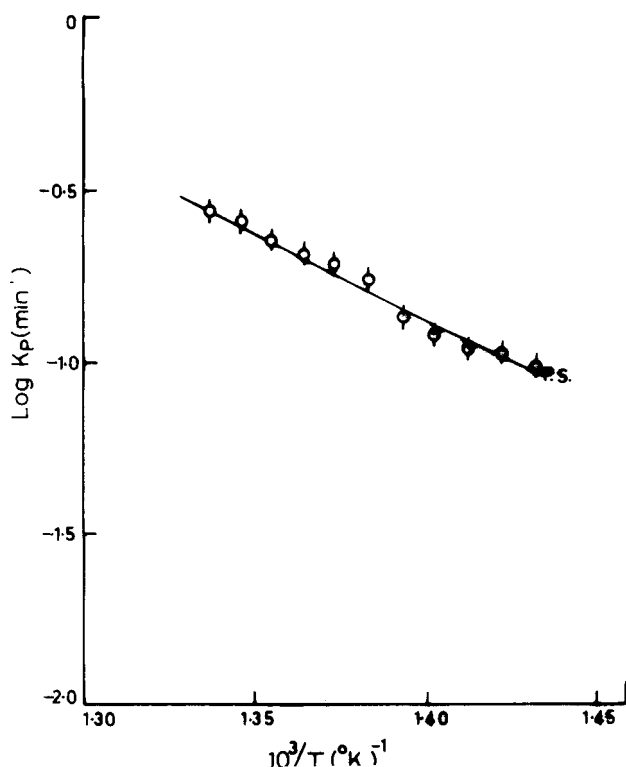


Figure 8 Arrhenius plot for the decomposition of polystyrene.

terms of loss percentage at the end (upto 500°C) are shown in the Table IV. From Table IV, it is observed that all blends and resin except polystyrene have a residue at 500°C. Decomposition curves contain the information necessary to evaluate kinetics of degradation by the method of Freeman and Carroll.¹⁹ Initial points do not fall on a straight line. So points corresponding to the degradation reactions are taken from 400°C. Temperature dependent Arrhenius plots are shown in Figures 5–9. Activation energies are calculated as shown in Table V. These results indicate that except polystyrene all degradation processes take place by two steps, one at low temperature and other at high temperature and thus two activation energies are evaluated. Between these two, low temperature value is always lower than high temperature value. Lower value is due to splitting of small molecules or monomers²⁰ while higher value indicates random cleavage (carbon-carbon bonds) mechanism of degradation.²¹ Hence, mechanism of degradation of blends and resin is a function of temperature and their rate parameters are different. Polystyrene degradation is caused by splitting off styrene monomer²⁰ due to its low activation energy (23.795 kcal/mol) of degradation. Effect of resin concentration in blends influences the normal degradation (Fig. 4). Polystyrene shows complete pyrolysis at 470°C and blends show higher than polysty-

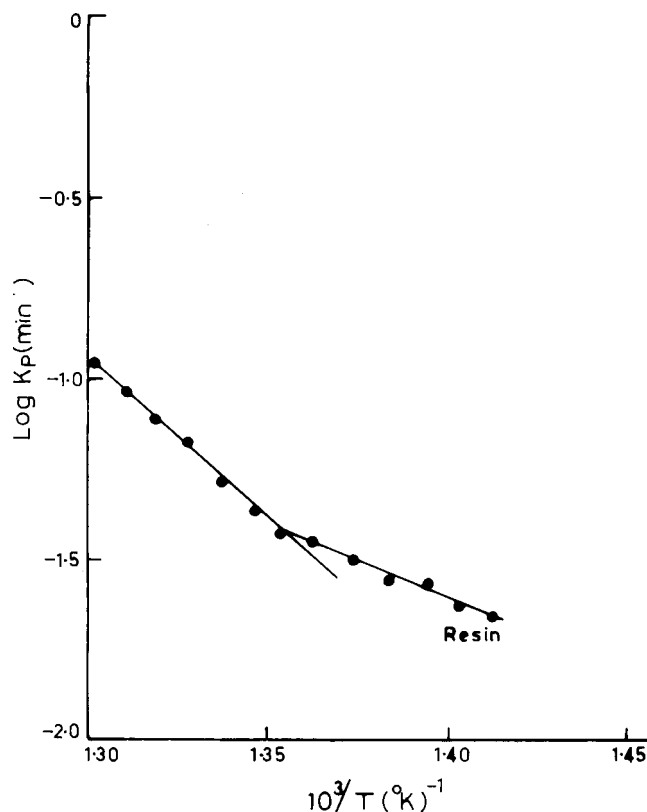


Figure 9 Arrhenius Plots for the decomposition of novolac resin.

rene. Therefore, kinetic parameters of blends are different from polystyrene. Addition of different amounts of resin causes increase in total activation energy (E_p) values. At the first part of degradation (lower temperature region), rate coefficient (k_p) of blends increase more than that of polystyrene and has a maximum value in blend "C" (82.5% greater than polystyrene and 77.3% than resin). Unsymmetric order of rate increase in blends can not be associated with resin amount but must be attributed to some destabilization of the polystyrene by the resin. The data of first activation energy as given in Table V also reveal that destabilization is insignificant in blend "B" (polystyr-

TABLE V
Activation Energy Values of PS/Novolac Blends

| Compound | First activation energy (EP) (kcal/mol) | Rate increase from PS (%) | Second activation energy (EP) (kcal/mol) |
|----------|---|---------------------------|--|
| PS | 23.79 | — | — |
| A | 17.60 | 26.0 | 36.23 |
| B | 21.97 | 7.6 | 50.34 |
| C | 4.16 | 82.5 | 19.61 |
| D | 8.32 | 65.0 | 20.02 |
| E | 19.89 | 16.4 | 29.29 |
| Resin | 18.30 | 23.1 | 41.18 |

ene:resin is 80:20). It is also interesting to note from the data that at higher temperature the degradation is C—C chain scission. Rate coefficient (k_p) is lowest in blend B (activation energy, E_{p2} , is 50.34 kcal mol⁻¹), which is also better than that of the pure resin (E_{p2} is 41.18 kcal mol⁻¹) signifying synergistic stabilization in blend B.

CONCLUSIONS

Infrared spectrum of polystyrene, resin, and their four different blends in the three important regions (4000–2000 cm⁻¹, 2000–1000 cm⁻¹, and 1000–200 cm⁻¹) have been studied. Band assigned to aromatic C—H stretching vibrations at 3095 cm⁻¹ in polystyrene has been found to shift towards lower wave number with decrease in amount of polystyrene in the blend. The maximum shift of 65 cm⁻¹ in blend-D (polystyrene/novolac: 80/40) definitely indicates strong intermolecular interaction between the components in the blend. It was also observed that band assigned for O—H stretching vibrations at 3620–3590 cm⁻¹ in novolac is unaltered in the blend signifying the absence of any hydrogen bonding in the blend.

Blends were also found to show better tensile strength properties to pure polystyrene. Among the blends, blend B showed highest strength. It is in line with the spectroscopic results (C—H stretching, C—C stretch vibration).

Degradation kinetics of the blends was also studied. Degradation initiation temperature was found to be maximum for blend-E (polystyrene/novolac 50/50). All blends and pure resin were found to show two step

process of degradation. Hence, two activation energies of degradation were found. Decomposition rates of the blends were found to have no definite relation with the amount of novolac resin in blends.

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