Solution blending of vinyl chloride-vinyl acetate-maleic acid terpolymer with butylated melamine-formaldehyde resin in tetrahydrofuran

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Investigations on the compatibility of (vinyl chloride)-(vinyl acetate)-(maleic acid) terpolymer (VMCH), blended with butylated melamine-formaldehyde resin (BMF) in tetrahydrofuran (THF) in various proportions are reported by using the mutual-solvent method, visible spectroscopy and polarizing microscopy. Intermolecular interactions have been examined by Fourier transform infrared spectroscopy. These studies evaluate the compatibility of VMCH/BMF blend by using different proportions of solvents.

A polymer pair incompatible in one solvent system will be incompatible in a range of solvents as the solvents play a secondary role in determining its incompatibility. These days, more emphasis is given to the role of solvents and their amount in blends for polymer-polymer compatibility. The present studies evaluate the influence of different proportions of solvents on the compatibility of VMCH/BMF blend as revealed by: The mutual-solvent methods; Visible spectroscopy; Polarising microscopy; and Fourier transform infrared (FTIR) spectroscopy to establish intermolecular interactions.

In the mutual-solvent method, freshly prepared blend solutions are kept under static conditions to study the layer separation of the blend solutions. Compatibility is said to prevail if phase separations do not occur. Compatibility between the polymers can be determined through measurement of transmittance of light. Discontinuous domains in incompatible polymer blends are often large enough to scatter light, forming a translucent or opaque blend when two transparent polymers are mixed. In a compatible blend (one-phase), no domains are present to scatter light, and hence the blend is transparent.

The theoretical transmittance of blend ($T_b$) can be calculated from the relation

$$T_b = W_1T_1 + W_2T_2$$

where $T_1$ and $T_2$ are transmittance (%) of the respective polymers and $W_1$ and $W_2$ are their weight fractions.

Compatibility of the blend may be explained from the measured transmittance ($T_m$) and $T_b$ values. The smaller the difference between $T_m$ and $T_b$, the greater is the compatibility. When $T_m = T_b$, it may be said that the domain size of the blend is less than the wavelength of the radiation used and the blend is optically perfectly compatible at the same wavelength.

Polarising microscopy is a useful technique to determine whether a blend is in a single phase (compatible) or multiphase (incompatible).

It is also well established that the intermolecular interaction between the polymers in a blend influences the compatibility of the blend. FTIR spectroscopy has recently been employed to study the intermolecular interaction between the polymer pairs in many polymer blends.

The major functional groups of VMCH are Cl and carbonyl (ester and carboxylic). The chlorinated polymer is a proton donor, the carbonyl in the ester is a proton acceptor and the carboxylic group is both proton donor and acceptor. The major functional groups of BMF are amine and hydroxyl.

The amine and hydroxyl groups are proton donor and acceptor. Consequently, dipole-dipole intermolecular interaction between chlorine-amine, chlorine-hydroxyl, ester carbonyl amine, ester carbonyl-hydroxyl, carboxylic group-amine and carboxylic group-hydroxyl may occur. For compatible blends, changes found in FTIR spectra for polymers having amine, chlorine, hydroxyl and carbonyl groups are: a. The N-H stretching band shifts; b. Syndiotactic C-Cl stretching band shifts; c. The hydroxyl stretching...
Table 1 — Compatibility study of VMCH/BMF blends by Mutual Solvent Method in tetrahydrofuran

<table>
<thead>
<tr>
<th>Weight fraction</th>
<th>Concentration of solution</th>
<th>Layer separation of blend solution after 48 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>VMCH</td>
<td>BMF</td>
<td></td>
</tr>
<tr>
<td>0.83</td>
<td>0.17</td>
<td>20 Y</td>
</tr>
<tr>
<td>0.62</td>
<td>0.38</td>
<td>20 Y</td>
</tr>
<tr>
<td>0.36</td>
<td>0.64</td>
<td>20 N</td>
</tr>
<tr>
<td>0.16</td>
<td>0.84</td>
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<td>0.84</td>
<td>10 N</td>
</tr>
</tbody>
</table>

Y: Layer separation; N: No layer separation

Experimental Procedure
VMCH (Union Carbide, U.S.A.) containing 86% by weight vinyl chloride, 13% by weight vinyl acetate and 1% by weight maleic acid and BMF (Himalaya Resins and Paints Pvt. Ltd, India) [% free formalin, max. 2%; acid value, 1.7; solid content, 61% (w/w)] were used.

VMCH and BMF were solution blended in 20, 15 and 10% THF solutions (w/v). The necessary amount of butanol was added to each blend to maintain the alcohol content at constant level. Thin films of VMCH/BMF blends were cast from the solutions on glass and mercury surfaces in a dust-free chamber at room temperature. After evaporation of the solvents, the films were dried under vacuum at 40°C for 7 days and used for blend characterization. The average film thickness was 2.3 x 10⁻⁶ m.

Layer separation of the blend solutions was studied after keeping the solutions under static conditions for 48 h. Transmittance (%) of the films was studied on a 6A Junior Spectrophotometer at 450 nm. A Leitz orthopla­nar polarizing microscope with plane polarized light, magnification 400 x, was used for morphology study. FTIR spectra were obtained on a Perkin-Elmer-1600 Series FTIR instrument. Sixty four scans at a resolution of 4 cm⁻¹ were signal averaged.

Results and Discussion
The study of layer separation of the blend solutions by the mutual-solvent method (Table 1) shows that VMCH/BMF blends at ratio of 36:64 and 16:84 are compatible at 20% (w/v) THF solutions as no layer separation takes place. However, 62:38 and 83:17 blends are incompatible at 20% solution. The 62:38 blend becomes compatible at 15% solution and the 83:17 blend at 10% solution.

The transmittance study (Fig. 1) shows that the VMCH/BMF blends at the ratios of 36:64 and 16:84 (Fig.1A) cast from 20% THF solution are compatible. The 62:38 and 83:17 blends cast from 20% solution (Fig.1A) show that the blends are incompatible as the \( T_m \) values do not deviate greatly from \( T_i \) values. The 62:38 blend becomes compatible at 15% (Fig.1B) and 83:17 blend becomes compatible at 10% (Fig.1C) respectively as the \( T_m \) values do not deviate greatly from \( T_i \) values.
Compatibility of the 36:64 (Fig.2G) and 16:84 (Fig.2H) VMCH/BMF blends cast from 20% solutions is also indicated by the phase morphology studies. Phase morphology of 62:38 VMCH/BMF blend cast from 20% (Fig.2D) solution shows prominent heterogeneity with respect to phase distribution. The same blend cast from 15% (Fig.2E) and 10% (Fig.2F) solutions, however shows much improved and more uniform phase distribution. For the 83:17 VMCH/BMF blend cast from 20% (Fig.2A) and 15% (Fig.2B) solutions, the phase morphology shows prominent heterogeneity. More uniform phase distribution is observed for the blend cast from 10% (Fig.2C) solution.

These conclusions are supported by the FTIR spectra of the blends. As shown in Fig.3A, the band around 3347.8 cm\(^{-1}\) consists of the sum of the OH and NH stretch signals from the methylol and amine group in pure BMF\(^6\). It has not been possible to resolve these bands. This band shifts to 3352.0 cm\(^{-1}\) (Fig.3B), 3370.0 cm\(^{-1}\) (Fig.3C), 3350.4 cm\(^{-1}\) (Fig.3D) and 3355.6 cm\(^{-1}\) (Fig.3E) for 16:84, 36:64, 62:38 and 83:17 VMCH/BMF blends cast from 20% concentration. On diluting the 62:38 blend to 15% (Fig.3F) and 83:17 blend to 10% (Fig.3G) concentration, this band shifts to 3364.4 cm\(^{-1}\) and 3376.0 cm\(^{-1}\) respectively\(^9,10\).

The absorptions assigned to carbonyl groups (ester around 1740.0 and 1736.0 cm\(^{-1}\) and carboxylic around 1718.0 cm\(^{-1}\)) shown in Fig.4A, do not change significantly with change in composition of the blend and concentration of the solution. However, new peaks or shoulders around 1763.0 cm\(^{-1}\) and 1754.0 cm\(^{-1}\) have been found for films cast from 20% solution at VMCH/BMF ratios 36:64 (Fig.4D) and 16:84 (Fig.4E), 15% solution at ratio 62:38 (Fig.4C) and 10% solution at ratio 83:17 (Fig.4F). Such peaks/shoulders are absent for pure VMCH (Fig.4A), and 83:17 (Fig.4B) and 62:38 (Fig.4C) VMCH/BMF blends cast from 20% concentration.

From the FTIR spectral study, it may be deduced that the predominant intermolecular interaction (dipole-dipole) between the polymers probably occurs between chlorine and hydroxyl and chlorine and amine groups, as the bands assigned to carbonyl groups show no great change.

If the cross-hydrogen-bonding between the OH and NH groups of the BMF and the carbonyl group of VMCH takes place, then one might expect a new hydrogen-bonded NH or OH and carbonyl peak below that of the 'free' NH, OH and carbonyl peaks\(^12\). Even if such cross-hydrogen-bonding between polymers takes place, one may obtain a reverse result as found by Chen and Kyu\(^10\) while studying the miscibility of poly (p-phenylene teraphthalalamide) and amorphous nylon copolymer. Again, if such hydrogen bonding takes place between OH and NH and carbonyl group, a new hydrogen-bonded carbonyl peak below that of the free car-
bonyl peak is expected. In this experiment, such a peak is absent, showing thereby that hydrogen bonding between OH and NH and ester has not occurred. In the blend system such as poly[1,3-phenylene (5,5'-bibenzimidazolyl)-2,2'-diyl] and the condensation product of 5,5'-carbonyl bis(1,3-isobenzofurandione) (3,3',4,4'-benzophenone tetracarboxylic dianhydride) and 5-amino-3-(4'-aminophenyl)-1,1,3-trimethylindan), cross-hydrogen-bonding between NH and carbonyl does not take place, but a dipole-dipole (charge or electron-transfer) interaction between the phthalimide and benzimidazole fused-ring or π-orbital interaction between imide and imidazole rings takes place. Again such dipole-dipole (charge or electron-transfer) interaction between OH and Cl in VMCH/nitrocellulose blends occurs. As such, interactions between carbonyl group and OH or NH may not occur readily and because of dipole-dipole (charge or electron-transfer) interaction between Cl and OH or NH, one may find a peak due to OH or NH above that of the original NH or OH band. So, it may be concluded that in the case of the VMCH/BMF blend, dipole-dipole (charge or electron-transfer) interaction between Cl and NH and/or OH has taken place.

For compatibility, when two polymers are blended, by whatever method, the Gibbs free energy of mixing ($G_m$) must be negative for the relation

$$G_m = H_m - T S_m$$

(2)

where $H_m$ is the enthalpy of mixing, $S_m$ is the entropy of mixing and $T$ is the absolute temperature. $H_m$ is essentially independent of molecular weight and is a measure of the energy change associated with intermolecular interactions. It is the dominating factor determining compatibility of high molecular weight polymers. The entropy ($S_m$) reflects the energy change associated with change in molecular arrangements. The magnitude of the entropy change is essentially an inverse function of the molecular weights of the polymers being mixed. The higher the molecular weight, the smaller is the number of possible arrangements available to the segments of the covalently linked molecules.

When mixing polar polymers, the polar molecules may contain different functional groups, which attract each other (intermolecular interaction) upon blending. Consequently, $H_m$ for polar polymers may be negative,
and since the entropy contribution is always negative, 
\( G_m \) can be negative. This satisfies the requirements for 
miscibility and explains why most miscible blends consist
of polar polymers. Again, it is difficult to define 
such interactions quantitatively in molecular terms so 
that there is no clear understanding even for such well-
known and well-studied interactions as those in PPO/PS 
and PVME/PS blends. This interaction is also dependent 
on blend composition.

If two polymers are dissolved in a common solvent 
and the solvent allowed to evaporate to produce a film, 
then one might expect intimate mixing without me-
chanical work. However, if the two polymers are mis-
cible, this method of preparation does not ensure a perfect 
blend since the polymers may phase separately in the 
presence of the solvent. This occurs if there is a difference 
in the interactions between the solvent and each of 
the two polymers. If one polymer interacts very strongly 
with the solvent then it will force the other polymer out 
of solution in order to maximize the number of favourable 
contacts.

The solvent, in general may ultimately modify the 
interactions between the polymer segments to a degree which is not readily determinable. This modification 
does not necessarily disappear smoothly with in-
crease in solute concentration due to evaporation of solvent. Thus, at 100% solid content (after evaporation 
of solvent), this polymer-polymer interaction probably 
does not change.

Conclusions

The conformational state of the polymers in solution 
varies sufficiently with concentration of solvent and 
with blend composition so that the intermolecular in-
teractions between polymer pair and polymer-solvent 
responsible for compatibility are altered enough to cause 
the observed dependence of compatibility on solvent 
concentration and blend composition.

The VMCH/BMF blends at 20% solution and in the 
films cast from the solutions are compatible up to 36:64 
blend ratio. Beyond this ratio, the polymers do not stay 
in single phase, as one of the polymers may interact very 
strongly with the solvent and force the other polymer 
out of solution. For blends up to 36:64 ratio, the excess 
solvent left in the system after its utilization to maximize 
the number of favourable contacts between one polymer 
(present in the blend) is used for favourable contacts 
with the other polymer resulting in both polymers to 
remain in a single phase.

Again with dilution, the incompatible blends (at 20% 
solution) show an increasing trend towards compatibility, 
because of the presence of a large volume of solvent 
in the system. The solvent molecules undergo favourable 
contacts with both polymers and both polymers 
remain in single phase.

The compatibility of polymers in solution is control-
led by the polymer-polymer and polymer-solvent inter-
actions. For blends up to 36:64 VMCH/BMF ratio at 
20% solution, the factors controlling the polymer-poly-
mer and polymer-solvent interactions lead to a confor-
mational state of these polymers, which in turn give 
compatible blends in solution and in cast films after 
removal of THF. Similarly, for incompatible blends at 
20% concentration with dilution, high polymer-solvent 
interactions are expected and the factors controlling the 
polymer-polymer and polymer-solvent interactions lead 
to a conformational state of these polymers which in turn 
give compatible blends in solution and in cast films after 
removal of THF. High polymer-polymer interactions 
in compatible blend films are confirmed by FTIR spec-
tral study.

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References

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