Study of surface morphology and characterization of polymethyl methacrylate:polychlorotrifluoro ethylene polyblend using SEM, DSC and X-ray diffraction techniques

P Agrawal+, P Parmar, R Mallick & R Bajpai*
Department of Electronics, St. Aloysius College (Autonomous), Jabalpur 482 001
+E-mail: dr_p_agrawal@hotmail.com
*Department of PG Studies and Research in Physics and Electronics, Rani Durgavati University, Jabalpur 482 001

Received 3 July 2007; revised 30 December 2007; accepted 10 January 2008

The effect of varying wt % ratio of PMMA:PCTFE polyblends on its surface morphology and structure has been reported. The value of intermediate glass transition temperature of the blend shows a homogeneous blending of the two polymers. The scanning electron micrographs also confirm the homogeneous blending of the two polymers for very low concentration of polychlorotrifluoro ethylene (PCTFE) in polymethyl methacrylate (PMMA) matrix. The role of PCTFE as plasticizer is confirmed by the decreasing glass transition temperature of the polyblend material with increasing concentration of PCTFE in PMMA matrix. At and after 5 wt % of PCTFE the blend shows heterogeneous surface morphology. Crystallinity of the blends is found to decrease with increasing PCTFE, concentration. X-ray diffractograms and SEM micrographs also show great amount of heterogeneity of the two constituents of PMMA:PCTFE polyblend at 95:5 wt% composition ratio. Appreciable blending and fascinating set of properties are found to be for lower wt% ratio of PCTFE in PMMA matrix.

Keywords: Plasticization, Morphology, DSC, SEM, X-ray diffraction

1 Introduction
Polymers are being widely used these days in almost all walks of life due to their fascinating and extraordinary characteristics. They are found to replace conventional materials because of their unique properties in terms of strength, stability and toughness. Since the beginning of the plastics industry, it has been observed that blending yields materials with property profiles superior to the features of the individual components. The blending of polymers provides a means of producing new materials, which combine the useful properties of all of the constituents. The tailoring of the properties of polymers is possible by blending them with some other polymers in different percentage ratios. Blending has been reported to produce definite and desirable set of properties in polymers and is found to have been giving rise to the formation of an entirely new class of materials enriched with the capabilities of suiting the specific needs of the users. The surface and morphological characterization techniques can be used to determine the surface morphology, mechanical strength and toughness of the polymeric materials. Microhardness measurements, differential scanning calorimetric analysis, scanning electron microscopy and X-ray diffraction analysis have been reported as the popular tools for investigating various aspects of polymers and their blends.

The blends of two polymers namely, poly (methylmethacrylate) (PMMA) and poly (chlorotrifluoroethylene) (PCTFE) have been investigated in the present paper. PMMA is a hard and rigid polymer. It is atactic, amorphous and has a high glass transition temperature (105°C). On the other hand, PCTFE is a white semi-crystalline solid which offers a unique combination of physical and mechanical properties, non-flammability, high optical transparency, chemical resistance, near zero moisture absorption and excellent electrical properties. PCTFE also has extremely low outgassing and therefore, it is suitable for use in aerospace and flight applications. Industrial applications of PCTFE include chemical apparatus, process equipment, cryogenic applications, valve seats, seals, gaskets, sight glasses (special process), laboratory equipment, medical equipment, gears, cams and bearings.

Compared to polytetrafluoroethylene (PTFE), PCTFE has a greater tensile strength, hardness and
resistance to creep. Crystallinities of poly (chlorotrifluoroethylene) and its copolymers by differential scanning calorimetry, X-ray diffraction, and density measurements have been reported\textsuperscript{13}. PCTFE shows by itself two sharp peaks in the 20 region of 15-20 degrees corresponding to 102 and 103 reflections\textsuperscript{13}. The miscibility of PMMA with fluoro-polymers like poly(vinyl formal\textsuperscript{6}) poly(vinyl fluoride\textsuperscript{14}), poly(vinylidene fluoride\textsuperscript{15}) and poly(chlorotrifluoroethylene\textsuperscript{16}) has been reported. The microhardness studies of PMMA:PCTFE blend have also been reported\textsuperscript{16}. The microhardness of the PMMA:PCTFE blend decreases with increasing wt% of PCTFE in the polyblend\textsuperscript{16}. This implies that PCTFE acts as a plasticizer for PMMA. The properties of this polyblend using the techniques of differential scanning calorimetry, scanning electron microscopy and X-ray diffraction have been investigated.

2 Experimental Details

For preparing various samples of different percentages, commercially available polymers PMMA and PCTFE were used. Wilson Laboratories, Mumbai, supplied the PMMA granules whereas Aldrich Chemical Company, Inc. Milwaukee WI 53255, USA, supplied PCTFE. The specific gravity, melting point and glass transition temperature of PMMA and PCTFE were 1.17-1.20, 225\textdegree C and 105\textdegree C, and 2.08-2.20, 220\textdegree C and 65-100\textdegree C, respectively.

The solution casting technique\textsuperscript{4,17} was utilized for preparing the blends of different compositional percentages of the two polymers. PCTFE was added in 1, 2, 3, 4 and 5 wt% ratio in the PMMA matrix for preparing the blends. The two polymers were dissolved in dimethylformamide at a temperature of 60\textdegree C with constant stirring. The solution was poured in a glass mould and it was kept inside the temperature-controlled oven for 6 h at 80\textdegree C. The temperature of the oven was controlled automatically. The samples were obtained in the form of pellets of size 6 sq cm and 0.04 cm thickness. After casting, the samples were kept at 60\textdegree C inside the oven for one hour and then annealed for 8 hours so as to eliminate the traces of solvent trapped in the blend due to blend vitrification during evaporation.

Differential Scanning Calorimetry of prepared samples were measured on a Modulated Differential Scanning Calorimeter in the temperature range 0-190\textdegree C at a heating rate of 10\textdegree C/min. The glass transition temperature of the polyblend specimens (PMMA: PCTFE) was measured using this technique.

The SEMs of prepared specimens were recorded on a scanning electron micrograph, JEOL JSM 5600, having the resolution of 3.5 nm and accelerating voltage of 0.5 to 30 kV.

The X-ray diffraction of the samples was carried out using high resolution X-ray diffractometer having 0-0 goniometer with 0.0001 deg step size and 3kW X-ray generator with Cu and Mo targets.

3 Results and Discussion

The thermal studies provide information related to the thermal properties of the material\textsuperscript{8}. They also give clues about the structure of the material as well\textsuperscript{18}. Fig. 1(a-f) show the DSC thermograms for pure PMMA and various PMMA:PCTFE blend specimens. The \( T_g \) s observed from the first negative peaks of different graphs of different blends are listed below:

Table 1 — Glass transition temperature of various polyblends of PMMA and PCTFE

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>105</td>
</tr>
<tr>
<td>Pure PCTFE</td>
<td>65</td>
</tr>
<tr>
<td>1 wt% PCTFE</td>
<td>96</td>
</tr>
<tr>
<td>2 wt% PCTFE</td>
<td>87</td>
</tr>
<tr>
<td>3 wt% PCTFE</td>
<td>80</td>
</tr>
<tr>
<td>4 wt% PCTFE</td>
<td>72</td>
</tr>
<tr>
<td>5 wt% PCTFE</td>
<td>68</td>
</tr>
</tbody>
</table>

Fig. 1—DSC thermograms for pure PMMA and PMMA:PCTFE polyblends (a) Pure PMMA (b) 1 wt% (c) 2 wt% (d) 3 wt% (e) 4 wt% and (f) 5 wt% of PCTFE
polyblends exhibit single glass transitions which can be considered as a clue of a homogeneous mixing of the two polymers. This $T_g$ value for the polyblend is also higher than that of pure PCTFE. Thus, the increase in the $T_g$ value of the polyblend with incorporation of PCTFE is indicative of cross-linking between the chains of two polymers. However, this degree of cross-linking decreases with increase in wt % of PCTFE.

This indicates that the addition of PCTFE is causing for a softening of the polyblend due to plasticization, which was observed through the specimens again confirms the reduction of steric hindrance between PMMA chain molecules due to the addition of PCTFE as was suggested in case of microhardness testing.

Figure 2 shows the scanning electron micrographs of pure PMMA and PMMA:PCTFE blend specimens.

**Fig. 2**—Scanning electron micrographs of pure PMMA PMMA:PCTFE polyblends (a) Pure PMMA (b) 1 wt% (c) 2 wt% (d) 3 wt% (e) 4 wt%, and (f) 5 wt% of PCTFE
with increasing wt % ratio of PCTFE in PMMA matrix. It can be observed that there is a homogenous mixing of PCTFE with PMMA for 1 wt % of PCTFE. This homogeneity seems to be declining with increasing wt % concentration of PCTFE. The blend having 5 wt % of PCTFE shows maximum heterogeneity and hence, may be considered as the non-preferable blend of the two polymers. The clarity of surface decreases with increasing wt % of PCTFE but a homogeneous distribution of PCTFE can be

![Fig. 3— X-ray diffractograms of pure PMMA and PMMA:PCTFE polyblends (a) Pure PMMA (b) 1 wt% (c) 2 wt% (d) 3 wt% (e) 4 wt%, and (f) 5 wt% of PCTFE](image-url)
observed on PMMA base. The formation of clusters of PCTFE at 5 wt% compositional ratio results in blend specimen with heterogeneous surface.

Figure 3 shows the X-ray diffractograms for pure PMMA and various blend specimens of PMMA:PCTFE. Figures 3(b-e) to 10 show the intensity patterns of PMMA:PCTFE blends ranging from 1 to 4 wt% of PCTFE, respectively. PMMA is known to be an amorphous polymer and shows three broad peaks at 20 values of 12°, 30° and 32°. The increasing content of PCTFE broadens these peaks to some extent. This can be understood as an evidence of decreasing homogeneity of the blends with increasing PCTFE content. Figure 3(f) reveals that the intensity pattern drastically changes when PCTFE is added in 5 wt % ratio. In this polyblend of PMMA and PCTFE, as PMMA settles, the crystallizable component is rejected by the amorphous component resulting in broad amorphous population which has been reported to often affect the properties of polymeric materials like glass transition temperature, crystal growth rate and bulk crystallization rate, etc. It is also possible to observe from the X-ray diffractograms that the intensity of diffracted X-rays decreases with increasing wt % ratio of PCTFE in PMMA matrix. This feature also suggests that the blending of two constituent polymers is tending towards heterogeneity with increasing PCTFE content. Hence, the amorphous nature of PMMA starts predominating as it is in a much higher percentage. The scanning electron micrograph of Fig. 2(f) shows that the homogeneity of mixing of the two components is lost at and above 5 wt% of PCTFE. Hence, it can be said that the results obtained from X-ray diffractograms and scanning electron microscopy have a good correlation.

4 Conclusions

The SEM, DSC and X-ray diffraction studies of the PMMA:PCTFE polyblends reveal similar information regarding the morphology and structure of the polyblends. The results obtained from these studies tally with those obtained from the microhardness studies also. PCTFE is found to act as a plasticizer for PMMA and the homogeneous blending of the two polymeric constituents is confirmed by DSC and XRD techniques as well. One Tg value for a polyblend specimen shows that the two components are blending with each other in a homogeneous manner. Minimum homogeneity is observed at and above 5 wt% ratio of PCTFE in PMMA matrix. It can be inferred from the X-ray diffractograms that PMMA and PCTFE make good and homogenous blends at lower wt % of PCTFE. This loss of homogeneity of the two components at 5 wt% of PCTFE is confirmed by the X-ray diffractograms also. It can be concluded that PCTFE, when added in small wt % makes a good homogeneous blend with PMMA thereby giving rise to new and interesting set of properties.

Acknowledgement

Authors are grateful to Inter University Consortium, Department of Atomic Energy, Indore, M P, India for providing the facilities of SEM, DSC and X-ray diffraction analyses. One of the authors (PA) would like to thank University Grants Commission, Central Regional Office, Bhopal for sanctioning a research project under which the work has been carried out.

References