Thermal behaviour of methylmethacrylate-grafted viscose fibres

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Graft copolymerization of methyl methacrylate on viscose fibre has been done using titanium(III) chloride-potassium persulphate redox initiator under visible light in limited aqueous system in presence of various solvents and grafted polymers have been characterized by DSC and TGA. The DSC results show a low compatibility in the thermal properties of viscose fibre and PMMA. The role of pendant PMMA chain produced in presence of different solvents and the thermal stability of graft copolymers have been analyzed by TGA study.

Keywords: Differential scanning calorimetry, Methylmethacrylate, Photografting, Thermogravimetric analysis, Viscose fibre

Modification of fibre properties by grafting has evoked considerable interest in recent years. Now-a-days, the development of thermostable polymers has become important and grafting has provided a suitable pathway. But only few reports are available in the literature1,2 regarding the studies on thermal behaviour of grafted rayon. The present paper reports the thermal behaviour of viscose fibres grafted with methylmethacrylate using titanium(III) chloride-potassium persulphate redox initiator under visible light in a limited aqueous system.

The methods for preparation of grafted fibres and the effects of various parameters on % grafting, % total conversion and grafting efficiency have been reported earlier3.

DSC measurements were done on a DSC-7 (Perkin-Elmer) under nitrogen atmosphere at a heating rate of 20°C/min. DSC range and sample weight of 5 mcal/s and 9 mg respectively were used.

TGA and DTGA curves of some selective fibres having approximately the same level of % grafting were recorded on a delta series TGA-7 (Perkin-Elmer) under nitrogen atmosphere at a heating rate of 20°C/min.

The DSC thermograms of ungrafted viscose fibre, MMA-grafted viscose fibres and MMA polymer are shown in Fig. 1. The thermogram 1b shows an endothermic peak at 339.1°C which is due to the thermal decomposition of viscose fibre. Similarly for PMMA, a sharp endothermic peak at 375.1°C is observed (thermogram 1a). Thermograms 1c and 1d relate to grafted viscose fibres with 128.85% and 207.18% grafting respectively. The double endothermic peaks exhibited on the DSC thermograms of the grafted fibres are due to the thermal decomposition of viscose fibre and PMMA present in the fibre. The DSC results suggest a low compatibility in thermal properties of viscose fibre and PMMA.

Table 1 shows the initial decomposition temperature ($T_d$); maximum pyrolysis temperature ($T_m$), % residual weight ($R_w$) and decomposition temperature ($T_o$) at different weight losses for MMA-grafted viscose fibres prepared in presence of different solvents. Residual weight is highest in the case of grafted fibre prepared in presence of methanol and lowest in the case of grafted fibre prepared in presence of formic acid. $T_o$ value is

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Table 1—Thermal analytical data of viscose fibre grafted with MMA in presence of different solvents

<table>
<thead>
<tr>
<th>Sample particulars</th>
<th>Swelling agent</th>
<th>( T_1 ) °C</th>
<th>( T_m ) °C</th>
<th>( T_{mll} ) °C</th>
<th>Temperature of decomposition ((T_0)) in °C at weight loss (%)</th>
<th>Residual weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.66% grafted</td>
<td>Methanol</td>
<td>282</td>
<td>407</td>
<td>332</td>
<td>371 392 408 421 430 470</td>
<td>8.33</td>
</tr>
<tr>
<td>65.66% grafted</td>
<td>Tetrahydrofuran</td>
<td>290</td>
<td>380</td>
<td>328</td>
<td>352 365 374 383 393 417</td>
<td>5.55</td>
</tr>
<tr>
<td>65.90% grafted</td>
<td>Dioxane</td>
<td>282</td>
<td>395</td>
<td>446</td>
<td>365 382 393 408 429 450</td>
<td>2.80</td>
</tr>
<tr>
<td>64.78% grafted</td>
<td>Formic acid</td>
<td>282</td>
<td>399</td>
<td>456</td>
<td>364 382 399 416 432 456</td>
<td>0.69</td>
</tr>
</tbody>
</table>

\( T_1 \)—Initial decomposition temperature; \( T_m \)—maximum pyrolysis temperature for 1st step; and \( T_{mll} \)—maximum pyrolysis temperature for 2nd step.

highest in the case of grafted fibres prepared in presence of methanol and lowest in the case of grafted fibres prepared in presence of tetrahydrofuran. From the results, it may be concluded that the thermal stability is highest in the case of grafted fibre prepared in presence of methanol and lowest in the case of grafted fibres prepared in presence of tetrahydrofuran.

This may be explained by considering the nature of the swelling agent or swelling power of the individual solvent. The swelling agent affects the rate of termination of the graft copolymerization as well as the rate of diffusion to the active sites and is considered to be rather identical to the gel effect observed in homopolymerization kinetics. Tetrahydrofuran (THF), a strong swelling agent for rayon, is also a very good solvent for MMA monomer and its polymer. Formic acid, a similarly strong swelling agent, is also a good solvent for MMA and its polymer. Dioxane, a poor swelling agent, is a good solvent for MMA and PMMA.

Methanol, on the other hand, is a better-swelling agent compared to dioxane but is not a solvent for PMMA. Tetrahydrofuran effects the most rapid grafting, presumably as a consequence of both high propagation rate (swelling effect) and termination rate (gel effect). The pendant chains of PMMA produced in presence of THF are shorter due to higher chain transfer constant. On the other hand, the pendant chains of PMMA produced in the presence of methanol are quite long because of moderate propagation rate and slow termination rate. The length of the pendant chains produced in presence of dioxane and formic acid fall in between those of chains produced in presence of methanol and tetrahydrofuran. It is known that the polymers degrade faster as molecular weight, i.e. chain length, is decreased. Therefore, the analysis made above is more or less consistent with the results of thermal degradation.

Table 2—Polymerization of MMA on viscose fibres

<table>
<thead>
<tr>
<th>Initiator system</th>
<th>Conditions of polymerization</th>
<th>Formation of PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_2 S_2 O_8 / TiCl_3 )</td>
<td>Dark, 40 ± 1°C, 3h</td>
<td>low</td>
</tr>
<tr>
<td>( K_2 S_2 O_8 )</td>
<td>Dark, 40 ± 1°C, 3h</td>
<td>low</td>
</tr>
<tr>
<td>( TiCl_3 )</td>
<td>Dark, 40 ± 1°C, 3h</td>
<td>nil</td>
</tr>
<tr>
<td>( K_2 S_2 O_8 / TiCl_3 )</td>
<td>Photo, 40 ± 1°C, 3h</td>
<td>low</td>
</tr>
<tr>
<td>( K_2 S_2 O_8 )</td>
<td>Photo, 40 ± 1°C, 3h</td>
<td>high</td>
</tr>
<tr>
<td>( TiCl_3 )</td>
<td>Photo, 40 ± 1°C, 3h</td>
<td>nil</td>
</tr>
</tbody>
</table>

The mechanism of the graft copolymerization of MMA on viscose using \( Ti^{+3}/K_2 S_2 O_8 \) in presence of light in limited aqueous system is complicated because of the heterogenous nature of the system. However, most likely the primary radicals to be generated in the system are sulphate ion radical \((SO_4^{2-})\) and hydroxyl radical \((\cdot OH)\). End group analysis of the free PMMA isolated from the polymer gave a positive test for sulphate and hydroxyl end groups. Thus, the probable mechanism may be described as:

\[
O_3^- + SO_4^{2-} + Ti^{+3} \rightarrow Ti^{+4} + SO_4^+ + SO_4^- \quad \text{(1)}
\]

\[
SO_4^+ + H_2O \rightarrow HS_O_4^- + HO^+ \quad \text{(2)}
\]

Eqs (1)–(3) are found to be faster in presence of light compared to dark (Table 2).

R cell - OH + SO_4^- \rightarrow HS_O_4^- + R Cell-O

R cell - OH + HO^- \rightarrow R cell - O^- + H_2O

Furthermore, decrease in per cent grafting with increase in \( TiCl_3 \) content may be assumed to be
caused by the consumption of $\text{SO}_4^2-$ by $\text{Ti}^{3+}$ ion according to the following equation:

$$\text{Ti}^{3+} + \text{SO}_4^2- \rightarrow \text{Ti}^{4+} + \text{SO}_4^2-$$

From the experimental results, it may be concluded that the present system of grafting produces a low compatibility in thermal properties of viscose fibre and PMMA, and the higher the length of the pendant PMMA chain, the higher is thermal stability.

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References