

Table 1

Properties of poly(vinyl alcohol)-g-poly(ϵ -caprolactone) (PVA-g-PCL) from melt-synthesis using MgH_2 as catalyst

| Run n ^o | Feed ratio (mmol) | | | Solvent DMSO mmol | Poly(vinyl alcohol)-g-poly(ϵ -caprolactone) | | | | | | |
|-----------------------|--------------------------|-------|------------------|-------------------------|---|-------------------------------|-------------------------------------|------------------------------------|-----------------------|-----------------------|--|
| | PVA ^a unit | CL | MgH ₂ | | DP _{exp} ^b | DP _{th} ^c | DS _{exp} ^d % | DS _{th} ^e % | Tg ^f °C | Tm ^g °C | Yield ^h (PCL) ⁱ wt % |
| 1 | 1.85 | 13.88 | 0.06 | | 5.9 | 115.6 | - | 6.5 | - 40 | 60 | 60 |
| 2 | 3.15 | 13.88 | 0.20 | | 8.1 | 34.7 | 4.9 | 12.7 | - 50 | 54 | 69(53) |
| 3 | 10.60 | 13.88 | 0.24 | | - | 28.9 | - | 4.5 | - 32 | - | 20 |
| 4 | 1.13 | 6.94 | 0.38 | | 4.6 | 9.1 | 16.7 | 67.2 | - 58 | 40 | 76(68) |
| 5 | 1.13 | 10.41 | 0.38 | | 5.4 | 13.7 | 29.4 | 67.2 | - 60 | 45 | 65(78) |
| 6 | 1.13 | 13.88 | 0.38 | | 6.8 | 18.3 | 24.3 | 67.2 | - 61 | 46 | 80(81) |
| 7 | 0.92 | 1.68 | 0.03 | | - | 28 | - | 6.5 | - 35 | - | 35 |
| 8 | 1.05 | 1.68 | 0.20 | | 1.2 | 4.2 | 13.3 | 38 | - 32 | - | 30(30) |
| 9 | 1.85 | 1.68 | 0.05 | | - | 16.8 | - | 5.4 | - 30 | - | 5 |
| 10 | 8.02 | 7.98 | 0.20 | | 3.4 | 19.9 | - | 4.9 | - 30 | - | 22 |
| 11 | 1.13 | 4.38 | 0.38 | 6.4 | - | 5.8 | 31.1 | 67.2 | - 56 | - | 85 |
| 12 | 1.59 | 4.38 | 0.38 | 6.4 | 3.1 | 5.8 | 18.3 | 47.8 | - 54 | - | 75(60) |
| 13 | 2.25 | 4.38 | 0.38 | 6.4 | 2.1 | 5.8 | 12.2 | 33.7 | - 34 | - | 88(40) |
| 14 | 4.58 | 4.38 | 0.38 | 6.4 | 3.7 | 5.8 | 9.8 | 16.6 | - 34 | - | 84(49) |

^{a)} PVA degree of hydrolysis 99 %, $M_w = 41000 \text{ g mol}^{-1}$

^{b) c)} Experimental (DP_{exp} from NMR spectra and equation (2)) and theoretical (DP_{th} from equation (4)) degree of polymerization of grafted poly(ϵ -caprolactone) chains based on ϵ -caprolactone monomer unit $-CO(CH_2)_5O-$

^{d) e)} Experimental (DS_{exp} from NMR spectra and equation (1)) and theoretical (DS_{th} from equation (3)) degree of substitution of PVA backbone chains (percentage of grafted PVA units)

^{f) g)} Glass transition temperature (Tg) determined for first heating run and melting temperature (Tm). PCL: Tg = - 65 °C and PVA: Tg = 68 °C.

^{h)} Yield in weight % of precipitated PVA-g-CL to PVA and CL in initial feed. Crude product was slowly dissolved in chloroform then precipitated in methanol

ⁱ⁾ PCL content in weight % from equation (9) and (10)

Table 2

Properties of poly(vinyl alcohol)-g-poly(ϵ -caprolactone) (PVA-g-PCL) from melt-synthesis using MgH_2 as catalyst

| Run n ^o | Feed ratio (mmol) | | | Solvent DMSO mmol | Poly(vinyl alcohol)-g-poly lactide | | | | | | |
|-----------------------|--------------------------|-------|------------------|-------------------------|------------------------------------|-------------------------------|-------------------------------------|------------------------------------|-----------------------|-----------------------|--|
| | PVA ^a unit | LA | MgH ₂ | | DP _{exp} ^b | DP _{th} ^c | DS _{exp} ^d % | DS _{th} ^e % | Tg ^f °C | Tm ^g °C | Yield ^h (PLA) ⁱ wt % |
| 1 | 0.53 | 13.88 | 0.20 | | | 69.4 | | 75.5 | 43 | - | 74 |
| 2 | 1.05 | 13.88 | 0.20 | | 7.9 | 69.4 | 15.8 | 38.1 | 48 | - | 70(67) |
| 3 | 2.10 | 13.88 | 0.20 | | | 69.4 | | 19.1 | 44 | - | 70 |
| 4 | 3.15 | 13.88 | 0.20 | | | 69.4 | | 12.7 | 42 | - | 35 |
| 5 | 5.34 | 13.88 | 0.20 | | | 69.4 | | 7.5 | 40 | - | 22 |
| 6 | 10.5 | 13.88 | 0.65 | | | 21.3 | | 12.4 | 40 | | 10 |
| 7 | 1.13 | 3.47 | 0.38 | | 8.2 | 9.1 | 17.9 | 67.2 | 50 | 115 | 38(71) |
| 8 | 1.13 | 4.86 | 0.38 | | 8.2 | 12.8 | 22.3 | 67.2 | 48 | - | 35(75) |
| 9 | 1.13 | 6.94 | 0.38 | | 9.6 | 18.3 | 23.6 | 67.2 | 49 | 118 | 65(79) |
| 10 | 1.13 | 10.41 | 0.38 | | | 27.4 | | 67.2 | 46 | - | 64 |
| 11 | 1.13 | 3.47 | 0.38 | 6.4 | | 9.1 | | 67.2 | 54 | 112 | 78 |
| 12 | 1.59 | 3.47 | 0.38 | 6.4 | | 9.1 | | 47.8 | 54 | - | 62 |
| 13 | 2.27 | 3.47 | 0.38 | 12.8 | 8.5 | 9.1 | 18.3 | 33.5 | 48 | 122 | 70(72) |
| 14 | 4.54 | 3.47 | 0.38 | 12.8 | | 9.1 | | 16.7 | 46 | 130 | 76 |

^{a)} PVA degree of hydrolysis 99%, $M_w = 41000 \text{ g mol}^{-1}$

^{b) c)} Experimental (DP_{exp} from NMR spectra and equation (7)) and theoretical (DP_{th} from equation (9)) degree of polymerization of grafted polylactide chains based on L-LA monomer unit -COCH(CH₃)O-

^{d) e)} Experimental (DS_{exp} from NMR spectra and equation (6)) and theoretical (DS_{th} from equation (8)) degree of substitution of PVA backbone chains (percentage of grafted PVA units)

^{f) g)} Glass transition temperature (Tg) determined for first heating run and melting temperature (Tm) for maximum heat of broad peak area on wide temperature range about 60 °C. PLA: Tg = 57 °C and PVA: Tg = 68 °C.

^{h)} Yield in weight % of precipitated PVA-g-CL to PVA and LA in initial feed. Crude product was slowly dissolved in chloroform then precipitated in methanol

ⁱ⁾ PLA content in weight % from equation (9) and (10)

Table 3
Wettability and surface energy of poly(vinyl alcohol)-g-poly(ϵ -caprolactone) films and poly(vinyl alcohol)-g-poly(lactide) films

| Polymer | Run (Table) | $\theta_{\text{H}_2\text{O}}$ ^a ($^\circ$) | $\theta_{\text{I}_2\text{CH}_2}$ ^a ($^\circ$) | γ_s^{p} ^b ($\text{mJ}\cdot\text{m}^{-2}$) | γ_s^{d} ^b ($\text{mJ}\cdot\text{m}^{-2}$) | γ_s^{b} ($\text{mJ}\cdot\text{m}^{-2}$) |
|-----------|----------------|--|---|---|---|--|
| PVA | | 54 | 55 | 29.1 | 23.2 | 52.3 |
| PVA-g-PCL | 4 (1) | 57 | 37 | 15.9 | 34.2 | 50.1 |
| | 5 (1) | 76 | 43 | 6.8 | 38.6 | 40.4 |
| | 6 (1) | 78 | 41 | 5.1 | 35.7 | 40.8 |
| PVA-g-PLA | 2 (2) | 66 | 43 | 12.0 | 32.4 | 44.4 |
| | 7 (2) | 78 | 40 | 5.0 | 36.3 | 41.2 |
| | 8 (2) | 81 | 46 | 4.5 | 33.4 | 37.9 |
| | 9 (2) | 84 | 48 | 3.6 | 32.8 | 36.4 |

^{a)} Contact angle ($\pm 1^\circ$) with water ($\theta_{\text{H}_2\text{O}}$) and diodomethane ($\theta_{\text{I}_2\text{CH}_2}$)

^{b)} Surface energy ($\gamma_s \pm 1 \text{ mJ}\cdot\text{m}^{-2}$), dispersive (γ_s^{d}) and polar (γ_s^{p}) components