Melting Behaviour of Triblock Polymers (Poloxamers) in Supercritical CO_2

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Carbon dioxide (CO_2) is the most commonly used SCF because of the relatively mild operating conditions (31.1°C and 72.8 bar) and easily tuneable properties. Moreover, the ability of CO_2 to act as a solvent and solute has made it highly desirable in the field of excipient processing, particle formation and drug encapsulation. The dissolution of CO_2 is known to affect glass transition or melting temperature of polymers and fats [1]. In this work, the effect of the dissolution of liquid (l.CO_2) or supercritical (sc. CO_2) was studied on the melting point of various poloxamers (Pluronic™ F77, F127, F38, F68, F108) at the pressure ranging from 70 to 250 bar in a supercritical phase monitor. The treated and untreated samples were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

The melting point depression between 14.6 °C to 19.3 °C was observed for poloxamers studied in this work. This decrease was dependent on the polyethylene content and the molecular weight of the polymer, where the trend in melting point depression was found to be F77 > F127 > F38 > F68 > F108. This phenomenon can be explained by the solubility behavior of CO_2 in the polymeric matrix. Here, CO_2 acts as a plasticizer which increases the free volume in the excipient by penetrating into the inter-molecular spaces and hence decreases the melting point substantially. The operating pressure was also an important factor. For all polymers; the melting point decreased rapidly before reaching to a minimum value with the increase in pressure. The comparison of DSC, SEM and XRD results of CO_2 treated and untreated samples showed no morphological changes in poloxamers due to sc. CO_2 treatment.

In conclusion, poloxamers showed a significant depression in melting temperatures in sc. CO_2 and analysis of treated and untreated samples confirmed that no morphological changes were made due to SCF processing at studied parameters. This approach can be used for the particle design and coating of thermo labile substances and biologics at considerably low temperatures.

[1] Lian, Z., Epstein S.A., Blenk, C.W., Shine, A.D. (2006). Carbon dioxide-induced melting point depression of biodegradable semicrystalline polymers. *The Journal of Supercritical Fluids*, 39(1), pp.107–117.

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