

ENHANCED PROCESSING OF POLYMERS USING SUPERCRITICAL CO₂

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A technology has been developed utilizing the plasticizing effect of supercritical CO₂ in a modified extrusion process. By this means it is possible to use supercritical CO₂ as a transient plasticizing aid combined with a capability to produce solid *foam-free* extrudate. This technology has been shown to reduce polymer processing pressures, motor power and melt viscosity, thus allowing processing at faster output rates, reduced temperature, and with lower energy consumption. Solidified extrudate made by this process was characterized by thermal, mechanical and X-ray techniques to determine changes in structure and properties during and after CO₂ diffusion from the polymer.

INTRODUCTION

Thermoplastics extrusion is one of the most important polymer conversion technologies, representing around 36% of all plastics processed. However, under standard processing conditions, thermoplastics have a relatively high melt viscosity, require large extrusion pressures and generally encounter some thermal degradation. Processing aids and plasticizers can help to ameliorate such problems, but these remain in the polymer after extrusion, thereby influencing mechanical properties.

The use of scCO₂ as a transient viscosity reducing aid [1-6] eliminates the disadvantages associated with many other industrial plasticizers. CO₂ is a gas under atmospheric conditions, thus it can be used as a processing aid and then be easily removed from a polymer through evaporation to obtain the original physical properties of the unplasticised polymer matrix. Its critical parameters ($T_c = 304.15$ K, $P_c = 7.38$ MPa, $\rho_c = 0.47$ g/cm³), readily enable its application in high pressure polymer melt extrusion technology.

When small molecules, such as CO₂, are added to polymer melts T_g is lowered by increasing free volume and making the molecules more mobile. Thus CO₂ can be considered as a 'molecular lubricant' [7].

MATERIALS AND METHODS

Commercially available pre-compounded rigid PVC with a K-value of 65 was used for this study. This material contained less than 3% of additives, including acrylic processing aid, hydrocarbon wax, polyethylene wax, and an ester of montanic acid wax and glyceryl monostearate. An extrusion grade high density polyethylene was also studied. Liquid carbon dioxide with purity of 99.9% v/v ratio was pressurized into a supercritical state using a Teledyne Isco A260D high pressure dual syringe pump.

A Collin 25mm 25:1 L/D single screw extruder fitted with a two-start uPVC screw or a general polyolefin screw was used for the experiments. The extruder barrel was fitted with four pairs of entry ports in the barrel wall, which were used for determining the melt pressures, temperatures and also as a point for CO₂ injection. The die had a slit width of 40 mm and a variable, but maximum die gap thickness of 2 mm. The CO₂ delivery system (Figure 1) comprised the high pressure dual syringe pump which accurately delivered CO₂ at a constant set flow rate and under controlled pressure. The CO₂ entered the polymer melt stream in the barrel through a specially designed injection valve. CO₂ was added at the metering zone, where polymer had melted and created a melt seal to prevent leak back of gas. Pressure transducers recorded the CO₂ pressure entering the barrel and the barrel pressures and temperatures were monitored before, at point of injection and at the end of the barrel.

Extrudate products were then characterized using thermal, mechanical, and X-ray techniques to ascertain possible structure and property changes. To this end, dynamic mechanical properties of the samples were determined using a Polymer Laboratories Mark II DMA at 1 Hz, a temperature scan of 40-100°C and at a heating rate of 2°C/min. Mechanical properties were also measured according to British Standard ISO 527-3 on a Universal Tensile Machine Instron 5564 at ambient temperature (20± 3°C). X-ray analysis was carried out using a Philip Xpert diffractometer with Cu K α radiation operated at 40 keV and 40mA at ambient temperature. Solid samples was placed in the sample holder and rotated at 16 revolutions per minute during the scanning procedure.

RESULTS

The effects of CO₂ addition to the polymer on melt pressure, motor current and output rate are shown in Figures 2 and 3 for uPVC and high density polyethylene respectively. The extent of the plasticisation effect was influenced not only by the amount of CO₂ added, but also on the ability of polymer to absorb CO₂, which in turn depends on its chemical structure. In particular, basic sites on the polymer acted as electron donors and favoured absorption CO₂, which acted as an electron acceptor [7]. In solid material this CO₂ sorption occurs more extensively in amorphous region of polymer, being more restricted by closely-packed crystalline regions.

Good dissolution between CO₂ molecules in the polymer is a requirement to maximize the plasticizing benefits of scCO₂. This can be enhanced by effective mixing combined with long

residence times of the gas-containing polymer melt in the extruder [8]. Also by increasing the die land-length, a higher pressure in the barrel resulted, which aided mixing and gas dissolution and allowed a more gradual pressure drop as the polymer cooled in the die. This influenced the morphology of the final product by inhibiting foaming (up to a limiting gas addition level), as the polymer exited from the die (Figure 4) [9].

The extrudate was characterized to study the effects of CO₂-assisted extrusion on the product structure and properties. Under optimum processing conditions, *foam-free* extrudate was produced, as shown in Figure 4. The results from thermal, mechanical, density (Table 1) and X-ray (Figure 5) analysis also show that there was no significant difference between products processed with and without CO₂. This means that the plasticizing benefits of CO₂ can be utilized during the extrusion process without influencing extrudate properties.

CONCLUSIONS

A CO₂ assisted polymer extrusion system has been developed to demonstrate the viscosity reducing effect of scCO₂, together with a capability to produce *foam-free* extrudate. This also gave a reduction in extruder motor power and an increase in material output. By controlling land-length and cooling conditions in the die, foaming of the melt was inhibited. No significant changes were seen in the properties of materials processed with and without CO₂. Therefore, CO₂ can be used as a temporary plasticizing aid during polymer extrusion without affecting the properties of the final product.

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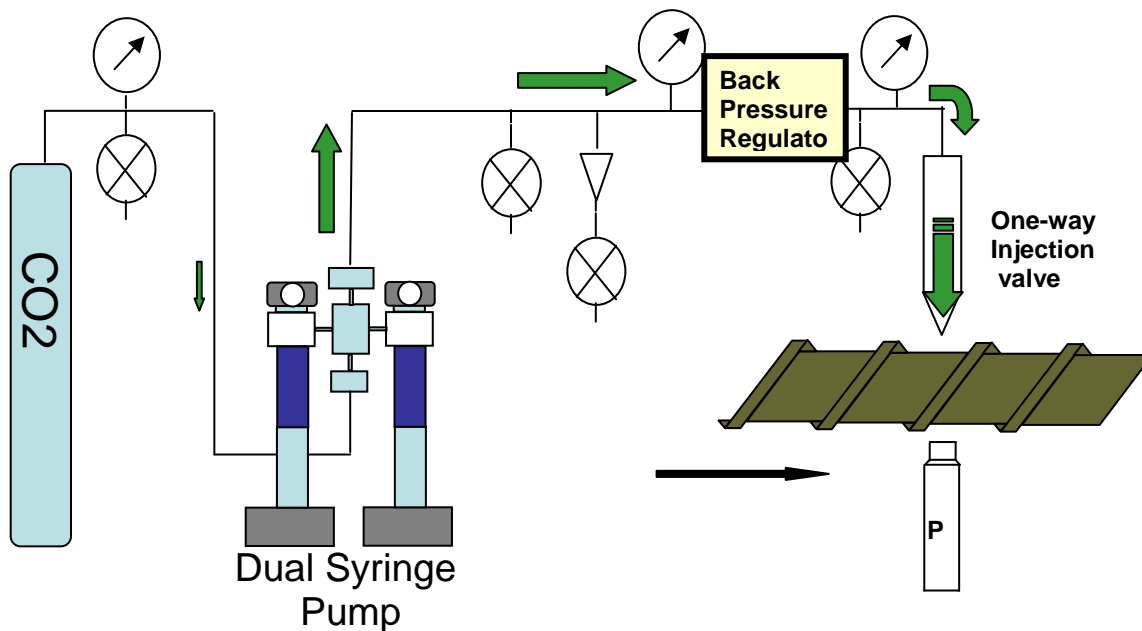


Figure 1: Schematic diagram of CO₂ delivery system

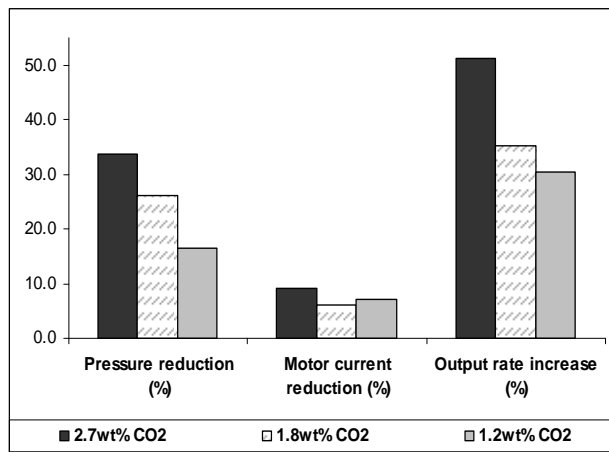


Figure 2: The effect of scCO₂ addition on reduction in pressure, motor current, and output increase for extruded uPVC. Changes are compared with unmodified polymer without CO₂ addition.

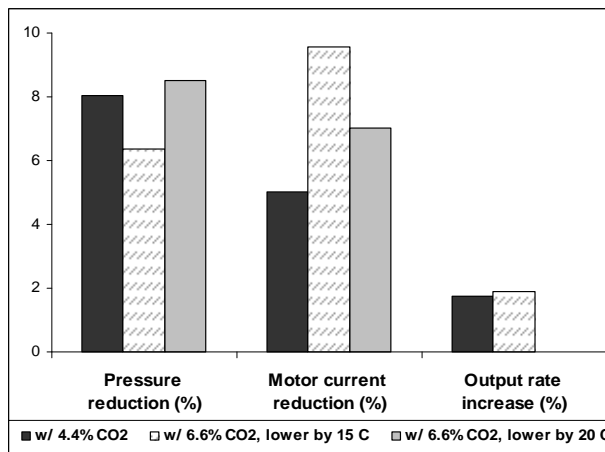


Figure 3: The effect of scCO₂ addition on reduction in pressure, motor current, and output increase for extruded HDPE. Changes are compared with unmodified polymer without CO₂ addition.

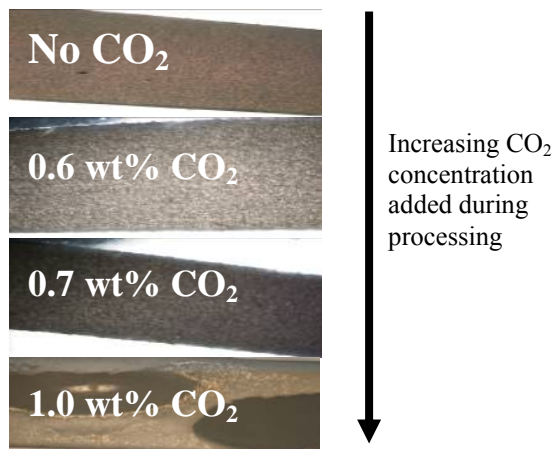


Figure 4: Cross-section (2mm thickness) view of the extruded uPVC with and without CO₂. Note that An excessive amount of CO₂ yielded large voids.

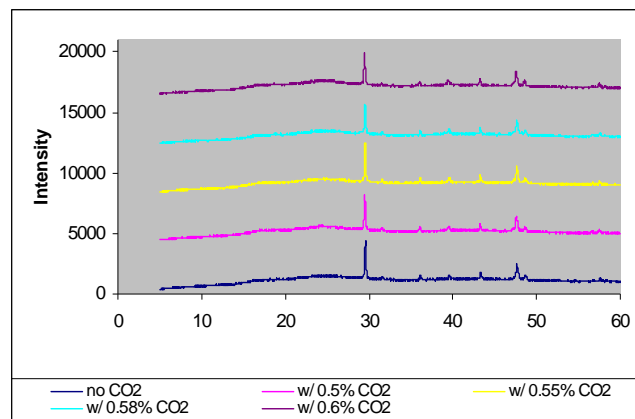


Figure 5: XRD traces of uPVC extrudate processed with various CO₂ concentrations.

CO ₂ added (%)	Density (Mg.m ⁻³)	Tensile Modulus (MPa)	Yield Stress (MPa)	Strain at Failure (%)
0	1421	1697± 90	48.6 ± 2.4	8.4 ± 0.5
0.5	1424	1486. ± 81	45.2 ± 1.1	7.5 ± 0.2
0.55	1420	1446± 209	44.5 ± 2.6	7.5 ± 0.4
0.58	1422	1515± 95	43.7 ± 2.0	7.1 ± 0.5
0.6	1418	1621± 212	42.6 ± 0.9	7.3 ± 1.5
0.65	1413	1464± 171	47.4 ± 1.5	7.4 ± 0.2

Table 1: Properties of uPVC extrudate processed with various CO₂ concentrations.