The Removal of Carbon Tetrachloride from Chlorinated Polyisoprene Using Carbon Dioxide

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SYNOPSIS

This study demonstrates the use of supercritical carbon dioxide in the removal of residual carbon tetrachloride from chlorinated polyisoprene in a packed column. The effects of varying temperature and pressure on the efficiency of extraction are examined. The data indicate that there exists an optimum combination of pressure and temperature and that quite small deviations from these conditions can produce substantially poorer extraction efficiency and lead to the destruction of the polymer particle morphology.

INTRODUCTION

It is commonly the case that polymeric materials prior to purification may contain unreacted monomer, solvent, or some other low molecular weight impurity. It is often desirable to reduce the level of these impurities on the grounds that they present some hazard to health which might limit the range of end uses of the polymer. To this end, the method most commonly employed is thermal stripping. This entails heating the polymer, preferably in a finely divided state, to elevated temperatures typically near to or in excess of the glass transition temperature T_g. Either hot air or steam may be used for this purpose, and the polymer may have had plasticizer specifically added in the formulation to aid in the process. Stripping times vary according to the nature of the polymer, the contaminant, and the residual level one is trying to attain. However, treatments in excess of 1 or 2 h are typical and may lead to difficulties with rapid and efficient throughput. In addition to this, the thermal stability of the polymer may present problems with respect to these lengthy exposures to high temperatures and may give rise to undesirable coloration effects.

The use of near-critical or supercritical carbon dioxide as a solvent of extraction has found a variety of applications in the food industry.[1] Of these, prob-

ably the best known is the Hag process for the decaffeination of coffee beans.[2] The particular attractions of carbon dioxide are that it is nonflammable, has low toxicity and low cost, and exhibits solvent selectivity. This selectivity arises from the fact that, at temperatures just above the critical temperature (31°C), the fluid is highly compressible, leading to the ability to modify the fluid's density with quite small changes in temperature or pressure. It has been established that the solvation power of a supercritical fluid is directly related to its density and its temperature. In general, two simple guidelines commonly apply regarding the solvating power of supercritical fluids with respect to a solute of low volatility, viz.:

1. At fixed density, solubility increases with temperature.
2. At fixed temperature, solubility increases with pressure.

It should be noted, however, that these are only guidelines and that exceptions are encountered in certain circumstances. The interested reader may seek a more detailed description of the phenomenon of supercritical solvation from one of the excellent reviews which exist (e.g., Refs. 3 and 4).

More recently, supercritical extraction has been extended to the field of polymers,[5] with some patents also beginning to emerge (e.g., Refs. 6 and 7). Despite the numerous examples that can now be found in the literature, however, to the authors' knowledge

there have been no systematic studies published on the efficacy of extraction with temperature and pressure for any given polymer/impurity system.

In this work, the removal of carbon tetrachloride (CTC) from chlorinated rubber using carbon dioxide has been studied over a wide range of temperature and pressure. It is believed that the results of this study help to shed some light on the processes involved.

EXPERIMENTAL

The polymer used in this study was chlorinated polyisoprene (trade name "Alloprene," manufactured by ICI Chemicals & Polymers Ltd.). The chlorination process entails bubbling chlorine gas through a solution of polyisoprene in CTC plus added plasticizer and catalyst. The converted polymer is precipitated into water, and the entrapped CTC is then removed by thermal stripping in rotary driers. For the purposes of this study, unplasticized polymer that had not been through the thermal stripping stage was used. The residual CTC of this polymer was $6.25 \pm 0.03\%$ by weight.

The experimental setup used in this study comprised a stainless steel extraction column of internal dimensions 102×8.5 mm containing 2.80 g fresh polymer held in place by metal frits. The column was mounted vertically in a well-thermostatted air circulating oven set at the desired operating temperature. Liquid carbon dioxide was pumped at a flow rate of 16.5 cm^3 min^{-1} through a length of coiled capillary tubing also placed in the oven and then on into the bottom of the extraction column. The desired pressure was maintained by a back pressure regulator (Tescom Corp.) mounted after the column and outside the oven.

The extraction time employed was 40 min in all cases and the levels of CTC remaining in the polymer were determined using head space analysis by gas chromatography. The lower limit of detection for this method is estimated to be 0.1% w/w in this case.

Extractions were performed in the pressure range 55–207 bar and the temperature range 40–110°C.

RESULTS AND DISCUSSION

The residual CTC levels measured in the polymer after removal from the extraction column are illustrated in Figure 1. It can be seen that, from a starting level of 6.25% w/w, it is possible to reduce the CTC

content to below detectable limits in 40 min at only one combination of the conditions explored, namely, 60°C and 207 bar.

The trends observed for the extractions carried out at lower temperatures [Figs. 1(a)–(c)] are what one would expect from the normal rules given in the introduction concerning supercritical solvation: Extraction at a fixed temperature improves with increasing pressure. However, the results depicted for the higher temperature extractions [Figs. 1(d)–(h)] reveal a more complicated situation. It is clear that there exists an optimum combination of temperature and pressure and that deviation from these conditions can produce considerably poorer results.

Figure 2 represents these same data replotted isobarically. From this representation of the data, it is clear that extraction at fixed pressure improves with increasing temperature, but only up to some limiting point, beyond which extraction efficiency becomes rapidly poorer. The failure to achieve good extractions at higher temperature and pressure may be readily explained by the physical state of the polymer which emerges from the extraction column. The starting polymer was a free flowing powder of mean particle size 95 μm. In those cases where conditions of temperature and pressure were modest, up to and including the optimum conditions, the extracted polymer emerged from the column unaltered in appearance and habit. However, under the more severe conditions of temperature and pressure, the extracted polymer was found to be progressively more aggregated and, in the worst case, emerged from the column as a solid rod of polymer. Thus, the likelihood is that the falloff in extraction efficiency is due to a reduction in surface area, which is in turn due to the softening of the polymer particles under these conditions.

The effects of compressed gases and supercritical fluids on polymers have been previously reported.[8–10] It has been shown that, for glassy polymers, carbon dioxide induces swelling in the polymer and that in some cases (e.g., PMMA and polystyrene) it is possible to observe a glass transition pressure. This is a gas pressure at which, for a given temperature below the normal T_g, a transition from the glassy to the rubbery state may be observed. In other words, large depressions in glass transition temperature may be brought about by the plasticizing effects of carbon dioxide at high pressure.

The extraction data presented here are a reflection of these phenomena. The extraction efficiency of the CTC is presumably related to the extent of swelling of the polymer particles allowing diffusion out of the polymer matrix. However, at higher tem-
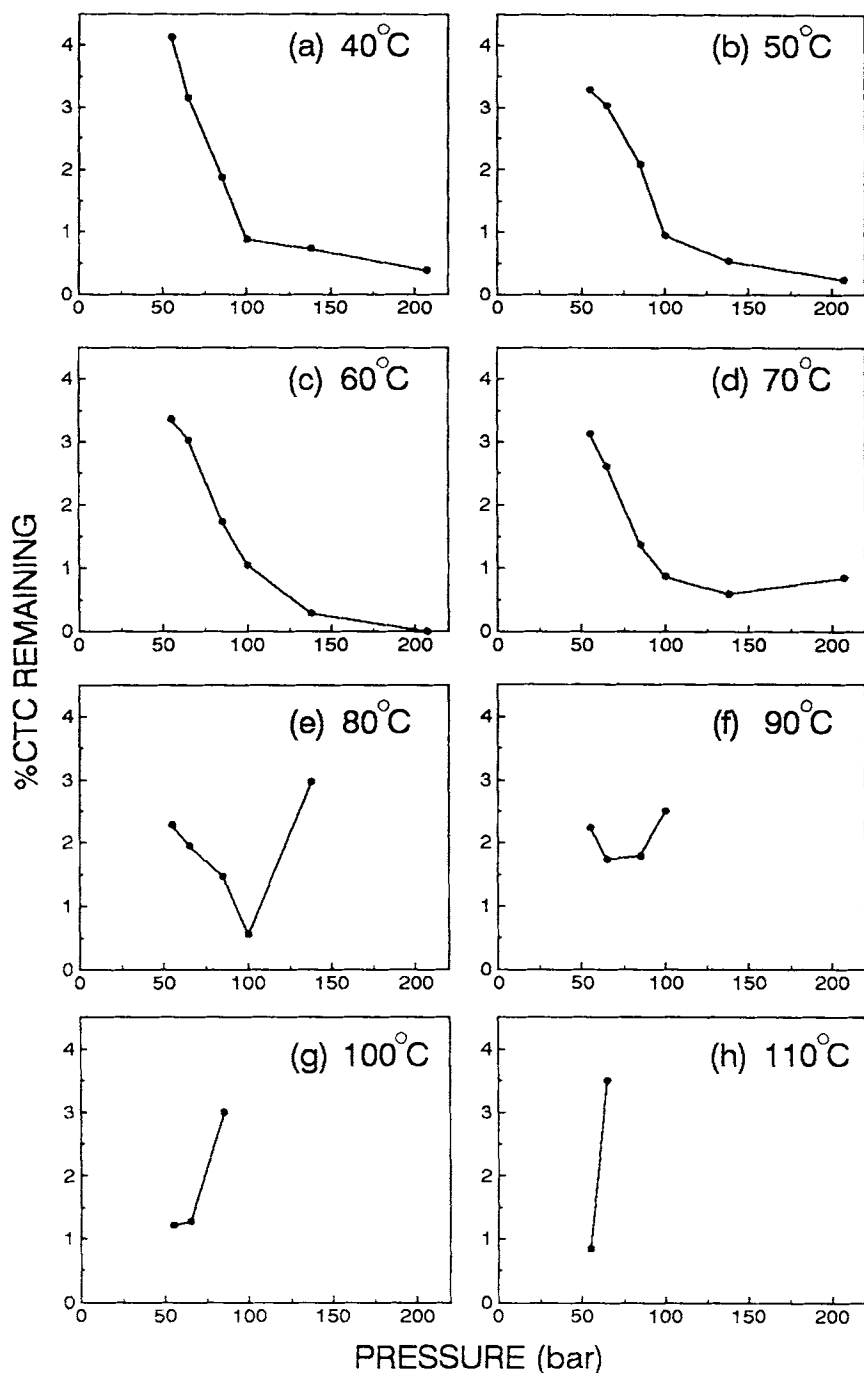
Figure 1 Residual CTC determined in polymer samples after extraction for 40 min plotted as a function of pressure at a range of temperatures as indicated. Data points are connected by solid lines purely as an aid to clarity.

peratures and pressures, particle aggregation occurs due to the transition from the glassy state to the rubbery state for polymer particles swollen and confined in a packed column. Thus, Figure 1 is an illustration of the effects of the glass transition pressure in this situation.

Similarly, although somewhat approximate, it is possible to derive, from Figure 2, the softening temperature as a function of pressure for the system under study here. This result is displayed in Figure 3 and is, in this case, an illustration of the depression in T_g induced by the carbon dioxide (note that the
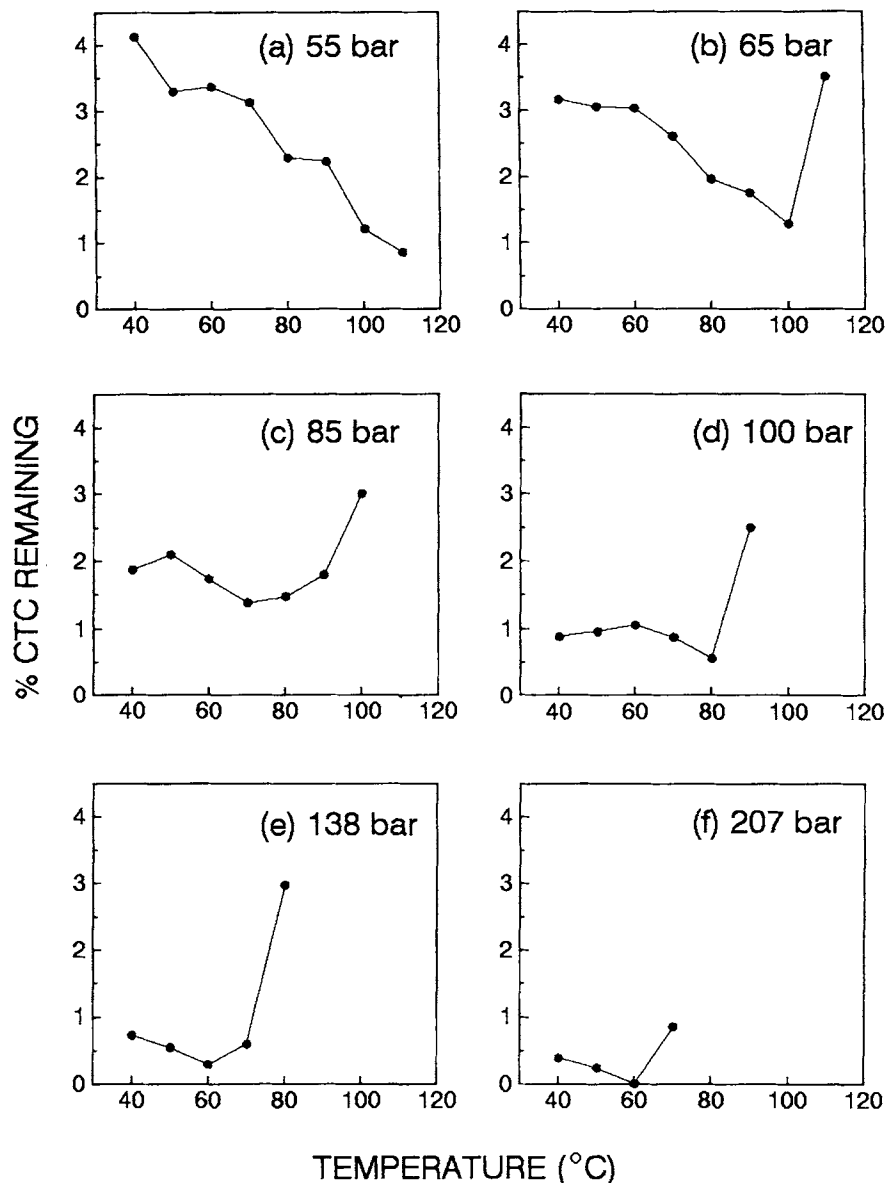
Figure 2 Extraction data plotted as a function of temperature at a range of pressures as indicated. Data points are connected by solid lines purely as an aid to clarity.

T_g of the unplasticized polymer as measured by DSC is 120°C). Extractions performed above this softening line result in a loss of surface area and the poor extraction efficiency associated with this.

This is an extremely important aspect to consider with respect to the application of supercritical extraction to other polymers. In particular, difficulties will be encountered for those polymers whose softening temperature at an appropriate system pressure is less than the critical temperature of the extracting gas. In these cases, it is not possible in a straightforward manner to achieve true supercritical extraction without resulting in particle aggregation.

CONCLUSIONS

It has been demonstrated that carbon dioxide may be used to reduce the CTC levels in chlorinated rubber to below detectable limits under modest conditions of temperature, pressure, and time. It has further been shown that there exist optimum conditions of temperature and pressure which, if exceeded, can produce catastrophic results in terms of extraction efficiency and particle habit. This can be related to the plasticizing effect of carbon dioxide, which can lead to a drastic reduction in the surface area of polymer particles in a packed column.
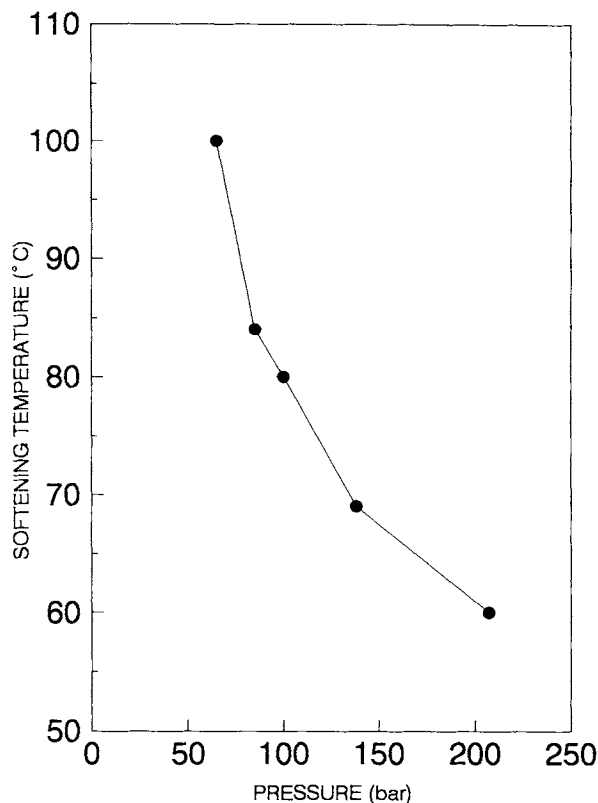
Figure 3 Softening temperature of chlorinated polyisoprene estimated from Figure 2 as a function of carbon dioxide pressure. Data points are connected by solid lines purely as an aid to clarity.

It is believed that carbon dioxide has many potential advantages in polymer processing as a means of facilitating the removal of low molecular weight impurities at relatively low temperature. The carbon dioxide emerging from the extraction column can be reduced in temperature or pressure sufficient to precipitate the extract and then recycled. Suitable use of heat exchangers or turbo-expanders can reduce the energy cost of this extraction cycle. Add to this a system of column switching for semicontinuous processing, and the prospect begins to increase in appeal. At a time when there exists increasing environmental pressure to reduce the use of organic solvents in industrial processes, carbon dioxide holds many potential attractions.

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