ABSTRACT

Recently, Supercritical fluids have been used in material synthesis and processing because of their special properties such as high diffusivity, low viscosity, and low surface tension. Supercritical carbon dioxide is the most attractive because it is non-toxic, non-flammable, and has moderate critical temperature and critical pressure. Moreover, and can also swell most polymers. In this study, we prepared the polymer/clay nanocomposites using supercritical fluids. Cloisites 10A,15A,25A,30B used in this study are natural montmorillonites modified with a quaternary ammonium salt. The nanocomposites of polymer/clay were characterized by XRD,TGA and DSC.

Keywords: supercritical, HCFC-22, nanocomposites, poly(methyl methacrylate), polyethylene oxide, carbon dioxide

1 INTRODUCTION

The application of supercritical fluids (SCFs) to composite material synthesis is developing in materials chemistry. [1,2] SCF solvents are an attractive alternative to incompressible organic liquid solvents, since they can have liquidlike dissolving power while exhibiting transport properties of a gas. Carbon dioxide (CO2) is the favorite solvent in SCF processes. However, it is generally not a good solvent for dissolving high molecular weight polymers.[3] On the other hand, hydrocarbon solvents and hydrochlorofluoromethane (HCFCs) have been known to be good solvents for a variety of high molecular weight polymers.[4] Chlorodifluoromethane(HCFC-22) is a good solvent which has critical point (Tc=96.2 °C, Pc=49.7bar). In this paper, the polyethylene oxide/clay and the poly(methyl methacrylate)/clay nanocomposites using SCF process have been studied. We present novel manufacturing technology of polymer/clay nanocomposites using supercritical fluid. Also, thermal property of polymer/clay nanocomposite using supercritical fluid process was enhanced than using melt intercalation method.

2 EXPERIMENTAL

1.Material

Sodium montmorillonite(Na+-MMT) and Cloisites 10A, 15A, 20A, 25A, 30B-MMT was obtained from Southern Clay Product, Inc. and poly(methyl methacrylate) of average molecular weight 350,000 was supplied by Aldrich Chemical Co. Inc. And poly(ethylene oxide) of average molecular weight 1x10^5 was supplied by Aldrich Chemical Co. Inc.

2.Procedure

2-2-1. PEO/clay nanocomposites Procedure in Supercritical CO2

Polymer/clay nanocomposite was conducted in a 150mL stainless steel high-pressure cell equipped with a magnetic stirring bar and an electrically heating jacket and window cell that allow visual observation of the mixture. Polyethylene oxide (0.6g), sodium montmorillonite or Organo clay(0.4g), were added to the cell. The cell was then filled with CO2 to 70bar, and heated to 70°C. After the desired temperature was reached, the desired pressure(250bar) and the cell was allowed to proceed with stirring for 2hr, and then the cell was cooled, and the CO2 was slowly vented. The final product was taken out and dried at room temperature in a vacuum oven overnight.

2-2-2. PMMA/clay nanocomposites Procedure in Supercritical HCFC-22

Poly(methyl methacrylate) and clay were added to the cell. The reactor heated to 50°C, and purged with nitrogen for 5 min. When the reactor was cooled to room temperature, it was evacuated for 2h using vacuum pump.
The cell was then disconnected from the nitrogen line, evacuated, and connected to the HCFC-22 feed system. The cell was filled with liquid HCFC-22 to 30 bar at 30°C by using an air-driven gas compressor and then gradually heated to 100°C to achieve a pressure 200 bar. After the desired temperature was reached, the cell was allowed to proceed with stirring for 2hr, and then the cell was cooled, and the HCFC-22 was slowly vented.

3. Characterization

XRD data (2θ = 2–10°) were collected on a Rigaku multiflex diffractometer using Cu Kα radiation (30kv,100mA) at a scan rate of 4°/min. DSC was used for measuring Tm of Nanocomposites at a heating rate of 10°C/min. TGA was performed using a Perkin Elmer system in an nitrogen atmosphere at a heating rate of 20°C/min.

3 RESULTS & DISCUSSION

PEO/clay nanocomposites were successfully prepared using supercritical fluid process. Fig.1 shows the X-ray diffraction patterns of PEO/MMT nanocomposites. As the amount of Na+-MMT was increased from 10 wt% to 40 wt%, the d-spacing of MMT was increased from 1.2 nm to 1.8 nm. Moreover, Fig.2 shows the thermal stability of nanocomposites using supercritical fluid process was more enhanced than using melt intercalation method.

![Figure 1. XRD patterns of PEO/Na+-MMT nanocomposites form different content](image)

PMMA/clay nanocomposites was also successfully prepared using SCF process. The XRD results are shown in the Fig. 3. The amount of clay was 10 wt%. Both PMMA/30B clay nanocomposites and PMMA/25A nanocomposites show the fully exfoliated structure.

![Figure 2. TGA curves of PEO/clay nanocomposites using SCF and melt intercalation method](image)

![Figure 3. X-ray of PMMA/30B-MMT and PMMA/25A-MMT nanocomposites](image)

4 CONCLUSION

PEO/clay nanocomposites were prepared using supercritical fluid process. PEO intercalation was shown by shifting of X-ray diffraction peaks. The thermal stability of nanocomposites using supercritical fluid process was more enhanced than using melt intercalation method. This result seems to be due to the powerful dissolving and high diffusion coefficient of supercritical fluid. And the clays of both PMMA/30B and PMMA/25A clay nanocomposites were fully exfoliated.

REFERENCES