Subcritical and Supercritical Fluid Technology for Recycling Waste Plastics

Fig. 2 Pilot Plant for PET Recycling Using Supercritical Methanol

random scission to polymers of smaller molecular weight, which are then continuously depolymerized to yield monomer components by end scission. The estimated molecular weight distribution well simulated the experimental data obtained by size exclusion chromatography. The monomer yield was also calculated and compared as a function of reaction time. Mitsubishi Heavy Industries, Ltd., Japan, has developed a chemical recycling process using supercritical methanol for depolymerizing post-consumer PET bottles on the pilot scale as shown in **Fig. 2**⁹⁾.

Nylon 6 is a polymer synthesized by ring-opening polymerization of ϵ -caprolactam, and has been depolymerized by hydrolysis in subcritical and supercritical water¹⁰⁾. The liquid phase contained ϵ -caprolactam and ϵ -aminocaproic acid with total yield of almost 100 %. Therefore, Nylon 6 was decomposed by hydrolysis to ϵ -aminocaproic acid followed by cyclodehydration to ϵ -caprolactam or further decomposition to smaller molecules, which indicates that the cyclodehydration reaction proceeds in water near the critical temperature.

Polycarbonates are widely used as commodity plastics and engineering plastics. Several depolymerization processes using alkali catalysts, can decompose polycarbonate synthesized from bisphenol A and phosgene, to produce bisphenol A. Decomposition of polycarbonate in subcritical water at 403–573 K resulted in the main products of phenol, bisphenol A, and *p*-isopropenylphenol¹¹⁾. The reaction was accelerated by the addition of Na_2CO_3 .

Polyurethanes are produced by the reaction of polyisocyanate with polyalcohol (polyol). Hydrolysis of polyurethane in water forms the polyol and diamine corresponding to the starting isocyanate¹²⁾. Decomposition of polyurethane was almost 100 % at temperatures above 543 K. Both polyol and diamine were recovered almost completely. Decomposition of polyurethane foam in subcritical water at 423–623 K

Fig. 3 Concept of Chemical Recycling of TDI to TDA

Fig. 4 Commercial Plant for TDI Residue Recycling

formed tolylenediamine (TDA) and polyol with the highest yield of almost 90 %¹³⁾.

Kobe Steel, Ltd. developed a chemical recycling process at Mitsui Takeda Chemicals, Inc. in 1997 by applying noncatalytic hydrolysis in subcritical water. Tolylenediisocyanate (TDI) distillation residue, which is typically incinerated, was successfully converted to TDA as shown in **Fig. 3**. The commercial plant has been operating since 1998 with a capacity of 10 t/day (**Fig. 4**). The process consists of a reaction process in subcritical water and a purification process. The recovered TDA was of high quality and more than 99.5 % pure. Expansion of the plant was completed in 2003. Hanhwa Chemical in Korea has commercialized a solid TDI residue recycling process and constructed a plant at Korea Fine Chemical in 2007 with capacity of 20 t/day³⁾.

2. 2. Addition Polymerization Plastics

Recycling of thermosetting resins, which are widely used for electronics, is important. Phenol resin has high thermal stability because aromatic units are connected by methylene bonds. Prepolymers of phenol resin were decomposed into their monomers in sub-

critical and supercritical water¹⁴). The total yield of identified products depended on the type of prepolymer; the maximum yield reached 78 % in a reaction at 703 K. The decomposition was accelerated by the addition of Na_2CO_3 , and the yields of monomers were more than 90 %. Decomposition in subcritical and supercritical water was applied to printed circuit boards¹⁵) and the liquid phase contained phenol, *o*-cresol, and *p*-cresol.

Flame-retardant plastics (Br-ABS and Br-HIPS) was decomposed in supercritical water in the absence and presence of the alkaline additives NaOH and $\text{Ca}(\text{OH})_2$ ¹⁶). The main reaction products were oils containing ethylbenzene. The bromine atoms in the plastics were removed into the aqueous phase, and all antimony remained in the solid residues.

Polyethylene is a commodity thermoplastic extensively used in consumer products. Higher yields of shorter chain hydrocarbons, higher 1-alkene/*n*-alkane ratio, and higher conversion rates were obtained in supercritical water¹⁷). Polyethylene cracking in supercritical water was compared with water-free thermal cracking. Yellow-brown grease was produced from supercritical water cracking¹⁸). The yield of oil products was higher and coke production was lower in supercritical water cracking than in thermal cracking.

2. 3. Crosslinked Polyethylene

Crosslinked polyethylene (XLPE) is a thermosetting resin which is difficult to recycle because of its low fluidity and low moldability due to the crosslinking. XPLE is classified into three types based on the crosslinking: peroxide-crosslinked polyethylene, radiation-crosslinked polyethylene, and silane-crosslinked polyethylene. If only the crosslinking points in XLPE are decomposed, the polymer can be effectively recycled, which does not require decomposition into smaller molecules. Since selective decrosslinking at crosslinking points is difficult in conventional processes, XLPE is usually converted into oil by thermal and catalytic cracking.

Hitachi Cable Ltd. has developed recycling of the insulation of crosslinked polyethylene cable^{19)~21}). The crosslinking element that consists of a siloxane bond in silane-crosslinked polyethylene (silane-XLPE) was selectively decomposed in supercritical alcohol or water as shown in **Fig. 5**. The crosslinking element was completely decomposed without reduction of the polymer molecular weight by reaction at 573-613 K in methanol. Supercritical methanol achieved selective decomposition at the crosslinking points, whereas supercritical water was less selective. The mechanical and electrical properties of the recycled polyethylene satisfied the requirements for use as cable insulation. A pilot-scale continuous process consisting of a reactor extruder and a degasser extruder was developed.

Decrosslinking of polyethylene in supercritical meth-

Cross-linking bond

Fig. 5 Decrosslinking of Silane Crosslinked Polyethylene in Supercritical Fluid

Fig. 6 Concept of FRP Recycling Using Subcritical Water

anol confirmed that the molecular weight of decrosslinked polyethylene was only slightly lower than that of raw polyethylene²²).

3. Materials Recovery from Waste

Fiber-reinforced plastics (FRPs) have been widely used as a high-strength material in recent years. FRP containing glass fiber (GFRP) is a composite material manufactured by laminating unsaturated polyester resin with glass fiber and filler. FRP containing carbon fiber (CFRP) usually consists of carbon fiber and epoxy resin.

Decomposition of FRP in subcritical and supercritical water resulted in almost complete decomposition at 653 K in 5 min^{23),24}). Decomposition of epoxy resin containing carbon fiber in supercritical water reached 79.3 wt% at 673 K and 95 wt% with alkali catalyst²⁵). The tensile strength of the reclaimed fibers was close to the virgin fibers.

Panasonic Corp. has developed FRP recycling technology since 2002 using hydrolysis in subcritical water^{26)~28}). After subcritical water hydrolysis of FRP, the resin was dissolved into a reaction liquid. The recovered unsaturated polyester components, such as glycols and fumaric acid, were separated from the aqueous reaction liquid and polymerized into polyester with new raw resin materials to produce recycled resin. Styrene-fumaric acid copolymer obtained in the aqueous phase was also separated and can be used as a low-profile additive for FRP formation (**Fig. 6**). The recovered inorganic materials can be used as inorganic

Fig. 7 Pilot Plant for FRP Recycling Using Subcritical Water

Fig. 8 Recovered Glass Fiber (left) and Carbon Fiber (right) from Treatment in BZA

filler to produce FRP. A pilot plant with a reactor capacity of 2.9 m³ was operated in Tochigi, Japan as shown in Fig. 7.

Hitachi Chemical Co., Ltd. investigated the dissolution process of the resin part of FRP by the “ambient pressure dissolving method” using various solvents with or without catalysts to develop a recycling technology for FRP²⁹⁾. The highest conversion was observed using K₃PO₄ as the catalyst and diethyleneglycol monomethylether as the solvent. The second highest conversion was observed for benzyl alcohol (BZA).

Operation temperature can be increased under pressures higher than the vapor pressure^{30),31)}. Reactions were carried out with or without a catalyst (K₃PO₄) in BZA under subcritical states at temperatures ranging from 463 to 623 K for 1–8 h in a batch reactor. Conversion of unsaturated polyester (UP) was faster at higher catalyst/solvent molar ratio and was enhanced in the presence of catalyst in subcritical BZA. The glass fibers recovered after FRP treatment in subcritical BZA were relatively long. Carbon fiber was also recovered successfully by treatment in BZA with K₃PO₄. **Figure 8** shows the fibers recovered by treatment in BZA. Recycling technology using subcritical and supercritical fluid for CFRP has been reviewed⁴⁾.

4. Conclusions

The development of chemical recycling of waste plastics by decomposition reactions in subcritical and supercritical fluids is reviewed from fundamental investigations to commercial scale processes. Condensation polymerization plastics are relatively easily depolymerized to their monomers. Crosslinked polymers can be recycled by selective decrosslinking reactions without severe decomposition of the backbone chains. Fiber reinforced plastics can also be recycled by depolymerization of the resin component to yield recovered fibers and monomers.

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要 旨

亜臨界・超臨界流体を用いた廃プラスチックのリサイクル技術

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超臨界流体は臨界温度と臨界圧力を超えた状態であり、反応や分離溶媒として注目されている。亜臨界・超臨界流体を用いた分解反応による廃プラスチックの化学リサイクル技術について基礎から商用プラントに至るまで総括する。従来プロセスに比べて超臨界流体中では分解反応が迅速かつ選択的に進行する。PET やナイロンなどの縮重合系プラスチックは超臨界水や

超臨界アルコール中で比較的容易にモノマーに解重合される。架橋高分子は主鎖の過度の分解を伴わずに選択的脱架橋化反応によりリサイクルできる。繊維強化プラスチックは樹脂部分を解重合することにより繊維や化学原料として回収できる。廃プラスチックのリサイクルのために亜臨界・超臨界流体を用いたパイロット規模や商用規模のプラントが開発されている。