Aminolysis and Aminoglycolysis of PET

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Aminolysis process of poly(ethylene terephthalate) using diethylenetriamine, triethylenetetramine, hexamethylenediamine, diethanolamine and triethanolamine is described. The products of PET aminolysis/ glycolysis are applied for epoxy resin hardening and rigid polyurethane foam synthesis. Two other potential fields of application i.e. surface active substances and feedstock for polyamide synthesis are also considered.

Introduction

The recycling of waste polymers including poly(ethylene terephthalate) (PET) can be carried out in many ways. PET belongs to condensation polymers very vulnerable to solvolytic chain cleavage. The polymer might be chemically recycled with a wide spectrum of degrading agents thus resulting in a great variety of products [1]. Besides conventional degrading agents such as methanol, (methanolysis), glycols (glycolysis), mineral acids, alkalis, water or steam (hydrolysis) an increasing tendency to use less common chemicals for PET chemical recycling is observed [2].

Aminolysis is not so often used as the other methods of poly(ethylene terephthalate) chemical recycling. The processes of partial, superficial aminolytic degradation of PET fibers have been subjected to numerous research studies (see ref. in [2]) and are practically applied on industrial scale. Such modification processes improve the quality of fiber dyeability and other technical and application parameters of the fibers.

Literature references concerning the deep aminolytic degradation of PET are very few (e.g. [2,3]) and application of the products of such a process on a commercial scale are rather unknown.

In this contribution results of investigation of poly(ethylene terephthalate) with selected amines and aminoalcohols are presented. Directions of application of the respective degradation products of PET, as feedstock materials are proposed.

Materials and Methods

Waste PET from packaging (beverage bottles) was used for chemical recycling after desintegration on flakes ca. 1x1 cm.

The following amines were applied for the polymer degradation: diethylenetriamine (DETA), triethylenetetramine (TETA), both from Riedel-De Haen A.G., Hannover, Germany, hexa-methylenediamine (HMDA) from E.

Merck, Darmstadt, Germany; diethanolamine (DEA) and triethanolamine (TEA) both products of Z.Ch. Rokita S.A., Brzeg Dolny, Poland.

Epoxy resin: Epidian 6 - bisphenol A type low molecular, liquid resin, RE=186, product of Z.Ch. Organika-Sarzyna, Sarzyna, Poland was hardened with some PET degradation products.

Polyol: Rokopol PT 44, polyoxypropylene tetrol, hydroxy number L_{OH} = 435, product Z.Ch. Rokita,S.A. was used for dilution PET degradation products with ethanolamines (DEA and TEA) and next applied for rigid polyurethane (PU) foam synthesis. Other PU components: diisocyanate Ongronat CR-30-20 (oligomeric MDI), product of Borsod Chem., Hungary; catalyst Niax A-1 and surface active agent Niax L-6900 both from Osi Specialtias S.A., Switzerland; blowing agent: pentane + water.

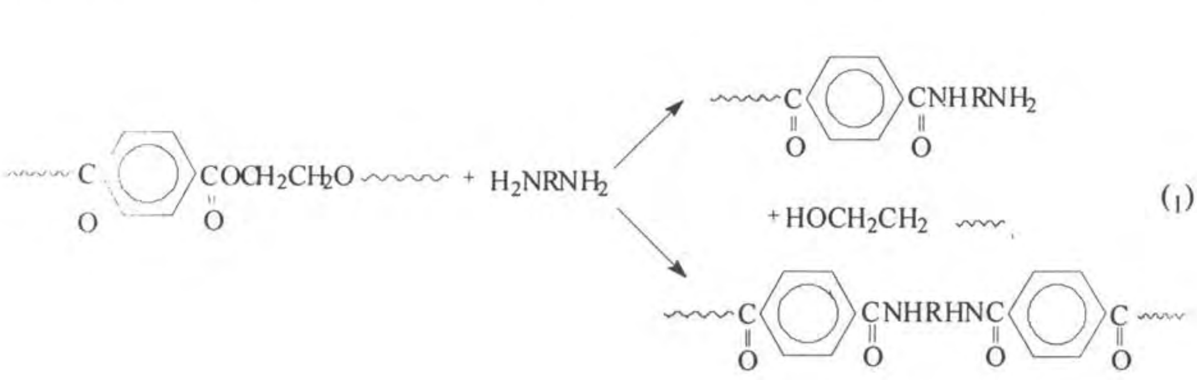
Long chain alkyl derivatives C_{12}, C_{14} and C_{16} from E. Merck, Darmstadt were used as reagents for surface active substances synthesis using PET/TEA degradation products.

Solvolysis of the waste PET with DETA, TETA, DEA and TEA was performed in a temperature range 100-215 °C. Time and molar ratio of reagents i.e. PET/ amine were also subjected to changes. Aminolysis with HMDA was carried out in ethylene glycol as a reaction medium at temperatures 120-140 °C. By-products of PET aminolysis/ glycolysis i.e. mainly ethylene glycol, were distilled off before using the products as feedstock for PU foam synthesis or the epoxy resin hardening.

Products of PET aminolysis (or glycolysis) were investigated by ^{1}H NMR, DSC or hydroxyl number was determined [4]. New materials obtained from the feedstock based on PET aminolysis products were characterized by methods of DSC, rheometry ARES (epoxy materials) or specific for rigid PU foams.

Results and Discussion

In effect of aminolytic solvolysis of PET chains by polyamines such as DETA, TETA and HMDA the following type amide derivatives are created:



(1)

In the cases of PET degraded by DEA or TEA solvolysis reaction may be considered as aminoglycolysis (DEA) or glycolysis catalyzed through tertiary amine groups (TEA).

All the PET degradation products with polyamines or ethanolamines were multicomponent mixtures as found by DSC and ^{1}H NMR. Their properties were dependent on PET/ amine molar ratios, temperature and time of the process.
Table 1 presents progress of PET glycolysis process in the system PET/TEA as expressed by values of hydroxyl numbers measured successively during process. It is seen from Table 1 that the final degradation product has L_{OH} substantially lower than that for theoretically expected 4,4'-bis(triethanolmonoamide) derivative of terephthalic acid.

Independently on a complex composition of PET aminolysis/ glycolysis degradation products we tried to apply them as feedstock materials. PET/DETA, PET/TETA and PET/TEA were used as epoxy resin hardeners. The former two products act as curing agents in polycondensation whereas the latter as inducing polymerization mechanisms of hardening.

Table 1. Hydroxyl number L_{OH} of PET degradation products taken during process (210 °C: PET 1 mol + triethanolamine 2 moles)

sample	time [min]	L_{OH} [mg KOH/g]	
		air	nitrogen
1	30	531	461
2	60	447	406
3	90	373	397
4	120	289	292
5	150	260	-

L_{OH} of triethanolamine = 1128
L_{OH} of 4,4'-bis(triethanolmonoamide) of terephthalic acid = 523

Fig. 1 presents viscosity-temperature curves for particular compositions of epoxy resin Epidian 6 (E 6) and PET degradation product, with TETA and TEA, respectively. For comparison data for E 6 cured with TETA and with modified hardeners PET/TEA/PAC are placed in Fig.1 also. It was found that useful epoxy mateirals can be obtained on a basis of PET/TETA or PET/TEA aminolysis products.

Rigid polyurethane foams can be synthesized using PET/TEA degradation product diluted with commercial polyol Rokopol PT 144. Properties of such PU foams are comparable with those synthesized of pure commercial polyol, up to content of the recycled component equal 30 wt. % [5].

Two other areas of use of PET/TEA and PET/HMDA products look promising i.e. synthesis of cationic emulgators and components for polyamide type polymers, respectively.

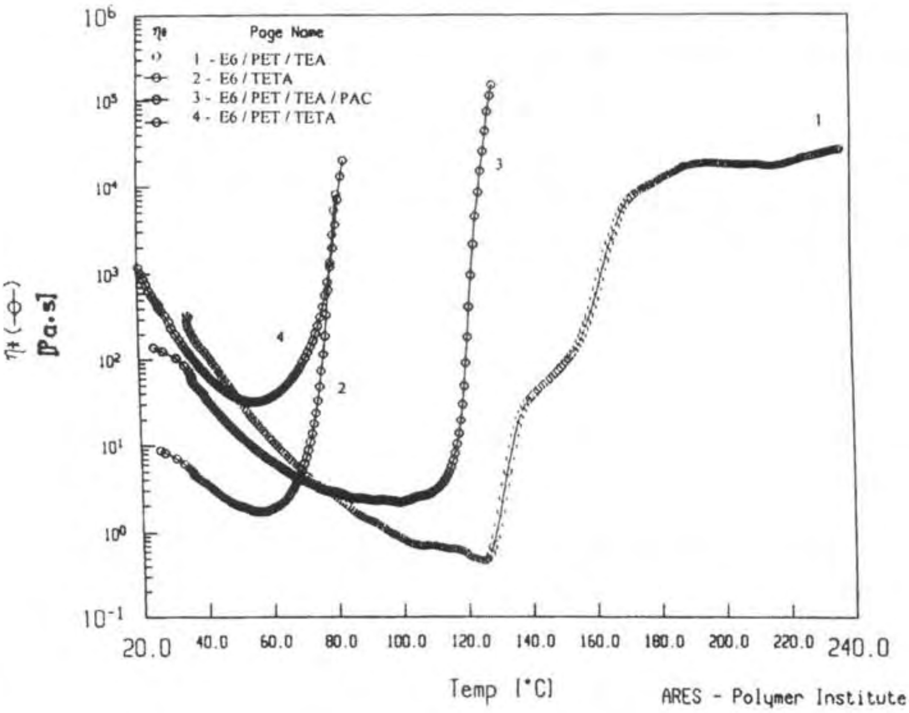


Fig. 1. Viscosity of epoxy compositions during heating with rate 5°/min.

Conclusion

Products of PET aminolysis/glycolysis may be applied as feedstock materials for epoxy resin hardening and rigid polyurethane foams synthesis. Some other areas of usage are also possible.

References

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