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Mechanical and Migration Properties of PVC/Waste PET Depolymerization Products Blends

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Waste poly(ethylene terephthalate) (PET) flakes were depolymerized by using trimethylol propane (TMP) in the presence of zinc acetate as catalyst. Molar ratio of PET/TMP was used as 1/2 and 1/4 in the alcoholysis reactions. In order to obtain PVC plastisols, PVC powder was dispersed into a plasticizer mixture composed of di-isononyl phthalate (DINP) and alcoholysis products by using a high-speed mixer (65% PVC, 35% plasticizers w/w). Alcoholysis products were used 20 and 40% of DINP by weight in the plasticizer mixture. Plasticized PVC sheets were prepared from these plastisols. Migration properties, mechanical properties and T_g of plasticized PVC sheets were determined. Results showed that the alcoholysis products of waste PET are compatible for using as secondary plasticizer for PVC.

Keywords waste PET, alcoholysis of PET, recycling, secondary plasticizer

Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely used in the packaging industry. The interest in recycling of waste PET is continuously growing because of environmental and economic factors. In Europe, the amount of collected waste PET increased almost ten-fold, from 45000 tons in 1995 to 499000 tons in 2003 (1). Mechanical recycling (2, 3), as well as chemical recycling, is being considered and chemical recycling is being used to obtain the monomer for use in further synthesis (4). The process of chemical recycling of waste PET (5) involves neutral (6), alkaline (7–9), acidic (10) hydrolysis, glycolysis (11, 12) and simultaneous hydrolysis-glycolysis (13). Although chemical depolymerization of waste PET by glycolysis (in excess diol, such as ethylene glycol (14), propylene glycol (15) and diethylene glycol (16)), by alcoholysis (in methanol) (17–20) has been studied for many years, and there is no report on using trimethylol propane (TMP). So far, most of the studies conducted are related to the industrial production of polyols, unsaturated polyesters (21, 22) and polyurethanes (23).

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Poly(vinyl chloride) (PVC) plays an important role in the plastic industry and is one of the most versatile thermoplastics, but it must be combined with a number of additives before processing. Low-molecular-weight plasticizer is one of the major additives used in PVC compounding. The addition of plasticizers to a PVC formulation decreases many mechanical properties such as hardness, tensile strength, modulus, etc. of the PVC product; however, low temperature flexibility, elongation and the ease of processing are all improved (24). The most widely used plasticizers are di-octyl phthalate (DOP) and di-isononyl phthalate (DINP) for PVC. These types of PVC- plasticizer blends present serious problems of high migration. One alternative to this problem is the use of polymeric plasticizers (25).

In this work, we investigated that the use of the alcoholysis products of waste PET with TMP as a secondary plasticizer for PVC.

Experimental

Materials

Waste PET flakes from grinding post consumer water bottles was sieved to obtain an 8–10 Mesh fraction. The viscosity average molecular weight ($\bar{M}_v$) was found to be 37000 (13). PVC was from Elf Atochem Ltd. DINP was from Plastay Chem. Ltd. The thermal stabilizer (Ca/Zn based) was from Akdeniz Chem. Ltd. The remaining materials were of synthesis and analytical grade.

Alcoholysis Reactions

The waste PET was depolymerized in TMP (PET/TMP molar ratio 1/2, 1/4) using 1% (w/w) zinc acetate, based on the weight of waste PET, as catalyst. The alcoholysis reactions were carried out at 230–240°C for 6 h in a 500 mL five- necked conventional glass reaction kettle equipped with a mechanical stirrer, heating mantle, reflux condenser, temperature control system and N_2 gas inlet. The reaction kettle was cooled and the alcoholysis products were directly used in preparation of the plasticizer mixture. In the case of PET/TMP molar ratio 1/2 and 1/4, alcoholysis products were called as A1 and A2, respectively. Hydroxyl value (HV) of A1 and A2 were determined by the acetylation method (26).

Preparation of the PVC Plastisols and Plasticized Sheets

PVC was dispersed into a plasticizer mixture composed of DINP and A1 or A2 and heat stabilizer in a high speed mixer (1400 rpm) in the following proportions: 65% of PVC, 35% of plasticizer mixture (w/w). A1 and A2 were used 20 and 40% of DINP by weight. Heat stabilizer (Ca/Zn based) was added at the level of 5% (w/w) based on the weight of plastisol. The PVC plastisols were plastered to a flat paper and were heated at 180°C in an oven for 2 min and plasticized PVC sheets (0.5 mm thickness) were obtaining.

Table 1 summarizes the composition of the plasticized PVC sheets. In order to obtain glass transition temperature (T_g) of the plasticized PVC samples, Differential Scanning Calorimetry (DSC) (SETARAM DSC 131) was used with a heating rate of 10°C/min under nitrogen atmosphere.

Table 1
The composition of plasticized PVC samples

Sample code	Plastisol Composition (wt%) PVC	Ca/Zn Stab.	DINP	A1	A2
R	100	5	65	—	—
A1-20	100	5	52	13	—
A1-40	100	5	39	26	—
A2-20	100	5	52	—	13
A2-40	100	5	39	—	26

Mechanical properties of plasticized PVC sheets were determined by a Hounsfield H10KS Universal Testing Machine.

Migration Test

Migration (liquid transfer) properties of plasticizers from plasticized PVC sheets were investigated by using a combined method that includes thermogravimetric analysis (27) and ASTM D2199-68 method. Small squared strip of polystyrene (PS) (2.5 cm × 2.5 cm) with approximately 0.5 mm of thickness were placed between two plasticized PVC sheets of 1 mm of thickness, and aged under low-pressure 100 kPa in an oven at 70°C for 3 days. PS/R, PS/A1-20, PS/A1-40, PS/A2-20 and PS/A2-40 denoted to the PS samples aged with plasticized PVC sheets.

Subsequently, migration of the plasticizer was determined by thermogravimetric analysis in a Shimadzu TGA 50A, by heating the aged PS samples from 25 to 500°C at 10°C/min heating rate under nitrogen flow.

In order to examine the changes of the surface of the PS films (before and after the migration test), an Olympus BX/40 microscope with a magnification of 3.3 × 10 was used.

Results and Discussion

Alcoholysis Reactions of Waste PET

In this study, the possible application of alcoholysis products obtained from waste PET as polymeric plasticizer for PVC was investigated. The alcoholysis of waste PET was carried out by using TMP (PET/TMP molar ratio 1/2, 1/4) in the presence of zinc acetate as catalyst at 230–240°C. HV of A1 and A2 were found to be 725 and 925 mgKOH/g, respectively.

The results indicate that the HV of alcoholysis products (A1 and A2) increase with the amount of TMP. This means that (1) the extent of polymerization increases with the amount of TMP (2) excess TMP. Alcoholysis products were used as plasticizer 20 and 40% of DINP by weight.

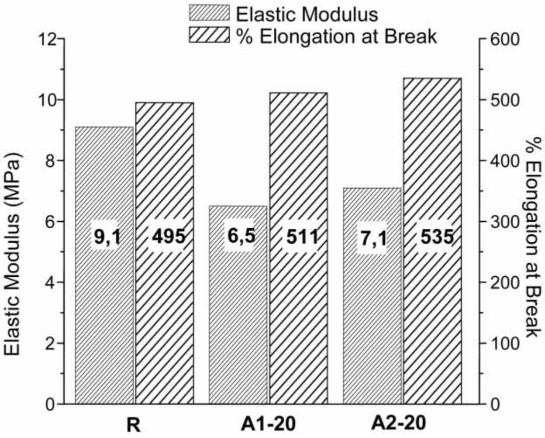

Figure 1. Mechanical properties of plasticized PVC samples.

Mechanical Properties

The elastic modulus and elongation at break (%) of the plasticized PVC sheets that plasticized by using only DINP (R) was found to be 9.1 MPa and 495%, respectively. The elastic modulus decreased by using A1 and A2 products 20% of DINP by weight, but elongation at break (%) increased. The decrease amount of elastic modulus is 29% and 22% according to R for A1-20 and A2-20, respectively. But, elongation at break (%) was improved as 3.5 and 8% by using A1 and A2 products 20% of DINP by weight (Figure 1). Decreased elastic modulus and increased elongation at break (%) indicate that A1 and A2 products can be used as a plasticizer for PVC 20% of DINP by weight.

In the case of using A1 and A2 40% of DINP by weight, the elastic modulus of plasticized sheets were increased, but elongation at break (%)decreased slightly. Elastic modulus of A1-40 sample increased 23% according to R and similarly elongation at break (%) decreased 15%. Similarly, elastic modulus of A2-40 sample increased 31% and elongation at break (%) decreased 16% according to R (Figure 2). Since the elastic

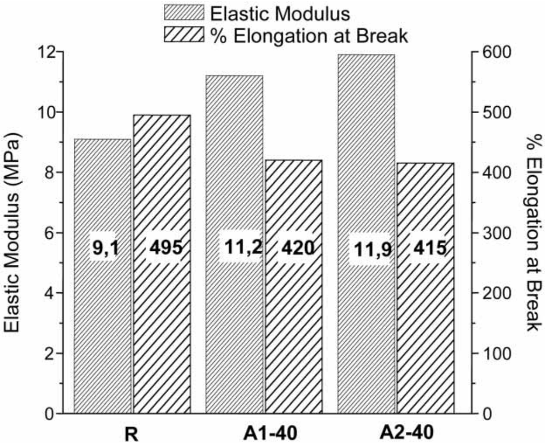

Figure 2. Mechanical properties of plasticized PVC samples.

modulus and elongation at break (%) changes slightly, it can be said that using A1 and A2 products 40% of DINP by weight is acceptable for some applications.

Migration Properties of Plasticizers

The method (27) used to investigate migration properties of plasticizers based on thermogravimetric analysis of PS samples aged with plasticized PVC sheets. Thermogravimetric analysis results of blank PS, A1 and PS samples aged with different PVC sheets (PS/R, PS/A1-20, and PS/A1-40) are given in Figure 3. As seen from Figure 3, the TGA

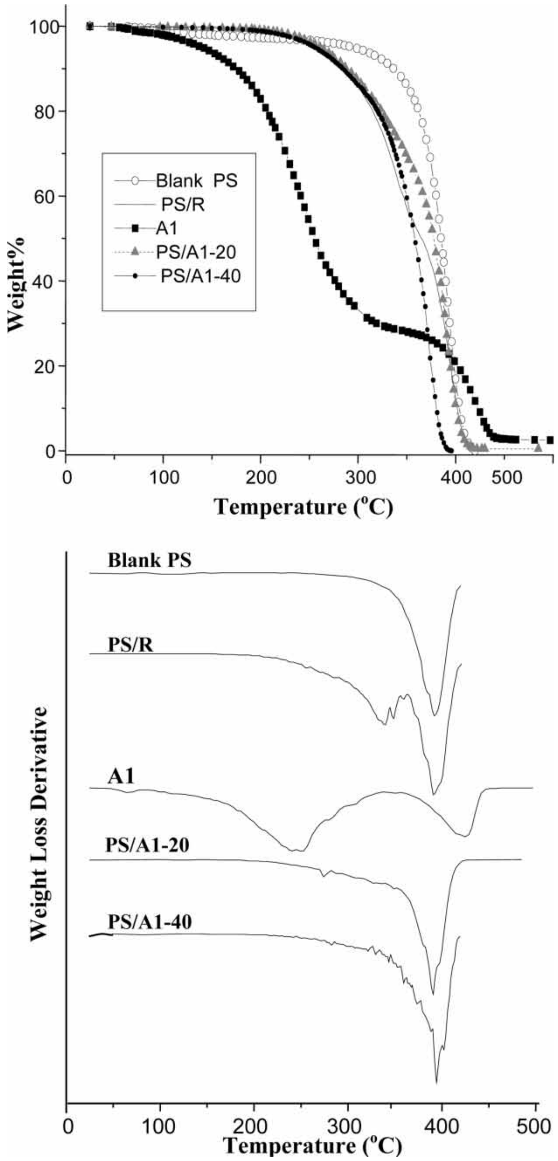

Figure 3. Weight % and weight loss derivative curves of PS samples aged with plasticized PVC.

curve of the blank PS shows one step attributed to the polymer degradation. However, the thermogram of PS/R has one additional step corresponding to the boiling point (at 384°C) (28) of migrated DINP to PS. The weight loss derivative curve of A1 has two degradation peaks (maxima at 249°C and 420°C) corresponds to the thermal degradation of A1.

Choice of terminated groups and total architecture of the plasticizer molecule is especially critical to good compatibility with PVC. In application, high molecular weight polymeric plasticizers (i.e., polyesters) and polymerizable plasticizers (i.e., trimethylolpropane bis(methacrylate), 2-ethyl-2-hydroxymethyl-1,3-propanediol dimethacrylate) are used to provide good resistance to extraction, migration, and volatile loss (29). The thermograms of the PS/A1-20 and PS/A1-40 have only one degradation step, such as blank PS. It means that there is no migration of plasticizers from PVC to PS matrix. It can be said that A1 product is highly compatible with PVC due to its molecular structure.

Microscopic observations of these samples were also in compliance with thermogravimetric studies. Figure 4 shows a comparison of migration properties of the plasticizers from PVC sheets. At the blank PS micrograph (Figure 4a), it is seen that the PS sample has a smooth surface. When the PS sample aged with R (PS/R), it is observed on the surface that there are numerous small transferred liquid drops on the surface, which attributed to the migrated DINP. In the case of PS/A1-20 and PS/A1-40, the micrograph has smaller amounts of transferred liquid drops dependent on a decreased amount of DINP used (Figure 4(b,c,d)). Decreasing the DINP amount (increasing A1 amount) decreases the migration. Microscopic observations and thermogravimetric studies show that A1 does not migrate to the PS and can be used as a low migrated plasticizer.

Figure 5 shows the behavior of a blank PS sample, A2 and PS samples aged with plasticized PVC sheets (PS/R, PS/A2-20 and PS/A2-40). A2 has three degradation steps in the weight loss derivative curve (maxima at 211, 306 and 420°C). However, there was not step at these temperatures in the thermograms of PS/A2-20 and PS/A2-40, which means that there is no migration of A2 to PS such as A1. At the micrographs of these samples, the surfaces of the PS films are seen homogeneous (a little amount of transferred liquid was

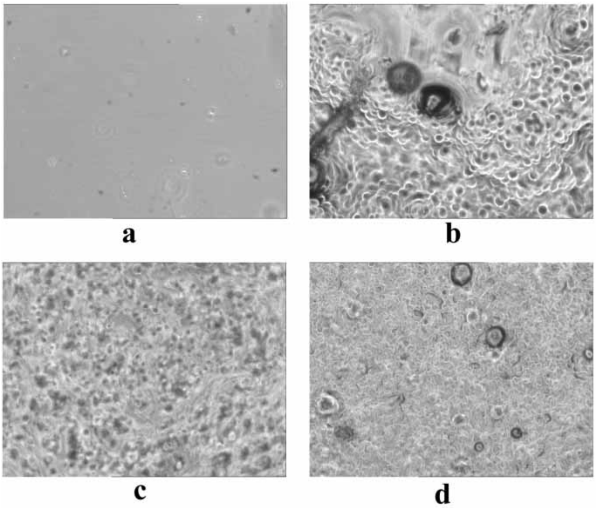

Figure 4. Micrographs of PS sheets after the migration tests a) Blank PS, b) PS/R, c)PS/A1-20, d) PS/A1-40.

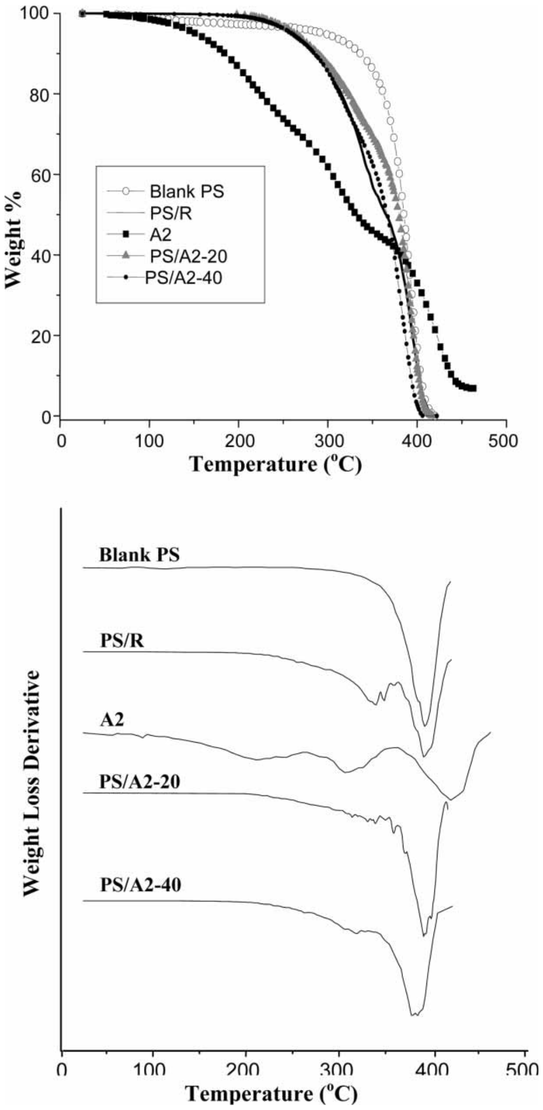

Figure 5. Weight % and weight loss derivative curves of PS samples aged with plasticized PVC.

observed). Since the amount of A2 in the plasticizer mixture increases, the transferred liquid drops on the sample surface decreases. This shows that A2 does not migrate to PS matrix (Figure 6).

T_g Determination

Figure 7 shows the T_g of plasticized PVC sheets. T_g of R was determined as −37°C. T_g of A1-20, A1-40, A2-20 and A2-40 are −40°C. Since these products have similar elastic modulus and elongation at break (%) values and have approximately the same T_g that R has, it can be said that A1 and A2 (20 and 40% of DINP by weight) can be used as a secondary plasticizer with DINP for PVC.

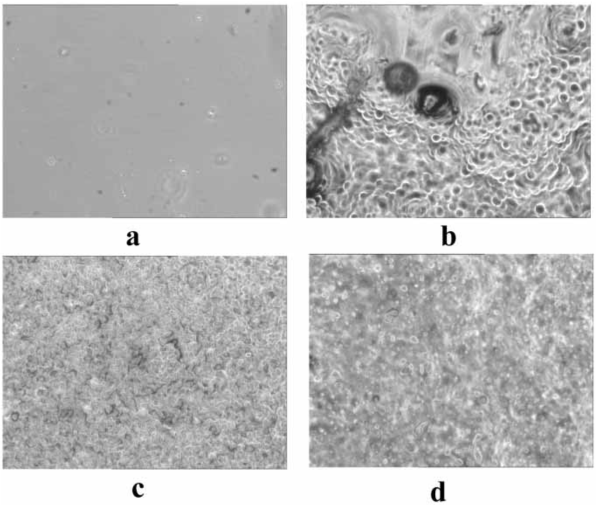

Figure 6. Micrographs of PS sheets after the migration tests. a) Blank PS, b) PS/R, c) PS/A2-20, d) PS/A2-40.

Conclusions

A1-20, A1-40, A2-20, and A2-40 have approximately the same mechanical properties. Also, these products have a lower T_g than R. Migration tests showed that all products obtained by using A1 and A2 have a lower migration than R.

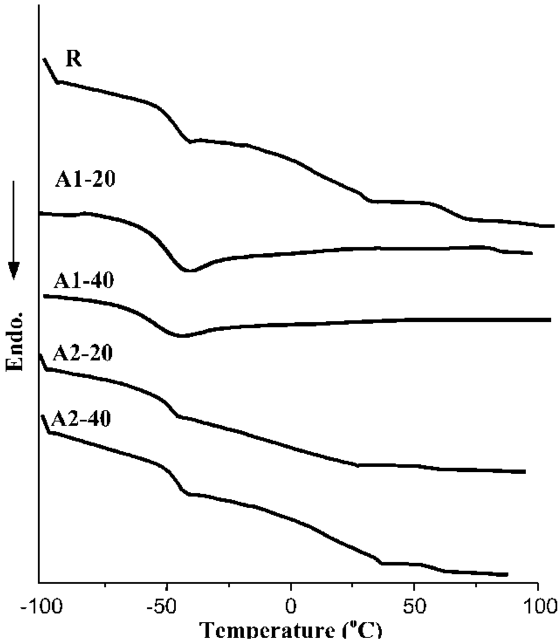

Figure 7. T_g of the plasticized PVC sheets.

These results show that:

Using A1 and A2 products as secondary plasticizer 20% of DINP by weight, improves elongation at break (%) slightly, but decreases elastic modulus. T_g of these samples are approximately the same and lower than R, but the migration of the plasticizer mixture decreases significantly.

Using A1 and A2 products as a secondary plasticizer 40% of DINP by weight, improves elastic modulus, but decreases elongation at break (%). T_g of these samples are approximately the same and slightly lower than R, but the migration of the plasticizer decreases significantly.

According to all results, A1 and A2 products obtained from alcoholysis of waste PET by using TMP can be used up to 40% of DINP by weight as a secondary plasticizer for PVC.

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References

1. PET Core News No.1, April 2003, PET Container Recycling Europe (Petcore). Belgium.
2. İyim, T.B., Özgümüş, S., and Orbay, M. (2002) Blend and Reaction Products Prepared from Phenolic Resin and Waste PET: I. Mechanical Properties. *Polymer-Plastics Technology and Engineering*, 41 (5): 917–931.
3. İyim, T.B., Özgümüş, S., and Orbay, M. (2003) Blend and Reaction Products Prepared from Phenolic Resin and waste PET: II. Thermal Oxidative Degradation. *Polymer-Plastics Technology and Engineering*, 42 (1): 17–32.
4. Mishra, S., Zope, V.S., and Goje, A.S. (2002) Kinetic and Thermodynamic Studies of Depolymerization of Poly(ethylene terephthalate) by Saponification Reaction. *Polym. Int.*, 51: 1310–1315.
5. Paszun, D. and Spychaj, T. (1997) Chemical Recycling of Poly(ethylene terephthalate). *Ind. Eng. Chem. Res.*, 36: 1373–1383.
6. Güçlü, G., Yalçınyuva, T., Özgümüş, S., and Orbay, M. (2003) Hydrolysis of Waste Polyethylene Terephthalate and Characterization of Products by Differential Scanning Calorimetry. *Thermochimica Acta*, 404 (1–2): 193–205.
7. Wan, B., Kao, C., and Cheng, W. (2001) Kinetics of Depolymerization of Poly(ethylene terephthalate) in a Potassium Hydroxide Solution. *Ind. Eng. Chem. Res.*, 40: 509–514.
8. Kao, C., Cheng, W., and Wan, B. (1998) Investigation of Alkaline Hydrolysis of Polyethylene Terephthalate by Differential Scanning Calorimetry and Thermogravimetric Analysis. *J. Appl. Polym. Sci.*, 70: 1939–1945.
9. Karayannidis, G.P., Chatziavgoustis, A.P., and Achilias, D.S. (2002) Adv. Poly(ethylene terephthalate) Recycling and Recovery of Pure Terephthalic Acid by Alkaline Hydrolysis. *Polym. Technol.*, 21 (4): 250–259.
10. Yoshioka, T., Motoki, T., and Okuwaki, A. (2001) Kinetics of Hydrolysis of Poly(ethylene terephthalate) Powder in Sulfuric Acid by a Modified Shrinking-Core Model. *Ind. Eng. Chem. Res.*, 40: 75–79.
11. Güçlü, G., Kaşgöz, A., Özbudak, S., Özgümüş, S., and Orbay, M. (1998) Glycolysis of Poly (ethylene terephthalate) Wastes in Xylene. *J. Appl. Polym. Sci.*, 69: 2311–2319.

12. Chen, C.H., Chen, C.Y., Lo, Y.W., Mao, C.F., and Liao, W.T. (2001) Studies of Glycolysis of Poly(ethylene terephthalate) Recycled from Postconsumer Soft-Drink Bottles. I. Influences of Glycolysis Conditions. *J. Appl. Polym. Sci.*, 80: 943–948.
13. Güçlü, G., Yalçınyuva, T., Özgümüş, S., and Orbay, M. (2003) Simultaneous Glycolysis and Hydrolysis of Poly(ethylene terephthalate) and Characterization of Products by Differential Scanning Calorimetry. *Polymer*, 44: 7609–7616.
14. Vaidya, U.R. and Nadkarni, V.M. (1988) Polyester Polyols for Polyurethans from PET Waste: Kinetics of Polycondensation. *J. Appl. Polym. Sci.*, 35: 775–785.
15. Vaidya, U.R. and Nadkarni, V.M. (1987) Unsaturated Polyester Resins from PET Waste. I. Synthesis and Characterization. *Ind. Eng. Chem. Res.*, 26: 194–198.
16. Aslan, S., Immirzi, B., Laurienzo, P., Malinconico, M., Martuscelli, E., and Volpe, M.G. (1997) Unsaturated Polyester Resins from Glycolysed Waste Polyethylene Terephthalate: Synthesis and Comparison of Properties and Performance with Virgin Resin. *Journal of Materials Science*, 32: 2329–2336.
17. Dimov, K. and Terlemezyan, E. (1972) Catalytic Action of Calcium Acetate and the Manganese Acetate-Sodium Acetate Mixture in the Pre-Esterification of Dimethyl Terephthalate with Ethylene Glycole. *J. Polym. Sci., Part 1*, 10: 3133.
18. Grushke, H., Hammerschick, W., and Nauchem, B. (1968) Process for Depolymerizing Polyethylene Terephthalate to Terefthalic Acid Dimethylester. U.S. Pat. 3,403, 115.
19. Marathe, M.N., Dabholkar, D.A., and Jain, M.K. (1980) Process for the Recovery of Dimethyl Terephthalate from Polyethylene Terephthalate. GB. Pat. 2,041,916.
20. Michel, R.E. (1992) Recovery of Methyl Esters of Aromatic Acids and Glycols form Thermoplastic Polyester Scrap Using Methanol Vapor. Eur. Pat. 484 963.
21. Suh, D.J., Park, O.O., and Yoon, K.H. (2000) The Properties of Unsaturated Polyester Based on the Glycolysed Poly(ethylene terephthalate) with Various Glycol Compositions. *Polymer*, 41: 461–466.
22. Öztürk, Y., and Güçlü, G. (2004) Unsaturated Polyester Resins Obtained from Glycolysis Products of Waste PET. *Polymer-Plastics Technology and Engineering*, 43 (5): 1539–1552.
23. Halacheva, N. and Novakov, P. (1995) Preparation of Oligoester Diols by Alcoholytic Destruction of Poly(ethylene terephthalate). *Polymer*, 36 (4): 867–874.
24. Ovchinnikov, Y.V., Tetel'Baum, B.Y., and Maklakov, A.J. (1971) Effect of Aging and Temperature on Changes in the States of Poly(vinylchloride)-plasticizer Systems. *Vysokomol. Soedin. Ser. A*, 13 (11): 2422–2428.
25. Pita, V.J.R.R., Sampaio, E.E.M., and Monteiro, E.E.C. (2002) Mechanical Properties Evaluation of PVC/Plasticizers and PVC Thermoplastic Polyurethane Blends from Extrusion Processing. *Polymer Testing*, 21: 545–550.
26. Pierson, R.H. (1975) *Standard Method of Chemical Analysis*; Welcher, F.C., and Roberts, E., eds.; Krieger Publishing Company Inc.: New York Chap. 32.
27. Marcilla, A., Garcia, S., and Garcia-Queseda, J.C. (2004) Study of the Migration of PVC Plasticizers. *J. Anal. Pyrolysis*, 71 (2): 457–463.
28. Riddick, J.A., Bunger, W.B., and Sakano, T.K. (1986) *Organic Solvents: Physical Properties and Methods of Purification-Techniques of Chemistry*, 4th Ed.; Wiley-Interscience: New York, 443.
29. Weber, J.M. (1982) *Encyclopedia of Chemical Technology. Plasticizers*; John Wiley-Interscience: New York; Vol. 18, 111–181.