

Pure Component Recovery from Polyamide 6/6 6 Mixtures by Selective Dissolution and Reprecipitation

C. N. Kartalis, J. G. Poulakis, C. J. Tsenoglou, C. D. Papaspyrides

Laboratory of Polymer Technology, Department of Chemical Engineering, National Technical University of Athens, Zografou, Athens 157 80, Greece

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ABSTRACT: A selective dissolution/reprecipitation technique was applied for the effective recovery of Polyamide 6 (PA 6) and Polyamide 6 6 (PA 6 6) from their mixtures. The proposed process comprises mainly selective polyamide dissolution in an appropriate solvent at a specific temperature, reprecipitation of the polymer from the solution by addition of a nonsolvent, washing, and drying. A model mixture of virgin PA 6 and PA 6 6 pellets was initially tried, whereas in a following stage the selective dissolution technique was applied for the recovery of a PA-copolymer layer from a three-layered bottle end product also containing HDPE and EVA. End-group analysis, dilute solution viscometry, and

differential scanning calorimetry were used to assess the molecular weight preservation and crystallizability of the recycled polyamides. The recycled materials demonstrated excellent retention of the properties studied, although in the copolymer case, due to hydrolysis, a molecular weight decrease was detected, accompanied with a slight compositional shift, favoring the PA6 6 presence in the final product. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1924–1930, 2002

Key words: solvent-based recycling; recovery; polyamides; dissolution/reprecipitation; poly- ϵ -caproamide; polyhexamethyleneadipamide

INTRODUCTION

Technology development concerning the recycling of polyamides is of great industrial interest due to the excellent performance in valuable applications characterizing these materials, but also because of the significant cost and environmental benefits associated with their recovery. For example, DuPont Co. has been evaluating the chemical recycling of nylons, whereas in other pilot projects, conventional melt reprocessing is being implemented on nylon automotive parts.¹ Following another approach, Ciba-Geigy Ltd. is proposing an effective recycling/reprocessing method for old polyamides by repairing them from prior damage.² A widely implemented chemical recycling method is polyamide (PA) depolymerization under high pressure, which leads to the production of monomers and other chemicals; however, extensive purification is necessary for recovering monomers of quality sufficiently high for reuse.^{3,4}

Polyamide recycling, based on solution processing, is still at a research stage. The crucial point here is to achieve polyamide recovery in a pure form. Based on this philosophy, there are interesting investigations concerning the separation of polyamides from different polymeric mixtures.^{5–8} For example, Subramanian⁵ patented a dissolution process for recovering PA

6 6 and/or PA 6 from admixtures with foreign materials. His method comprises dissolving the polyamide in a solvent, combining this polyamide solution with an additional quantity of essentially the same solvent at a temperature sufficiently lower than the solution temperature. This results in quenching the solution to cause polyamide precipitation.⁵ Earlier, Moran patented a method for separating nylon 6 from mixtures with nylon 6 6. That process includes treating the mixture with an aqueous solution of an aliphatic carboxylic acid at a concentration and temperature capable of dissolving nylon 6 only, followed by separating the nylon 6 solution from nylon 6 6.⁶

Another route pertaining to polyamide recycling via dissolution is polyamide layer recovery from multilayer packaging products. Highly layered films are tailored to create specific levels of barrier protection for food packaging by keeping out oxygen or certain wave lengths of light, while keeping in flavors and perfumes. Polyamides are usually used as inner barriers in multilayer products (bottles or films) together with a thin slice of ethyl vinyl alcohol (EVOH) or ethylene vinyl acetate (EVA). These three resins are polar, so no tie layer is needed.^{9–11} There are added difficulties in recycling multilayer products because of the different polymer types contained. In this case, direct mechanical recycling is only feasible if one of the different polymer types contributes a very high portion on the multilayer product.⁹ Even in this case, though, the quality of the recycled material is questionable because of the interference of the other poly-

Correspondence to: C. D. Papaspyrides (kp@softlab.ecp.ntua.gr).

mer species. Because, as a rule, mechanical delamination of the different layers is not feasible, the dissolution technique presents the only viable alternative for separating specific layers. In dissolving a multilayer structure, the inner polymeric layer is often well shielded from the solvent by an outer layer that only dissolves at a higher temperature. It would therefore be expected that no dissolution occurs in such a system until the application of the higher temperature at which the polymers codissolve. Nevertheless, experience indicates the opposite. It has been discovered that for thin layers, representing the typical thickness of coextruded packaging films, the inner layers are not that well shielded from the solvent, and selective dissolution can occur even when the ordering of the individual polymers is inappropriate, based on the criterion that the outermost layers must dissolve at the lowest temperatures. It appears that solvent diffusion through the undissolved outer layer causes delamination of the internal polymer-to-polymer interface, thus causing the collapse of the entire structure into the solvent.¹²

In our previous study,¹³ a model dissolution/precipitation process was investigated for the single polymer recycling of poly- ϵ -caproamide (PA 6) and polyhexamethyleneadipamide (PA 6 6). This process comprises dissolution of each of the aforementioned polyamides in an appropriate solvent, reprecipitation by addition of a nonsolvent, and, finally, recovery of the polymers through washing and drying. Dimethylsulfoxide/methyl ethyl ketone (DMSO/MEK) proved to be the most suitable solvent/nonsolvent system for PA 6 recovery, whereas formic acid/MEK was used effectively as a solvent/nonsolvent pair in the case of PA 6 6 recovery. The recycled polyamides were analyzed with respect to their molecular weight, crystallinity, and grain size. In all cases, the recycled materials demonstrated excellent retention of the properties studied.

The aim of the present work is to investigate the separation of polyamide mixtures using the aforementioned dissolution/precipitation technique. Emphasis is also given again on recycling the solvents employed. Initially, we study component recovery from a model mixture of virgin PA 6 and PA 6 6. Following that, the selective dissolution technique is applied for the recovery of a PA-copolymer layer from a three-layered bottle. By using the appropriate solvent, the PA-copolymer layer is selectively dissolved and recovered from the multilayer product. A nonsolvent is then used for PA precipitation from the solution. Finally, in both cases (model mixture and multilayer product), characterization studies focus on molecular weight retention (based on end-groups analysis and viscometry) as well as on the crystallizability (through thermal analysis) as prime indicators of material quality of the recovered polyamides.

EXPERIMENTAL

Materials

The composition of the model mixture is as follows: 66.67% w/w virgin PA 6 pellets, under the trade name ULTRAMID BS416 (BASF Co., Ludwigshafen am Rhein, Germany), and 33.33% w/w virgin PA 6 6 pellets, under the trade name 126 AM, 30 P (Rhône-Poulenc Co., Courbevoie, France).

DMSO (Merck Co., Darmstadt, Germany) is used as the solvent for the recovery of the PA 6 from the model mixture, whereas formic acid (Kemira Co., Helsinki, Finland) is used as a solvent for the dissolution of PA 6 6. In both cases, MEK (Merck Co.) is employed as a single nonsolvent for the reprecipitation stages.

The multilayer product examined is the granules from a three-layer packaging bottle. The outer layer is high-density polyethylene (HDPE; Finathene 58070, Fina Co.). The inner layer consists of the recycle; a PA 6/PA 6 6 copolymer (Ultramid C 35, BASF Co.), with a blue pigment, that participated in the multilayer structure in a concentration level of $\sim 5\%$ w/w. Between these two layers, there is an EVA copolymer-based tie layer (Orevac 9314, Atochem Co.). The molecular composition of the polyamide copolymer recycle was initially unknown but, as it will soon be explained in the Discussion, it was deciphered to be 76/24% on a molar basis (or 61/39% w/w) by analyzing the DSC measurements under the light of the Flory-Mandelkern model for explaining melting point depression in the presence of impurities.

Formic acid (Kemira Co.) is chosen as the solvent for the PA 6/PA 6 6 copolymer layer dissolution, whereas after separation MEK (Merck Co.) is again employed as the nonsolvent for the reprecipitation of the PA copolymer.

In all cases, analytical grade solvents are used.

Dissolution/precipitation procedure

Pellets of a model mixture consisting of PA 6 and PA 6 6 were treated with DMSO at 125°C for the selective dissolution of the PA 6. PA 6 is readily dissolved in DMSO at a temperature level of 110–130°C, whereas for PA 6 6 a higher temperature is required (160–180°C). An upper concentration level of 0.15 kg L⁻¹ (0.1 kg L⁻¹ for PA 6 and 0.05 kg L⁻¹ for PA 6 6) was employed because by further increasing the concentration the solution became too viscous to be processed within the limitations of our experimental apparatus. A 2-L reaction vessel, fitted with stirrer, reflux condenser, and thermometer was employed. To avoid any oxidation of the polyamide grades, pure nitrogen was used for the creation of an inert atmosphere. After the selective dissolution of the PA 6, the solution obtained was filtered under pressure through a Seitz Merkur EF 6/03 device, with a volume capacity of 300 mL, using 5500 Seitz-T-Filter sheets of exclusion size in the range of 20–70 μm . Through this filtration pro-

cedure, the two polyamide types were separated: PA 6 obtained in the filtrate solution, while PA 6 6 pellets remained intact in the filtration device. The undissolved polyamide (PA 6 6) was then washed with hot (125°C) DMSO, to remove any amounts of remaining PA 6.

In a subsequent stage V_1 L of MEK was properly added in the filtrate solution and that caused the precipitation of the contained polyamide (PA 6). The polymer grains were isolated by filtration under vacuum. The mixture of the solvents was then replaced by V_2 L of MEK and the stirring was again applied for 30 min. This washing procedure was repeated once more (V_3 L MEK employed). Finally, the polyamide grains were dried in vacuum, at 80°C, for 24 h.

Using the same route, the undissolved/separated PA 6 6 pellets were dissolved in formic acid at room temperature. Inert atmosphere was again employed to avoid any oxidation during dissolution. After dissolving the polymer, V_1 L of MEK was properly added in the solution, and the PA 6 6 contained was precipitated. The aforementioned washing procedure was employed again in this case, using V_2 L and V_3 L of MEK. Finally, the polyamide grains were again dried for 24 h, in a vacuum chamber, at 80°C.

In both cases, the solvent/nonsolvent mixtures collected were separated for reuse in a 0.85-m high-distillation column, filled with Raching rings, and equipped with a side condenser on the top.

The three-layered packaging bottles, after being cut into pieces, were treated with formic acid under nitrogen and at room temperature for dissolving the polyamide layer. A 2-L reaction vessel, fitted with stirrer, reflux condenser, and thermometer was used for that purpose. The concentration was kept at a 0.5 kg L⁻¹ level, corresponding to a PA-copolymer concentration of about 0.025 kg L⁻¹. The solution obtained after the selective dissolution of the PA layer was filtered under pressure through the aforementioned Seitz Merkur EF 6/03 device. Through this filtration procedure, the PA was obtained in the filtrate solution. The undissolved parts were then washed with formic acid for the removal of any remaining PA. The unperturbed HDPE and EVA layers remained in the filtration device; they were recovered clean but no further work was done on separating them or studying their key properties.

Again using MEK as nonsolvent, the aforementioned reprecipitation and washing technique was employed for precipitating and recovering of the polyamide contained in the filtrate solution. The recovered polymer grains were isolated by filtration under vacuum and were finally dried in a vacuum chamber at 80°C for 24 h.

Characterization of the recovered polyamides

End-group determination

Free amine and carboxyl end-group determination was carried out on both the virgin and the recovered

polyamide grades. This was accomplished by titration as follows: For the carboxyl groups, benzyl alcohol at 150°C was used as solvent for both polyamides, while a 0.05N KOH alcohol solution was employed as the titration solution. In this case, cresol red was used as indicator. On the other hand, for amine group determination, the titration solution, a mixture of perchloric acid with methanol, was properly added in the polyamide solutions at room temperature. A 3:1 ratio phenol/glycol mixture was used as solvent for the preparation of the polyamide solutions. During titration a mixture of benzyl orange with methylene blue in a 2:1 ratio was used as an indicator. In both cases, the number of free end-groups was calculated in terms of gram-equivalents per 10⁶ g of polymer.

Dilute solution viscometry

The Intrinsic Viscosity was measured for both the virgin and the recovered polyamide grades. The viscometer utilized is an ASTM Cannon 75 B11, Ubbelohde type. In the PA 6 case, an 85% (w/v) aqueous solution of formic acid at 25°C was used as a solvent, while for PA 6 6 and the PA-copolymer, H₂SO₄ 96% w/v solution in water, at 25°C, was employed.

Molecular weight determination

The number-average molecular weight M_n was calculated using two different methods, as follows.

(1) By applying the Mark-Houwink-Sakurada (MHS) correlation on the intrinsic viscosity data, $[\eta]$, and translating the results to molecular size information through the expression¹⁴: $[\eta] = KM^a$. For the formic acid solution used in the PA 6 case, $K = 22.6 \times 10^{-3}$ ml/g and $a = 0.86$. For the H₂SO₄ solution used in the PA 6 6 case, the constants are $K = 115 \times 10^{-3}$ ml/g and $a = 0.67$.

(2) By measuring the total number of the free end-groups. Because there are two ends to every linear polyamide molecule, the number-average molecular weight is calculated as¹⁵:

$$\bar{M}_n = \frac{2 \times 10^6}{\text{equiv. of (amine + carboxyl)ends}/10^6 \text{ g}} \quad (1)$$

These number-average molecular weight M_n estimates were only implemented for the PA 6 and PA 6 6 grades that were separated and recovered from the model mixture and not for the PA-copolymer for which the composition was initially unknown.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC-4 calorimeter was used to obtain thermograms of the virgin and recovered materials. The measurements were carried out under nitrogen,

TABLE I
Operating Conditions and Results on PA Recovery from the Model Mixture and the Multilayer Product

	PA 6	PA 6 6	PA-copolymer
Concentration of PA in the solvent	0.10 Kg/L	0.05 Kg/L	0.025 Kg/L
Dissolution temperature	125°C	25°C	25°C
Solution volume	0.5 L	0.5 L	0.2 L
MEK volume (V_1)	1.5 L	1.5 L	0.6 L
MEK volume for washings ($V_2 + V_3$)	1 L	1 L	0.4 L
PA 6 recovered	~100%	~100%	~100%
Solvent (DMSO) recovered	97%	97%	96%
Nonsolvent (MEK) recovered	82%	83%	80%

between 25 and 250°C for the PA 6, and between 25 and 300°C for the PA 6 6 and PA-copolymer, using an empty capsule as reference. Sample weights varied from 4.5 to 5.5 mg and the heating rate was fixed at 10°C/min.

RESULTS AND DISCUSSION

Yield of polyamides and solvent/nonsolvent systems

Typical operating conditions and results pertaining to PA 6 and PA 6 6 recovered from the model mixture and results for the PA-copolymer recovery from the multilayer product are presented in Table I.

The recovery values quoted always represent the mean value derived from five recycling runs. Within our experimental conditions, the polymer yield always attains the theoretical value, whereas the separation and recovery of the solvents and the nonsolvents used stands at very satisfactory levels. Eventual goal is a closed-loop recycling of all solvents, which could be feasible by developing the process in a pilot scale.¹⁶

Characterization of the recovered polyamides

Number-average molecular weight

Table II presents the free end-group data determined for the virgin and the PA 6 and PA 6 6 grades recovered from the model mixture. For both recovered polyamides, the number of the terminal groups is basically the same with the virgin grades. This indicates that the selective dissolution procedure seems to

have a negligible effect on the molecular structure and composition of both polymers.

For PA 6, much lower amine end-groups seem to be present than carboxyl end-groups. This may imply the following:

1. The manufacturer uses a possibly monocarboxylic acid (e.g., acetic acid) as a chain stopper. In that case, in addition to the acid and amine end-groups, a third type of end-group should be present, which cannot be titrated. If this is the case, the total number of end-groups is higher than the titrated groups and the real M_n should be calculated by using the following equation:

$$\bar{M}_n = \frac{2 \times 10^6}{\text{equiv. of (amine + carboxyl + nonfunctional ends)/}10^6 \text{ g}} \quad (2)$$

2. The manufacturer uses a dicarboxylic acid (e.g., adipic or terephthalic acid) as a chain regulator. In this case, the right number of end-groups is titrated.

In our polyamide samples, the type of chain stopper employed is not available and therefore a simplification of the aforementioned equation was used.

The intrinsic viscosity values for the recovered PA 6 and PA 6 6 from the model mixture, as well as for the PA-copolymer which originated from the multilayer product, are presented in Table III, where they are compared with the values of the virgin materials.

In the case of the model polyamide mixture, the recovered polymers present nearly the same intrinsic viscosity with the virgin grades. In other words, the results indicate that the dissolution/precipitation

TABLE II
End-Group Determination Data for the PA 6 and PA 6 6 Grades Recovered from the Model Mixture

	Equiv. —COOH/10 ⁶ g PA	% Standard deviation	Equiv. —NH ₂ /10 ⁶ g PA	% Standard deviation
PA 6				
Virgin material	68.3	2.85	29.6	2.94
Recovered material	68.0	1.55	25.7	2.78
PA 6 6				
Virgin material	40.8	3.94	88.5	3.77
Recovered material	40.3	2.93	86.4	2.39

TABLE III
Intrinsic Viscosity Data for all Polyamide Grades (in dL/g)

	Virgin material [η]	% Standard deviation	Recovered material [η]	% Standard deviation
PA 6	70.72	1.15	72.95	1.10
PA 6 6	73.55	0.85	74.46	1.28
PA 6/PA 6 6 copolymer	153.4	2.13	114.3	1.59

technique does not induce any changes in molecular weight or architecture. This is not the case for the A-copolymer recovered from the multicomponent bottle, where a 25% reduction in intrinsic viscosity is detected. For an estimated MHS exponent value of $a \approx 0.70$, typical of polyamides in sulfuric acid solutions,¹⁴ this translates into an $\sim 35\%$ decrease in molecular weight.

Data concerning the number-average molecular weight of the virgin and the recovered PA 6 and PA 6 6 grades from the model mixture are presented in Table IV; they are based on both viscometric and end-group determinations. For PA 6, the slight increase of the end-group-based \overline{M}_n values compared to those derived from viscometry may be attributed to the existence of some undetermined end-group presence, as discussed above. More importantly, the values between the virgin and the recycled homopolymer grades are almost the same, independent of the method of measurement. This proves that no degradation due to oxidation occurs during the recovery stage and can be attributed to the mild operating conditions and inert atmosphere encountered throughout the process. A slight molecular weight increase encountered in some recycled grades could probably be attributed to fractionation phenomena (i.e., some lower molecular weight fractions may remain soluble in the solvent/nonsolvent phase).¹⁷

On the other hand, the PA-copolymer recovered from the multicomponent bottle demonstrates a molecular weight decrease in comparison to its pristine precursor. This copolymer size reduction is accompanied with a small compositional shift and is explained at the end of the Discussion. It may be due to the hydrolytic action of formic acid utilized in the recovery or due to the completely different processing history and exposure to additives that this material was subjected to during manufacturing.

Melting ranges and degrees of crystallinity

DSC runs were performed to study the thermal profile of all polyamide grades recovered. Heat of fusion data for both virgin and recycled materials are listed in Table V; this quantity represents the amount of energy necessary for transforming a crystalline or partially crystalline polymer to a completely disordered amorphous one. Effective heat of fusion values may be computed from the area under a well-defined DSC

thermogram peak. The percentage crystallinity of a polymer sample tested, c , may then be determined by comparing the actual heat of fusion of this sample, ΔH_{exp} , with ΔH_f , the heat of fusion of a perfectly crystalline PA:

$$c = (\Delta H_{\text{exp}}/\Delta H_f) \times 100 \quad (3)$$

For PA 6, ΔH_f is taken equal to 46.82 cal g⁻¹, whereas for PA 6 6 equal to 50.45 cal g⁻¹.¹⁸ By linear weighted averaging and for an estimated 61/39% w/w PA 6/PA 6 6 composition, the corresponding ΔH_f value for the copolymer is 48.24 cal g⁻¹.

Degree of crystallinity estimates for the PA 6 and PA 6 6 recovered from the model mixture and calculated from eq. (3) are reported in Table V. Some increase in the PA 6 crystalline content may be attributed to the very mild cooling rates prevailing during the recycled polyamide precipitation. In other words, the recycling process itself serves at the same time as a sort of an annealing treatment. Yet, this does not seem to be the case with the recycled PA 6 6, where crystallinity actually decreases a little, whereas for the copolymer recycled from the multilayered product, crystallinity practically remains unchanged.

Table V also summarizes the collected melting point temperature data. Results obtained from the polyamide model mixture components indicate that recycling leaves the material microstructure unaffected, in harmony with the rest of the properties. On the other hand, a significant increase in the melting temperature of the polyamide copolymer recovered from the multilayer mixture was detected. As it becomes apparent in the next section, the magnitude of the melting tem-

TABLE IV
Number-Average Molecular Weight (\overline{M}_n) Estimates for the PA 6, PA 6 6, and Copolymer, Obtained by Applying Either the (Mark-Houwink-Sakurada) Viscometric Approximation or the Free End-Group Correlation

	Viscometric approximation	Free end-group approximation
PA 6		
Virgin material	18,300	20,400
Recovered material	19,000	21,350
PA 6 6		
Virgin material	15,500	15,500
Recovered material	15,700	15,800

TABLE V
Thermal Analysis (DSC) Results

	Melting point (°C)	Actual heat of fusion ΔH_{exp} (in cal/g)	ΔH_f (cal/g)	Crystalline content (%)
PA 6 (model mixture)				
Virgin material	224.44	11.99	46.82	25.6
Recovered material	224.65	16.52	46.82	35.3
PA 6 6 (model mixture)				
Virgin material	263.55	15.61	50.45	30.9
Recovered material	263.72	13.42	50.45	26.6
PA-copolymer (multilayer product)				
Virgin material	198.08	13.63	48.24	28.3
Recovered material	221.83	13.21	48.49	27.2

perature shift is crucial in deciphering microstructural and compositional changes in the recycled product.

Microstructural changes in the recovered PA-copolymer

The accumulated thermal analysis results (Table V) in conjunction with the intrinsic viscosity measurements may be utilized to decipher the dissolution/precipitation-induced physicochemical changes during recycling. These happen exclusively on the copolymer recycle. As already explained, small variations in the effective fusion enthalpies between original and recycled pure PA samples from the model mixture are only due to inevitable differences in the degree of crystallinity caused by the alternative paths followed during postprocessing polymer solidification.

As already mentioned, in the case of the PA 6/PA 6 6 copolymer, lower dilute solution viscosity values measured after recycling indicate a marked decrease in molecular weight; this is most likely due to partial chain fracturing caused by selective hydrolysis while in formic acid.

This comes to an apparent contradiction with the fact that, upon recycling, there is a 24-degree melting point elevation in the recovered copolymer (from 198 to 222°C); it has long been known that molecular size reduction causes a directly opposite effect.¹⁹ A way of explaining this seeming paradox is by stipulating that, along with molecular size reduction, there is a compositional shift in the copolymer structure occurring during recycling.

Of assistance in the quantitative analysis of the thermal measurement data is the work of Flory and Mandelkern on the effects of moieties on melting point depression.¹⁹ When applied to an AB copolymer (here, A = PA 6 and B = PA 6 6), it states that:

$$\frac{1}{T_m} - \frac{1}{T_{mi}} \approx \frac{R}{m_i \Delta H_i} \ln\left(\frac{1}{x_i}\right) \quad (4)$$

where T_m (in Kelvin) is the melting temperature of the copolymer; T_{mi} is the melting temperature of the pure

polymer i ($i = A$ or B); x_i is the mole fraction of the i component in the copolymer ($x_A + x_B = 1$); ΔH_i is the enthalpy of fusion per gram of i as discussed in the previous section; m_i is the molecular weight of the repeat unit of the i polymer ($m_A = 113$ and $m_B = 226$ g/mol); and R (≈ 2 cal/g) is the gas constant.

This last expression may first be used to characterize the original copolymer composition for which T_m is equal to 471.2 K (i.e., lower than either T_{mi} of the corresponding homopolymers) due to eutectic formation. By applying eq. (4) for $i = A = \text{PA 6}$, one finds that $x_A = 74\%$, because

$$\begin{aligned} \ln(x_A) &= -(46.82 \times 113)[1/(471.2) - 1/(497.6)]/2 \\ &= -0.298 \Rightarrow x_A = 74\% \end{aligned}$$

Physical symmetry requires that eq. (4) should also be equally applicable on the opposite end of the compositional spectrum (i.e., for $i = B = \text{PA 6 6}$) and, therefore,

$$\begin{aligned} \ln(x_B) &= -(50.45 \times 226)[1/(471.2) - 1/(536.7)]/2 \\ &= -1.48 \Rightarrow x_B = 23\% \end{aligned}$$

Remarkably (and, perhaps fortuitously), Flory's theory result is self-consistent by reproducing with a 97% accuracy the fact that the sum of calculated x_A and x_B should be equal to unity. The small discrepancy may be corrected by multiplying the first estimates above by 1.03 (=1/0.97) and, therefore, the initial molar fractions are

$$x_A = 0.76 \quad \text{and} \quad x_B = 0.24$$

This translates into a 61/39% w/w PA 6/PA 6 6 virgin copolymer content.

This same procedure may be repeated for investigating the character and composition of the harvested copolymer recycle, x'_A and x'_B , for which $T_m = 495$ K:

$$\begin{aligned} \ln(x'_A) &= -(46.82 \times 113)[1/(495) - 1/(497.6)]/2 \\ &= -0.0279 \Rightarrow x'_A = 97\% \end{aligned}$$

$$\begin{aligned}\ln(x'_B) &= -(50.45 \times 226)[1/(495) - 1/(536.7)]/2 \\ &= -0.895 \Rightarrow x'_B = 41\%\end{aligned}$$

The deviation from the sum-to-unity self-consistency criterion is now equal to 38%, significantly greater than in the virgin copolymer case. This comes as no surprise because T_m variation is now not only affected by compositional shifts, but also by the competing effects of molecular size reduction. Therefore, the need for a correction is now more urgent, and it is accomplished by multiplying the above results by 0.7246 (=1/1.38). After doing so, the corrected renormalized molar composition is

$$x'_A = 70.3\% \quad \text{and} \quad x'_B = 29.7\%$$

which translates into a 54/46% w/w content for the recovered product. This means that the recycled copolymer is 7% richer in PA 6 6 than its virgin precursor.

The whole sequence of events during polyamide copolymer recycling may therefore be described as follows.

Solution processing causes copolymer hydrolysis which is inevitably inducing chain fragmentation and, therefore, considerable reduction in the copolymer molecular weight; this explains the lower viscosity values of the recyclate. Molecular fragmentation is accompanied by shedding of small oligomer-size pieces from the edges of the new chains. PA 6-rich pieces are lost in significantly larger numbers than PA 6 6 pieces; this explains why there is a melting point shift along the eutectic of the recyclate. Stipulating preferential PA6 hydrolysis, and therefore PA 6 6 richer copolymer product, is in accord with experience, indicating that PA 6 6 is considerably more resistant to hydrolysis than PA 6.²⁰ Fortunately, and despite a molecular weight reduction, the crystallizability of the recycled copolymer remains intact.

CONCLUSION

A selective dissolution/reprecipitation process has been utilized to recycle PA 6 and PA 6 6 from a model mixture. Following that, the same selective dissolution/reprecipitation technique was applied for the recovery of a PA-copolymer layer from a typical multi-layer end product. In both cases, the polyamides reprecipitated from concentrated solutions through the

addition of a nonsolvent in the form of small grains. The yield of polyamide recovery was excellent, whereas that of the solvents and nonsolvents used stands at very satisfactory levels. The quality of the recyclates was excellent; the recovered polyamides of uniform monomer chemistry were identical to their virgin precursors, whereas a molecular weight reduction and a slight microstructural change suffered by the recovered copolymer did not affect its character.

Thus, consistent with our previous series of studies, this work develops fundamental knowledge and methodology on feasible ways of recycling valuable polyamides from mixtures of waste plastics, through selective dissolution and reprecipitation.

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