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Structural effects of diacidic and glycolic moieties on physicochemical properties of aromatic polyesterdiols from glycolysis/esterification of poly(ethylene terephthalate) wastes

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Abstract

Useful polyols for rigid polyurethane foam manufacture may be obtained by glycolysis of post-consuming poly(ethylene terephthalate) (PET) wastes. The physicochemical properties of about 100 polyesterdiols were measured, the polyol molecular structure being built on three diacidic moieties and three glycolic moieties in various proportions. Viscosity, foaming agent compatibility and storage stability are the most relevant physicochemical properties.

Statistical analysis was made over more than 50 polyols. Molar ratios of the constitutive moieties to terephthalic residue were taken as composition parameter. From a Principal Component Analysis (PCA) it was found that 141b compatibility is of opposite viscosity and independent of polyol storage stability, the properties being governed essentially by the glycolic moieties. Multiple regressions gave prediction equations for viscosity and 141b compatibility as a function of moieties amounts.

The own effect of each structural unit was also investigated through some more homogeneous panels of polyols. Lack of storage stability appears when the proportions of constitutive PET units in glycolic and acidic moieties overcome critical values. The viscosity of the polyols increases greatly with decreasing hydroxyl value or increasing the proportion of aromatic diacidic residues.

Keywords: Glycolysis; Aromatic polyesterdiols; Statistical analysis

1. Introduction

As the new regulations are appearing all over the world, the valorization of the polymer wastes is becoming a priority. Chemical valorization could take advantages either on physical regeneration (tolerance of some impurities, diversification of the outlets) and or on energy valorization (economy of the raw materials, safeguard of the ecological and commercial value of the matter).

The poly(ethylene terephthalate) (PET) waste is sourced from post-consumer scrap, such as bottle, films or fibers. PET is a polyester. Solvolytic chain cleavage is possible by reagents, such as water (hydrolysis), alcohols (alcoholysis), amines (aminolysis), acids (acidolysis), leading to a large variety of valuable products [1]. In view of chemical recycling, besides the monomers formation — dimethylterephthalate (DMT), terephthalic acid (TA), bishydroxyethylterephthalate (BHET) — one expects [1] the production of specialized oligomeric products such as α,ω dihydroxy materials (polyols) for the synthesis of polyurethanes, reactive materials (unsaturated polyesters, coatings) and non-functionalized esters (plasticizers).

The polyols obtained from PET are aromatic polyester polyols (APPs). Although APPs were initially introduced as low-cost extenders [2], it was soon found that they yielded foams with low flammability. As a result, they became the preferred polyol in boardstock applications [3].

Numerous polyols synthesis processes have been described in the literature, mainly in patents. It appears that some unfavorable physicochemical properties of aromatic polyester polyols may arise from the association of terephthalic and ethanediyl units:

- *Storage instability*. Solid products at room temperature, or liquids but some solids separate from solution over time.
- High viscosity.

Partial elimination of monoethyleneglycol [4] after the

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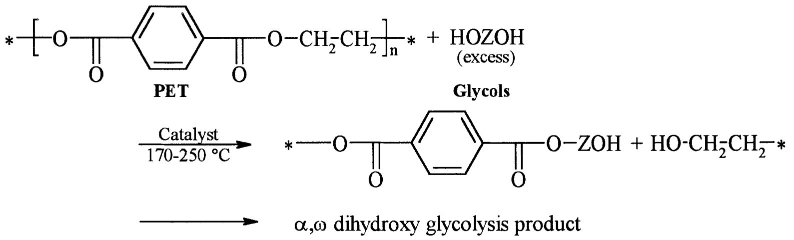
glycolysis step and chemical modification of the resulting polyol by ethoxypropoxylation [5] or esterification with a diacid (or a derivative) are the main procedures to overcome these deficiencies. Examples of diacidic reagents are adipic acid [6], glutaric acid [7], adipic, glutaric, succinic dimethylester mixture [8], phthalic anhydride [9], diacids found in industrial dimethylterephthalate process residue [2,10]. Diethyleneglycol is the most used glycol. Dipropyleneglycol affords secondary hydroxyls and a better compatibility with CFC 11 [2,11]. Increased functionality can be introduced by using triols or tetrols [7,12].

In this paper, we describe the properties of polyols prepared in two stages: firstly, a glycolysis of PET (use of a mixture of diols introduced in excess — Eq. (1)), followed by an esterification (us.e of a mixture of diacids — Eq. (2)), distilling off the formed water. The reagents were (mono)ethyleneglycol (MEG or EG), diethyleneglycol (DEG) and dipropyleneglycol (DPG) as glycols; adipic acid and phthalic acid (in fact the anhydride) as diacids



(1)

$$\alpha,\omega \text{ dihydroxy glycolysis product} + \underset{\text{(defect)}}{\text{dicarboxylic acid}} \xrightarrow[170\text{–}250°\text{C}]{\text{Catalyst}} \text{polyester(diol)} + H_2O \quad (2)$$

In such glycolysis/esterification processes, all expected alcoholysis reactions take place leading to a complex mixture of α,ω diols [13], all of global formula $HOZ(YZ)_nOH$, $n \geq 0$; Z and Y being glycolic and diacidic moieties, respectively. The diols differ by the moieties distribution and by the polymerization degree. A chemical equilibrium state is quickly reached [13] with the synthesis processes used in the present work (reactions at 200–230°C and titanium (IV) butoxyde as catalyst). Thus, these polyols may be distinguished by the sole composition of the diacidic and glycolic residues T/P/A/E/De/Dp. T and E are the terephthalic and ethanediyl units arising from the PET. P, A, De, Dp being the moieties derived from the reagents, i.e. (*ortho*)phthalic acid, adipic acid, diethyleneglycol and dipropyleneglycol, respectively.

Another important feature is the glycolic moieties to diacidic moieties molar ratio, RM, which determine the main polymerization degree: $RM = (\text{mol Z/mol Y}) = (\bar{n} + 1)/\bar{n}$.

The hydroxyl value (OHV) of the polyol is linked to the RM and the molecular weight of the moieties, and, thus, is correlated with the chemical composition of the polyol.

In our laboratory, we have synthesized about a 100 such different polyols [14], all in chemical equilibrium. The aim of this work was to correlate the properties of the polyols and their chemical composition. The properties evaluated were: the storage stability of the polyols (and also of the intermediate glycolysis products), the viscosity and the compatibility with a, today, largely used foaming agent: 1,1-dichloro, 1-fluoroethane (HCFC 141b). Firstly, we have used the statistical methods for the whole panel of polyols that were characterized by large variations of compositions and hydroxyl values. Secondly, more homogeneous panel of polyols was studied with graphical methods.

1.1. Identification of polyols and notations

The polyols, all in chemical equilibrium state, were identified by the molar ratios of constitutive moieties to terephthalic residue:

T, P, A: diacidic moieties derived from terephthalic, phthalic, adipic acids, respectively.

E, De, Dp: glycolic moieties derived from monoethyleneglycol, diethyleneglycol, dipropyleneglycol, respectively.

For the statistical analysis, the amounts of glycolic and diacidic moieties — expressed as number of moles for 0.5 mol T — were taken as constitutive parameters. These moieties amounts are written in italic characters: *P*, *A*, *E*, *De*, *Dp*.

Another useful classification, for PET based polyols (without DMT) is the composition of the original reactive mixture relative to 1 mol *PET*: *x* mol of added glycols, *y* mol of added diacids, composition of the added glycols and diacids, molar proportion of the glycolic and diacidic residues.

Example of notation:

DEG: glycol;
De: glycolic moiety;
De: moiety amount (in mol for 0.5 mol T).

2. Experimental

The polyols were prepared in two stages. The reactions were conducted under a nitrogen blanket, at 200–240°C. Firstly, PET (96 g; 0.5 mol) was glycolyzed with a mixture of diols (DEG + DPG + MEG) under reflux and with titanium (IV) butoxyde (TBT) as catalyst (0.48 g). One hour after the total disappearance of the solids, the reaction mixture was cooled and an aliquot of the resulting glycolysis product was taken. Appropriate amounts of adipic acid and phthalic anhydride were then added and the mixture was heated, with continuous stripping off the formed water, until the acid number falls below 1–3 mg KOH/g.

Some model products ($E < 0.5$ mol) were obtained from dimethylterephthalate instead of PET in the first step, and with methanol distillation.

The final reaction products were characterized [14] by:

- Hydroxyl value and acid number by chemical titration.
- Free glycols analysis by gas chromatography; polyester molecular distribution by SEC chromatography [13] with 254 nm absorbance detection.
- Viscosities were determined, at 25°C, by measurements in a coaxial cylinder rheometer, BAROID FANN 35S, at shear rate range $1–1000\ \mathrm{s}^{-1}$. All polyols were Newtonian.
- HCFC 141b compatibilities were determined by GC analysis of the polyol phase obtained after mixing equal amounts of the polyol and the blowing agent. If two phases were observed, the polyol phase was separated and, then, analyzed by GC (2 g probe dissolved in 8 ml chloroform and 0.5 g ethylacetate, as internal standard, column 10% FFAP on chromosorb WAW 80/100 mesh — 60°C). Compatibility is the concentration of the HCFC 141b, expressed in g per 100 g of the saturated polyol phase. If only one homogeneous phase was observed, more blowing agent was added. Compatibilities greater than 70% were called 'very high compatibilities'(VHC).
- Storage stability: at the end of the synthesis, all polyols were obtained as homogeneous limpid liquids. With cooling and room temperature storage, some of them lose slowly their homogeneous liquid character: some become homogeneously hazy, some evolve to white pastes, other let deposit a solid at the bottom. Short-term (three days) and long-term (three months) storage stabilities were evaluated for each polyol and intermediate glycolysis product.

Statistical results were obtained by STATGRAPHICS Plus Version 4.0 (Manugistics). Figures were drawn by using Microsoft® Excel 2000 according to STATGRAPHICS Plus results.

3. Results

3.1. Principal component analysis

Principal Component Analysis (PCA) is a multivariate method [15] that lends to reduce or simplify data, investigate the dependence among variables, etc. The data are a table matrix of descriptors (variables) and observations. PCA conducts to determine relationships among quantitative variables, keeping as much information as possible from the original variables. The recombined variable that accounts for the largest amount of variance forms the first principal component. Each successive component explains the decreasing amount of variance. Then, the data can be plotted with the most meaningful components. PCA is useful to locate outliers (in other words, data that have too much difference with the others) and to reveal links between data and variables. Thus, PCA and multivariate data analysis methods are used to extract meaningful information from a mass of data, typically in the analytical area. For example in polymer area: PET density and orientation determination [16], EVA copolymers discrimination [17], LLDPE density [18] were deducted from FT-Raman spectra. Hakkarainen et al. [19] use PCA and other multivariate data analysis to identify degradation products by GC–MS and to predict long-term properties of glassfiber reinforced polyester composites. Using multivariate and other chemometrics methods, Bystritskaya et al. [20,21] try to build prediction models for polymer ageing and polymer properties estimations.

We have conducted a PCA over five properties of use — 141b compatibility, viscosity, short- and long-term polyol stability, long-term glycolysis product stability. First, we have extracted two principal components from 62 polyols whose properties data are fully complete. The score plot (projection of polyols on the two first components plan), shows the great influence of a particular polyol due to its high viscosity. Thus, that polyol has been excluded from the PCA study. Then, we have extracted two new principal components from the 61 remaining polyols. These components account for 59.6% of total variance (40.1% by principal component 1, x-axis, and 19.5% by principal component 2, y-axis). Fig. 1 displays the projection of the properties on the two components plan (loading plot) and the projection of the polyols (score plot). Loading plot gives information on synergistic, antagonistic or independent behaviors.

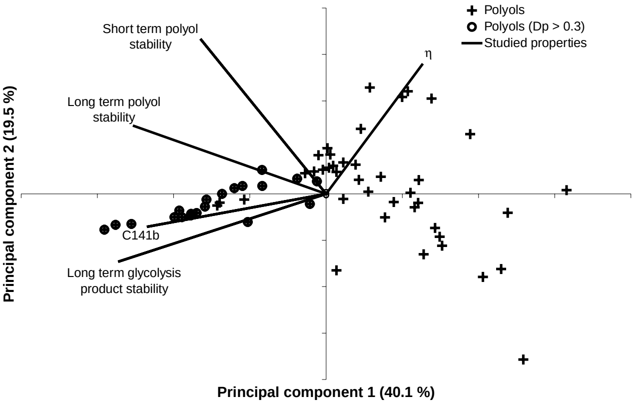


Fig. 1. Loading and Score plot. PCA of polyols. Properties are drawn in full line. +: Individual polyols; Polyols with high Dp moiety amounts ($Dp > 0.3$ mol) have been circled.

Variables, whose projections are close to, have synergistic variations. Opposite variables, projection reflects antagonistic behaviors. Variable projections drawing a right angle are independent. In our case, the loading plot of Fig. 1 shows three groups:

- 141*b compatibility and long-term glycolysis product stability*. Compatibility increase and long-term stability improvement are linked up.
- *Short- and long-term polyol stability*. Both polyol stabilities are connected.
- Viscosity.

First group is opposite the third, so viscosity decrease will improve 141b compatibility and long-term glycolysis product stability. The second group is nearly perpendicular to the first and the last. Consequently, polyol stabilities are independent of the properties of others.

We have plotted the scatterplot (projection of the polyols). Each polyol can be described with additional descriptors (variables that were not taken into account for the principal components determination). The aim is then to bring out possible correlations between the variables and the additional descriptors. We identify the polyols by moieties amounts (see notations). An example is given in Fig. 1 with the Dp moiety amount:

- Dp moiety amount (*Dp*) is in a quiet restricted range, 0–1.38 mol. Most of the polyols (about two-third) have *Dp* below 0.3 mol (polyols with *Dp* above 0.3 mol are circled in Fig. 1). *Dp* below 0.3 mol polyols are on the right side of the figure and particularly opposite the polyol stabilities. Consequently, low amount of *Dp* conducts low polyol stabilities. *Dp* above 0.3 mol polyols are distributed along 141b compatibility and glycolysis product storage stability. Thus high *Dp* affords compatibility with 141b foaming agent and glycolysis product storage stability.
- E moiety amount (*E*) is mostly about 0.5 mol. Lower amounts are distributed over the plan whereas higher amounts are opposite the polyol stabilities: *E* increasing conducts to decrease storage stabilities. Thus, glycolysis of PET by MEG drives to polyols lack of stability.
- De moiety amount (*De*) is widespread, between 0.31 and 6.22 mol and mostly includes between 0.92 and 1.14 mol. Low *De* decreases polyol stabilities. High amount favors 141b compatibility, long-term glycolysis product stability and decreases viscosity, especially very high amount.
- A moiety amount (*A*) seems to have no effects on the properties of use.
- P moiety amount (*P*) seems to have a light effect on polyol stabilities, in others words, increasing the amount tends to increase the stabilities. Very high amounts promote 141b compatibility and decrease viscosity.

Thus, to promote polyol stabilities, low *E* and high *De*, *Dp* and *P* are better. High *De*, *Dp* and *P* favor 141b compatibility and decrease viscosity.

3.2. Multiple regressions

To follow up the study, we have conducted multiple regressions over the properties. We presume a quadratic model (independent variables, squared and two-way interaction terms) to be fitted. Independent variables are the moieties amounts (see notations). For each obtained equation, data range and mean value of each moiety are indicated in Table 1.

3.2.1. 141b compatibility

For 141b compatibility, we get a correlation with an 88% determination coefficient for a 99% confidence level (Eq. (3)). The sample contains 67 polyols

$$C_{141b} = 23.9 + 52.9Dp + 14.9A - 27.5EP - 11.0De\,Dp + 20.3DeP - 76.5DpP \quad (3)$$

To validate the model, we plot 141b compatibility estimation against measured 141b compatibility (Fig. 2). For very high compatibility polyols (see Section 2), we report the estimated value on the 70% compatibility dashed vertical line: most of these polyols gets predicted values about or greater than 70%. Only one of the polyols has predicted value lower than 70%. In that case, we have reached limits of the model because that polyol presents, at the same time, high *Dp* and low *E* and *De* moieties amounts, close to the experimental area boundaries.

3.2.2. OH value

Hydroxyl value is correlated with the moieties amounts, with a 96.6% determination coefficient for a 99%

Table 1
Data range and mean value, moiety per moiety for each regression (in mol per 0.5 mol T)

Equation	*E* moiety amount		*De* moiety amount		*Dp* moiety amount		*A* moiety amount		*P* moiety amount	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
3	[0–0.78]	0.5	[0–6.22]	1.39	[0–1.38]	0.36	[0–3.2]	0.30	[0–3.2]	0.27
4	[0–3]	0.58	[0–6.22]	1.09	[0–2.69]	0.47	[0–3.2]	0.27	[0–3.2]	0.23
5	[0–3]	0.53	[0–6.22]	1.18	[0–2.69]	0.50	[0–3.2]	0.30	[0–3.2]	0.25
6	[0–3]	0.53	[0–6.22]	1.18	[0–2.69]	0.50	[0–3.2]	0.30	[0–3.2]	0.25

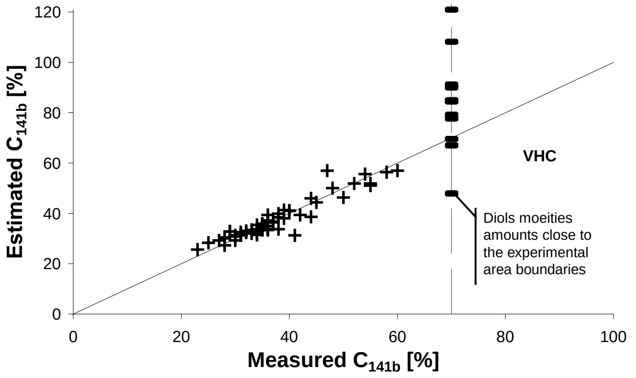


Fig. 2. Regression plot. +: Estimated against measured 141b compatibility, for polyols with measured $C_{141b} < 70\%$. −: Estimated 141b compatibility for polyols with experimental $C_{141b} \geq 70\%$.

confidence level (Eq. (4)). The sample contains 98 polyols

$$\begin{aligned}\mathrm{OHV} = {} & 67.6 + 268.8E + 328.3De + 230.9Dp - 654.5A \\ & - 678.4P + 53.4E^2 - 33.1De^2 - 52.5Dp^2 \\ & - 94.8A^2 - 121.9DeDp + 128.5DeA + 191.0DpA \\ & + 503.7DpP - 85.5AP \end{aligned} \tag{4}$$

Fig. 3 displays the estimated OHV against the measured one. Most of the polyols agree with the model, but some of them are deviated from the model by greater than 10%. In that case, the polyols have moieties amounts that are not in the 25–75% fractile. Thus, the model is unable to predict with reliability the OH value of polyols outside of the middle of the data range (Table 1).

3.2.3. Viscosity

For polyol viscosity, direct correlation cannot be established, but the viscosity logarithm is correlated with the moieties amounts, with a 92.6% determination coefficient for a 99% confidence level (Eq. (5)). The sample contains 86 polyols

$$\begin{aligned}\log \eta = {} & 5.46 - 1.61E - 2.38De - 0.98Dp + 1.94A \\ & + 4.66P + 0.35De^2 + 0.31Dp^2 + 1.80P^2 \\ & + 1.02DeDp - 1.37DeP - 3.04DpA - 3.82DpP \\ & + 1.82AP \end{aligned} \tag{5}$$

Fig. 4 shows the polyol estimated viscosity against the measured one. Polyols seem to have estimated viscosities close to the measured one. For increasing viscosity, polyols present increasing deviation from the model. Two highly viscous polyols present great deviation to the estimated model (circled in Fig. 4). One of them presents diacidic moieties amounts in the upper quartile of diacidic moieties variations. The second presents *De* and *Dp* in the lower quartile of glycolic moieties variations. But, the moieties variations are in the experimental area boundaries. Consequently, despite its good determination coefficient, the model can weakly describe some of the polyols. Another way to estimate viscosity would be preferable.

To find another way to estimate viscosity, we have studied viscosity against the OH value. We have found a relationship between viscosity and the OH value decimal logarithms, with an 83% determination coefficient for a 99% confidence level (Eq. (6)). The sample contains 86 polyols

$$\log \eta = 12.4 - 3.59 \log \mathrm{OHV} \Leftrightarrow \eta = 2.45 \times 10^{12} \mathrm{OHV}^{-3.59} \tag{6}$$

Fig. 5 shows the polyols estimated viscosity against the OH value, with confidence and prediction limits. The whole OH value and viscosity variations are taken into account, but some polyols are out of the prediction limits. Again, we get a model to estimate the viscosity property but the OH value is not a sufficient estimator.

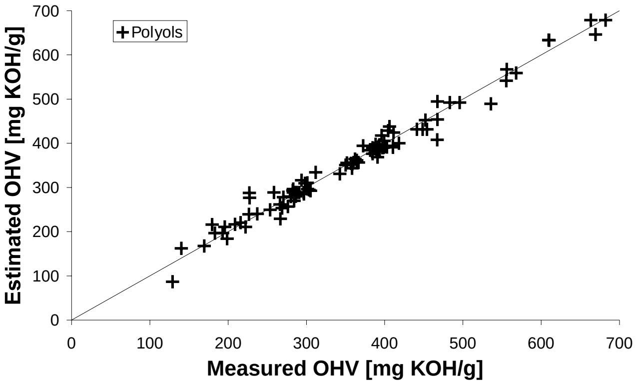


Fig. 3. Regression plot. +: Estimated against the measured OH value.

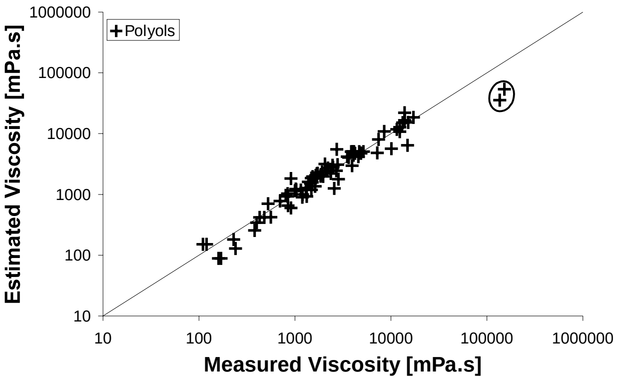


Fig. 4. Regression plot. +: Estimated against the measured viscosity.

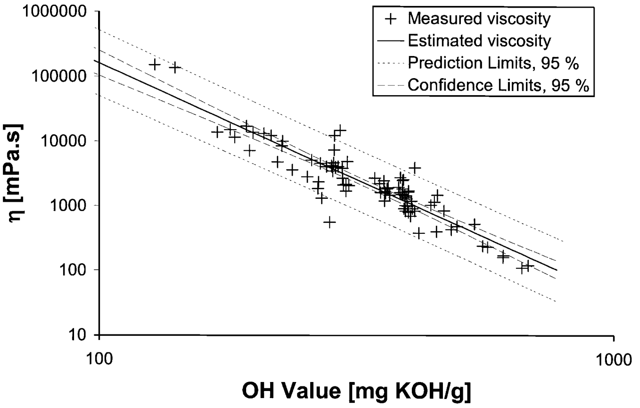


Fig. 5. Simple regression plot. +: Estimated viscosity against the OH value (full line) in log scale. Dotted lines: prediction limits. Dashed lines: confidence limits.

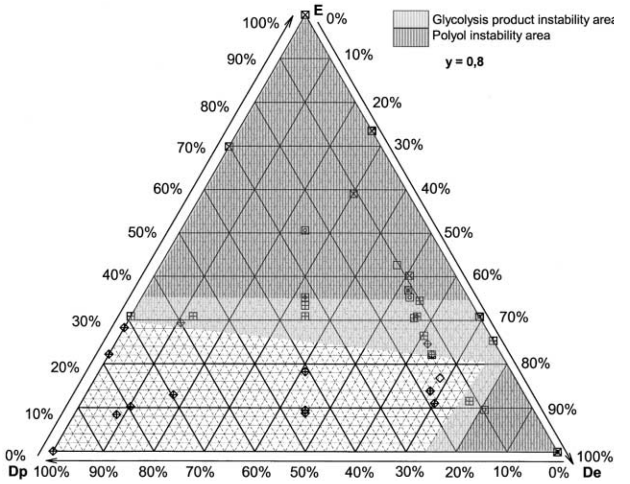


Fig. 6. Storage stability projected on the glycolic moieties composition ternary diagram. □: Unstable glycolysis products, ◇: stable glycolysis products. ×: unstable polyols, ○: short-term stable and long-term unstable polyols, +: long-term stable polyols.

3.3. More homogeneous panels of polyols

The own effect of each structural unit was also investigated through some more homogeneous panels of polyols.

3.3.1. Storage stability

A set of polyols was obtained with a diacidic units molar ratio $(P + A)/T = 0.8$; the ratio P/A was mostly taken as 1 and the hydroxyl values of the polyols were in the range 280–420 mg KOH/g. The long-term stabilities of the polyols and intermediate glycolysis products were evaluated. The storage stability seems to be correlated with the glycolic moieties repartition. From Fig. 6, it appears that lack of stability arise when the molar proportion of E moiety in the glycolic residues is higher than about 35 mol%. Note that, for polyols obtained from PET (without DMT) and glycols other than MEG, $E < 35$ mol% corresponds to RM $> \sim 1.6$ and OHV $> \sim 250$ mg KOH/g. Comparison of polyols differing only by P/A ratios show that slightly better stabilities occur with adipic moiety replacement by phthalic one. Another zone of instability is found when glycolic moieties are essentially DEG derived.

The intermediate glycolysis products, i.e. polyols with terephthalic unit as sole acidic residue, are still less stable: stability limit is about 20 mol% E moiety in the glycolic moiety, corresponding for PET based polyols to RM $> \sim 5$ and OHV $> \sim 720$ mg KOH/g. However, better stabilities are observed for high Dp/De ratios.

Another results confirm that storage stability is enhanced with higher (P + A)/T ratios. Thus, post-esterification of the PET glycolysis product has two favorable effects: T/(P + A) ratio lowering and, for convenient RM value attainment, introducing more glycols that allows a reduction of E proportion in glycolic moieties.

3.3.2. Viscosity

The multiple regression gave relations between the viscosity and both the composition variables and OH value of the polyols. In order to study the own effect of each parameter, we have tried polyols, as similar as possible in chemical composition.

A set of polyols was synthesized with a diacidic residues molar ratio P/A/T = 0.4/0.4/1 and with constant hydroxyl value of 400 mg KOH/g. Clearly, moderate increase of viscosity results from enrichment of MEG derived moieties, whereas replacement of DEG by DPG has only a slight positive effect (see Fig. 7).

Other polyols were synthesized, as a punctual modification of a reference polyol which was obtained from 0.5 mol PET, 0.2 mol adipic acid, 0.2 mol phthalic anhydride, 0.92 mol DEG, 0.2 mol DPG. The modified polyols correspond to the glycolysis of one PET mol by x mol of a fixed composition mixture of glycols (DEG/DPG = 4.6 mol/mol) and esterification by y mol of diacids. Values for the reference polyol were $x = 2.24$; $y = 0.8$ (P/A = 1); RM = 1.80 and OHV = 289 mg KOH/g. Fig. 8 shows the evolution of log (viscosity) as a function of log (OHV). Line 1 corresponds to polyols with variation of P/A ratio, as sole modification. Dramatic decrease of viscosity results from introduction of aliphatic A moieties. Comparatives polyols (circles; same RM, P/A = 1, but variation of y) show a high increase of viscosity with increasing PET content in reactant mixtures. Thus, aromatic moieties (phthalic and especially terephthalic) are responsible for higher viscosities. The own effect of hydroxyl value was investigated through polyols disposed in lines 2 and 3 in Fig. 8. Variations of OHV were obtained in line 2 by modification of x and in line 3 by modification of y (P/A = 1). Straight lines are observed, and OHV being inversely proportional to molecular weight, thus, we observe a law $\eta = kM^a$. Coefficients $a = 4.2$ and 3.3 for lines 2 and 3, respectively. The discrepancy could result from the fact that OHV enhancement is accompanied, in line 2, by a decrease in the proportion of MEG derived

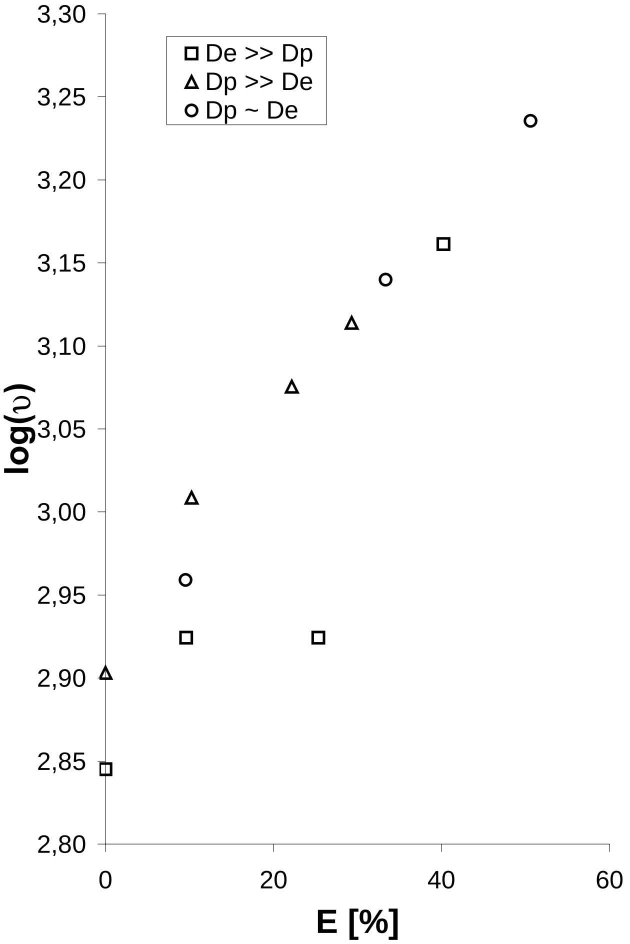


Fig. 7. Viscosity logarithm against E moiety proportion in glycolic residues.

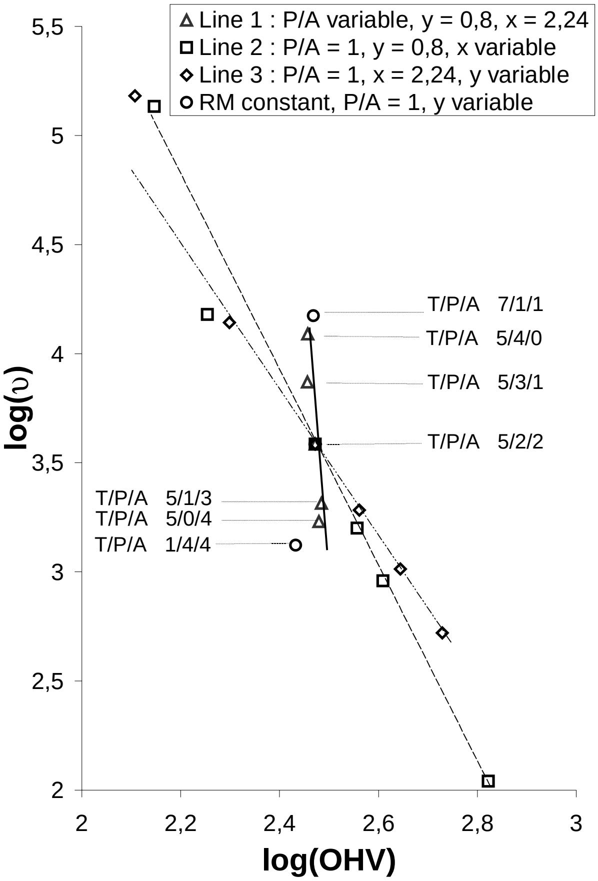


Fig. 8. Viscosity against OH value — log scale — according to reactants composition. Viscosity is expressed in mPa s and OH value in mg KOH/g; The center polyesterdiol belongs to the four data sets; polyol synthesis: 1 mol PET + x mol glycols(DEG/DPG = 4.6/1) + y mol diacids.

moiety in glycolic residues (thus lowering the viscosity), and, in line 3, by an increase in the proportion of terephthalic moiety in diacidic residues (thus enhancing the viscosity).

4. Discussion

The physicochemical properties of the polyols are profoundly affected by the chemical constitution. Prediction of properties is of interest for optimization purpose. Multiple regressions have given relations between properties and the moieties amounts for 141b compatibility, viscosity and OHV.

As OHV results from the composition and can be theoretically calculated (see Appendix A), the relation is not a surprise. The theoretical relation as a function of constitutive moieties is of a complex form, but in a limited area of the amounts, an approximation by a quadratic model is plausible.

Viscosity was found to be correlated with both constitutive parameters and hydroxyl values. The models can weakly describe some polyols, probably because of too high heterogeneity of the whole panel. From examination of a more homogeneous panel of polyols, it appears clearly that, at constant OH value, aromatic moieties (phthalic and especially terephthalic) and ethanediyl (E) units conduct much higher viscosities. For polyols of ‘homogeneous’ compositions, we found a relation between viscosity and number average molecular weight: $\eta = kM^a$. The power coefficient — ~3.6 — is close to the usual value (~3.4) for polymers with molecular weight higher than critical molecular weight. But, for our low molecular weight compounds, a value close to 1 is more likely expected. However, the composition of the polyols is not really homogeneous because OHV variations are obtained by modifying the RM — i.e. changing the glycolic to acidic moieties ratio and the amount of terminal groups.

Employing Doolittle equation based on free volume concept Kim [22] has determined that the viscosity of unsaturated polyols in concentrated solution of styrene is correlated with the T_g of the polyols. Polyols were obtained by glycolysis of PET with mono- and di-propyleneglycol and esterification with maleic anhydride. When the PET content decreases (higher y and RM values), the viscosity decreases (as for our polyols) and T_g decreases. Higher T_g

and viscosity of more aromatic polyester may result from conjugation between phenyl ring and carboxyl groups, making the structural framework stiffer [23]. For isophthalate polyols [24], it has been noticed that lower viscosity values are obtained by increasing the RM and also by glycolysis with linear diol instead of branched one. A liquid crystal structure was suggested for the low viscosity polyols.

An equation for HCFC 141b compatibility was found. It is important to note that, with the choice of the chemical constitution, varied values may be obtained. Relative high compatibility is desirable for polyisocyanurate technology, but too high solubility of the blowing agent in the foams polymer matrix causes plastification effect, leading to problems with dimensional stability and reduction in compressive strength [25].

As already mentioned in numerous patents (see e.g. Refs. [3,12]), the storage stability is greatly enhanced by lowering the amount of ethanediyl moieties. With the diols used in the present study, stable polyols with convenient hydroxyl value (<450) cannot be obtained by a single glycolysis step of PET and without elimination of monoethyleneglycol. A post-esterification step leads to better results, but it is difficult to obtain stable polyols when the molar ratio of added diacidic to terephthalic units is lower than 0.8.

Thus, it appears that the constitutive moieties of PET are accountable to non-desirable physicochemical properties: high viscosity, lack of storage stability. However, PET provides some other interesting properties: foams low flammability, polyol production cost (if wastes are used).

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Appendix A

Theoretical hydroxyl value for PET based polyols:

$$\mathrm{OHV} = 56.1 n_{\mathrm{OH}}/\mathrm{weight}$$

where n_{OH} is in meq and weight is in g and

$$n_{\mathrm{OH}} = (n_{\mathrm{OH}}\text{from added glycols}) - (n_{\mathrm{OH}}\text{consumed by esterification}),$$

$$\text{weight} = (\text{weight of reactants} - \text{weight of distillated water})$$

For a composition from 0.5 mol T and other moieties amounts equal to P, A, E, De, Dp:

$$n_{\mathrm{OH}} = 2000[De + Dp + (E - 0.5)],$$

$$\text{weight} = 96 + 62(E - 0.5) + 106De + 134Dp + 130P + 110A$$

Thus

$$\mathrm{OHV} = 11\,200 \times \left[\frac{De + Dp + (E - 0.5)}{96 + 62(E - 0.5) + 106De + 134Dp + 130P + 110A}\right]$$

The same equation is found for DMT based polyols.

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