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Procedure for the preparation of polymeric mixtures using vegetable oils and plastic packaging bottle wastes

Mérite Muntumosi-Senzedi, Jean-Pierre Mbungu-Tsumbu, Robert Muanda-Ngimbi, Richard Bopili-Mbotia-Lepiba, and Baudouin Zuka-Maniania

Department of Physics, Faculty of Sciences and Technologies, P.O.B. 190 Kinshasa XI, University of Kinshasa,
Kinshasa, RD Congo

ABSTRACT: The objective is to propose a solvent able to mix with polymers that hardly mix to based vegetable oils solvent (such as terephthalate polyethylene having undergone a certain crystallization or addition of additives). The methodology consists of measuring the unmixed solvent fraction through a series of experiments of partial cooking of the same polymer quantity. The solvent is a mixture of vegetable oils adjusted by the addition of a well-defined tiny sulfuric acid quantity. This methodology is based on the Hildebrand's approach in the Flory-Huggins theory of polymer mixtures according to which the best solvent is the one whose solubility parameter is the closest to that of the polymer. Then, hardly miscible polymers were successfully mixed to based vegetable oils solvent. The behavior of the obtained polymeric mixtures as a function of the added sulfuric acid tiny amount is in good agreement with the Hill-Langmuir models on the equilibrium between the adsorption and the desorption of species in well determined quantity. The «Solvent» entities are «Ligands», while the «Polymer» sites are «Receptors». This behavior also shows that, for a solvent adjusted by adding a well-defined tiny sulfuric acid amount, the mixing phenomenon can be an enduring process in time. The results of this work suggest that it is possible to adjust the solubility parameter of the previous study solvent to that of the polymer by adding a tiny amount of an appropriate element to the solvent/polymer mixture.

KEYWORDS: Polymeric mixtures, solubility parameter, vegetable oils solvent, plastics wastes, Hill-Langmuir models.

1 INTRODUCTION

The previous study proposes a method for obtaining a vegetable oils solvent capable of mixing with polyethylene and its derivatives. The authors succeeded in carrying out polymeric mixtures in the laboratory by the proposed method, using mainly samples of polyethylene and polymers derived from polyethylene taken from wastes of the packaging bags [1]. The results of this study thus raise great hopes in addressing the resolution of the environmental problem linked to the dispersion of plastic wastes in nature. They also open up a new perspective in the recovery of plastic wastes. The polymeric mixtures obtained can have interesting applications in a wide variety of fields [2], [3], [4], [5].

However, recent experiments carried out on mixtures of the proposed solvent with certain polymers, such as terephthalate polyethylene having undergone some crystallization or addition of additives, show only a very little amount of polymer that mixes with the solvent. Among the recalcitrant polymers (that mix very little with the proposed solvent) are samples of polymers taken from the waste of drinks packaging bottles. Water and sugary drinks packaging bottles are the most abundant plastic wastes found in nature.

According to Hildebrand's approach on polymer blends, it is always possible to obtain a satisfactory mixture by adjusting the solubility of the solvent to that of the polymer [1], [6], [7]. If certain polymers mix very little with the solvent proposed by the previous study, this means that the solubility of the proposed solvent is not sufficiently close to that of these polymers. The solvent proposed by the preceding study is a mixture of vegetable oils in well-determined proportions so as to approximate the solubility of this mixture of vegetable oils as closely as possible to that of the polymer.

The objective of the present work is to propose a solvent able of mixing with recalcitrant polymers (such as terephthalate polyethylene which has undergone a certain crystallization or addition of additives). It is a question either of proposing another solvent whose solubility is close to that of the polymer, or of continuing to adjust the solubility of the solvent by the procedure of the previous study.

2 METHODOLOGY

According to the same procedure described in the previous study, the methodology consists in measuring the fraction of the solvent unmixed with the polymer through a series of experiments of partial cooked of the same quantity of polymer [1].

The methodology is based on the Hildebrand approach in the Flory-Huggins theory on polymer mixtures. According to this approach, the best solvent is the one whose solubility parameter is closest to that of the polymer. The solubility parameters appear in the parameter of Flory [7, 8] given by the expression

$$\boldsymbol{\beta} = \frac{\boldsymbol{v_m}}{\boldsymbol{R\,T}} \left(\boldsymbol{\delta_{solvent}} - \boldsymbol{\delta_{polymer}}\right)^2 \qquad (1)$$

The Flory parameter "β" is involved in the enthalpy mixture expression "$\Delta\, H_{mix}$". $\delta_{solvent}$ et $\delta_{polymer}$ are solubility parameters, T is the temperature, R the ideal gas constant and v_m the molar volume of the polymer.

According to the Flory-Huggins theory, the mixture of polymers is controlled by the value of the free enthalpy "$\Delta\, G_{mix}$" whose expression is given by:

$$\Delta\, \boldsymbol{G_{mix}} = \Delta\, \boldsymbol{H_{mix}} - \boldsymbol{T}\, \Delta\, \boldsymbol{S_{mix}} \qquad (2)$$

The entropy term " $-T\, \Delta\, S_{mix}$" takes into account of the monomer units arrangements number in the solvent, while the enthalpy of the mixture "$\Delta\, H_{mix}$"describes the different interactions between the monomer units and the solvent molecules.

In the solvent consisting of a vegetable oils mixture, proposed in the previous study, a tiny well-determined quantity of sulfuric acid is added each time in attempting to approach the solvent solubility to that of the polymer.

3 MATERIALS AND EXPERIMENTS

The materials used in this work are mainly the same as those in the previous study [1]. The cooking was carried out in free atmosphere according to the same procedure using a hot plate (LABBOX SBS CE 2012) equipped with a magnetic stirrer and a temperature regulator. Once the regulator temperature adjusted, the cooking shows a rapid rising in temperature from room temperature during about 35 minutes, then followed by a nearby temperature stabilization during 10 minutes around 160 °C, and finally a free cooling down to room temperature as a result of stopping the heating. The magnetic stirrer remained operational throughout cooking. A mercury thermometer graduated from 0 °C to 250 °C was set in the vapor about one centimeter above the free surface of the mixture. A 500 ml Beaker (LABBOX LBG 3.3) was used as a cooking container. A balance (TANITA model 1230) was used for sample weighing. The same experimental setup was used.

Vegetable oils and kerosene were used in the proportions indicated by the previous study to constitute the solvent. Polymer samples were taken from drink waste packaging bottles. Tiny amounts of concentrated sulfuric acid (98 %) were used as additive to solvent / polymer mixtures.

The preparation of these polymeric mixtures consisted of adding to one hundred milliliters polymeric mixture respectively 0 ml, 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, 1 ml, 1.2 ml, 1.4 ml, 1.6 ml, 1.8 ml and 2ml of concentrated sulfuric acid. One series of cooking experiments with the same amount of polymer (0.5 gram) were then carried out in different polymeric mixtures. Before performing measurements, the final mixtures were each rested for 30 days at room temperature under atmospheric pressure.

A second series of cooking experiments with the same amount of polymer (0.5 gram) was carried out in polymeric mixtures of 100 milliliters each with an additive of one concentrated sulfuric acid milliliter (H2SO4) (98%). Before performing measurements, each final mixture was rested at room temperature under atmospheric pressure for 0 day, 3 days, 6 days, 9 days, 12 days, 15 days, 18 days, 21 days, 24 days, 27 days and 30 days, respectively.

4 RESULTS AND DISCUSSION

Concerning the first series of cooking experiments, the final mixtures obtained with less than 0.4 ml of sulfuric acid as additive show some polymeric lumps. While polymeric mixtures obtained with more than 0.4 ml of sulfuric acid as additive do not show polymeric lumps. Therefore, these facts indicate the existence of a threshold quantity of sulfuric acid as an additive to obtain mixtures without polymeric lumps (with all the polymer mixed in the solvent).

The amount of unmixed solvent to the polymer was plotted against the amount of sulfuric acid additive to the mixture (Fig. 1). One can observe in this graph that the amount of the unmixed solvent to the polymer decreases as the amount of sulfuric acid additive increases.

In Fig. 1, dots indicate measured values, while the solid curve derives from a growth model of the solvent amount effectively mixed to the polymer. The amount of unmixed solvent decreases with the amount of sulfuric acid additive while the amount of effectively mixed solvent increases. However, this growth in the amount of effectively mixed solvent to the polymer should remain limited both by the amount of available polymer and probably also by the resting time before measurements.

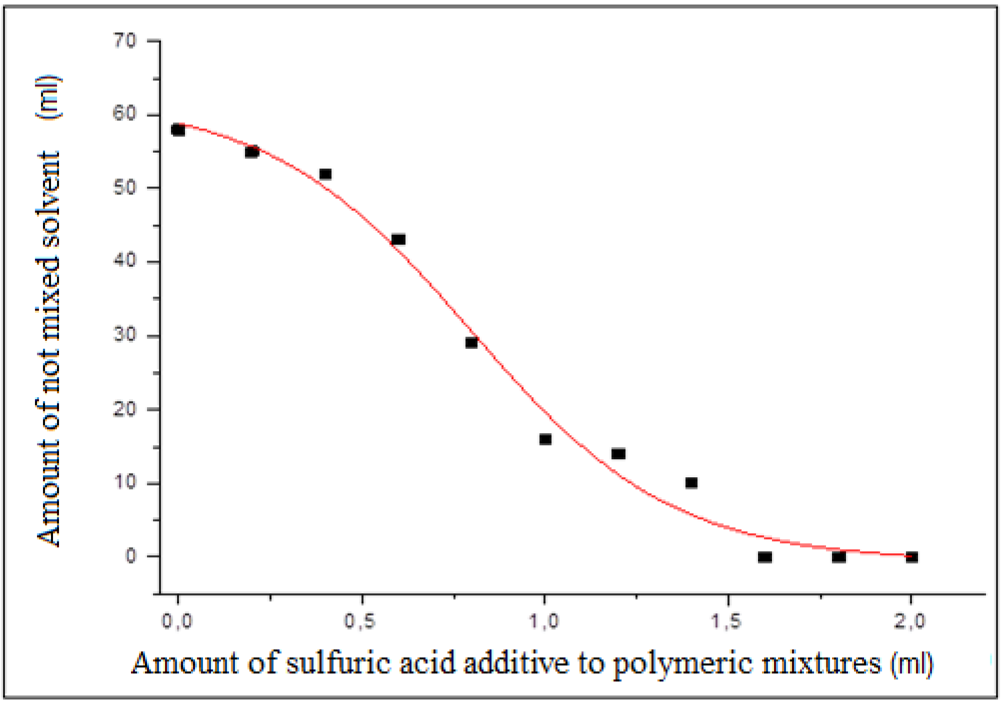

Fig. 1. Amount of unmixed solvent as function of sulfuric acid additive to polymeric mixtures

Using appropriate data analysis software, it appears that the growth logistic function better fits to measured values [9, 10, 11, 12]. Thus, using the logistic growth model, the function Y (x) in equation (3) describes the amount of unmixed solvent to the polymer as a function of the amount of sulfuric acid additive, while the amount of effectively mixed solvent to the polymer is described by the function Z (x) in equation (4).

$$\boldsymbol{Y}\,(\boldsymbol{x}) = \frac{\boldsymbol{a}}{\boldsymbol{1} + \boldsymbol{e}^{\boldsymbol{\mu}(\boldsymbol{x}-\boldsymbol{x_c})}} \tag{3}$$

$$Z\,(x) = a - \frac{a}{1 + e^{\mu(x-x_c)}} \tag{4}$$

Table 1 presents parameter values obtained by fitting the growth logistic function to measured values.

Table 1. Parameters of the growth logistic function fitted to experimental data

$a\ (ml)$	$\Delta a\ (ml)$	$x_c\ (ml)$	$\Delta x_c\ (ml)$	$\mu\ (ml)^{-1}$	$\Delta\mu\ (ml)^{-1}$	**Corr. coeff.**
61	3	0.79	0.05	3,8	0,5	0.987

The logistic growth model takes into account the environmental constraints involved and, in effect, slows growth when the size of the quantity $\boldsymbol{Z\ (x)}$ approaches a certain K value. The growth rate " $\boldsymbol{\mu\left(1-\frac{Z\ (x)}{K}\right)}$" is variable and depends on the size of the quantity $\boldsymbol{Z\ (x)}$. The logistic growth model is then described by the differential equation below:

$$\frac{dZ\ (x)}{dx}=\mu\left(1-\frac{Z\ (x)}{K}\right)Z\ (x) \tag{5}$$

The parameters μ and K are constants.

One can notice in this model that the coefficient $\boldsymbol{1-\frac{Z\ (x)}{K}}$ remains close to 1 when the size of the quantity Z (x) is very small, which causes the beginning of exponential growth. We also notice that this coefficient decreases until it tends towards 0 when the value of the quantity Z (x) increases and tends towards the value K. The parameter K therefore represents the limit value of the quantity of solvent which can participate in the mixing process.

In this model, the rate of growth of the amount of solvent actually mixed with the polymer is proportional to both the amount of solvent already mixed with the polymer and the amount of solvent that can still be mixed with the polymer. This looks like an autocatalytic reaction, the catalyst being "the amount of sulfuric acid added as an additive" [9, 10, 11, 12].

Regarding the second set of cooking experiments, observations made on the final product show a two-phase polymer mixture with an unmixed amount of solvent supernatant the mixture. The two phases of the polymeric mixture are a phase rich in polymer and a light phase poor in polymer. The amount of solvent unmixed with the polymer was plotted against standing time. It can be seen in this graph that the amount of solvent unmixed with the polymer decreases in a certain way as a function of the standing time (Fig. 2).

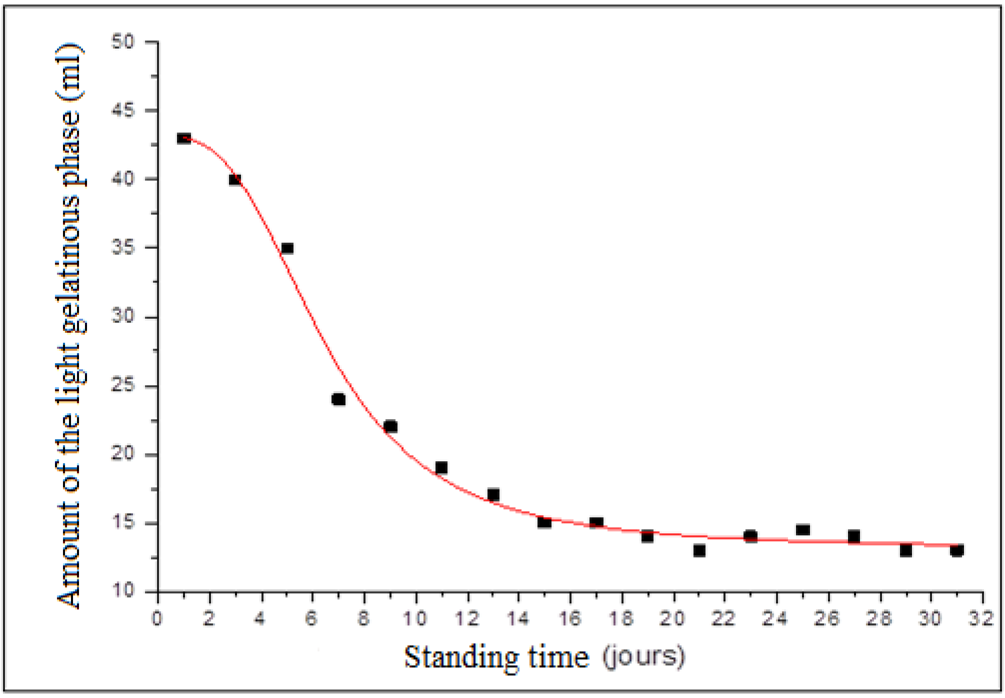

Fig. 2. Relative amount of the light gelatinous phase as a function of time

In the Fig. 2, the dots indicate the measured values, while the solid curve results from a growth model of the amount of solvent actually mixed with the polymer. The amount of solvent unmixed with the polymer decreases with standing time as the amount of solvent actually mixed with the polymer increases. At the zero moment of standing, some mixing had already taken place during the heating, i.e. a certain amount of solvent was already effectively mixed with the polymer. After a sufficiently long-standing time, the amount of solvent actually mixed with the polymer is maximum while the amount of solvent unmixed with the polymer becomes minimum.

Using the same data analysis software, it appears that the growth logistic function fits better to the measured values. Thus, from the logistic growth model, the function Y (t) expressed by equation (6) describes the quantity of solvent unmixed with the polymer as a function of the standing time, while the quantity of solvent actually mixed with the polymer is described by the function Z (t) expressed by equation (7).

$$\boldsymbol{Y\,(t) \;= A_2 + \frac{A_1 - A_2}{1 + \left(\frac{t}{t_0}\right)^p}} \tag{6}$$

$$\boldsymbol{Z\,(t) \;= b - \left[\frac{A_1 - A_2}{1 + \left(\frac{t}{t_0}\right)^p} + A_2\right]} \tag{7}$$

Table 2 presents the values obtained by fitting the logistic growth function to the experimental data.

Table 2. Values of fitted parameters from the logistic growth model

$A_1\ (ml)$	$\Delta A_1\ (ml)$	$A_2\ (ml)$	$\Delta A_2\ (ml)$	$t_0\ (days)$	$\Delta t_0\ (days)$	p	Δp	**Corr. coeff**
43,0	0,9	13,0	0,5	6,4	0,3	3,0	0,3	0,99

The parameter t_0 expresses the duration of the solvent / polymer mixing process.

Regarding this logistic growth model, its conception is based on the Hill-Langmuir equation which itself derives from the law of mass action [12, 13, 14]. Indeed, the Hill-Langmuir model sets in equilibrium the adsorption and desorption of species (L) called "Ligand" by another species (R) called "Receptor". The "Ligand" species can be found in varying concentration, while the "Receptor" species, the quantity of which is constant, is greatly exceeded by the quantity of the "Ligand" species. The "Receptor" sites are found in the polymer, while the "Ligand" species are in the solvent.

$$\mathbf{nL + R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} L_nR} \tag{8}$$

The factor n represents the number of coordination for the "Ligand" species in a "Receptor" site. The parameters $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$ are respectively the adsorption rate and the desorption rate. The action mass law is expressed as follows:

$$\boldsymbol{[L_nR] = \;[R_0]\,\frac{[L]^n}{[L]^n + K_d} = \;[R_0]\,\frac{[L]^n}{[L]^n + (K_A)^n}} \tag{9}$$

$\boldsymbol{[L_nR]}$ is the concentration of the "Ligand-Receptor" complex. $\boldsymbol{[R_0]}$ is the total concentration of "Receptor" sites. [L] is the concentration of free ligands (in practice considered as the total concentration of ligands). $\boldsymbol{K_d = \;k_2/k_1}$ is the dissociation equilibrium constant of the "Ligand-Receptor" complex. $\boldsymbol{K_A}$ is the concentration of the "Ligand" species when half of the "Receptor" sites are occupied.

In terms of concentrations, the equilibrium dissociation constant of the "Ligand-Receptor" complex $\boldsymbol{K_d}$ is given by the expression:

$$\boldsymbol{K_d = \frac{[L]^n[R]}{[L_nR]}} \tag{10}$$

While the equilibrium constant of association $\boldsymbol{K_a}$ of "Ligands" and "Receptors" to form the "Ligand-Receptor" complex is given by the expression:

$$\boldsymbol{K_a = \frac{[L_nR]}{[L]^n[R]}} \tag{11}$$

Authors have proposed practical modifications of equation (9) allowing the application of the Hill-Langmuir model to describe the phenomena of sigmoid and hyperbolic saturation under experimental conditions [15, 16].

Thus, the following equation, called the "MORGAN-MERCER-FLODIN equation" is often used:

$$\boldsymbol{[L_nR] = [R_0]\,\frac{[L]^n}{[L]^n + K_d} + \beta\, K_d \frac{1}{[L]^n + K_d}} \tag{12}$$

The parameter β allows the translation on the y-axis. Equation (12) can take the form (13).

$$\mathbf{[L_nR] = [R_0] - \frac{[R_0] - \boldsymbol{\beta}}{1 + \frac{[L]^n}{K_d}}} \tag{13}$$

The MORGAN-MERCER-FLODIN equation takes various forms depending on the considered case. For example, the function fitted to the experimental data is one of the forms of the MORGAN-MERCER-FLODIN equation presented as follows [**15, 16**]:

$$\mathbf{[L_nR] = [R_0] - \frac{[R_0] - \boldsymbol{\beta}}{1 + \left(\frac{t}{t_0}\right)^n}} \tag{14}$$

with $\left(\frac{t}{t_0}\right)^n = \frac{[L]^n}{K_d}$

Comparing equation (14) to the function fitted to the experimental data (see equation 7), we obtain that for a sufficiently long resting time, all the "Receptor" sites are occupied by the "Ligand" species, namely $(\boldsymbol{[L_nR]})_{t=\infty} = \boldsymbol{[R_0]}$, and there will be a residual amount of solvent. At the instant t = 0, a certain number of “Receiver” sites had already been occupied during the cooking, that is to say $(\boldsymbol{[L_nR]})_{\boldsymbol{t=0}} = \boldsymbol{\beta}$. We obtain 30 ml of solvent effectively mixed with the polymer during the thirty days standing time, each "Solvent-Polymer" complex consisting of a "Receptor" species linked to three "Ligands" species (see Table 2). About 13 ml of solvent remained residual without being able to mix with the polymer during the thirty days standing time.

The two series of experiments show that out of the 100 ml of solvent used for cooking 0.5 g of polymer, about 61 ml are needed to obtain the mixture, 13 ml are residual and 26 ml have probably evaporated during the cooking.

5 CONCLUSION

The present work completes and reinforces the results of the previous study. It proposes to continue to use the previous study procedure in the mixing of vegetable oils with recalcitrant polymers. This involves the cooking of the same quantity of polymer in solvents that consist of vegetable oils in different proportions in order to obtain the optimal solvent. For the recalcitrant polymers which uneasily mix with the previous optimal solvent, the present work has chosen to adjust the solubility of the optimal vegetable oils solvent by adding a tiny amount of sulfuric acid in the mixture. It is probably possible to use an acid other than the sulfuric acid as an additive to the mixture.

The results of this work certainly contain some originality. In fact, the amount of sulfuric acid added in tiny amounts as an additive promotes the solvent / polymer mixing process. These results show that the solvent / polymer mixing process is slow and may require the presence of some additional element that boosts the mixing process for recalcitrant polymers.

The description of these results is based on Hildebrand's approach in the Flory-Higgins theory of polymer blending. These results are in agreement with the Hill-Langmuir models that rely in equation the adsorption and the desorption of species (L) called “Ligand” by another species (R) called “Receptor”. "Solvent" entities play the "Ligands" role, while the "Polymer" sites play the "Receptors" role [14].

The results of this study raise high hopes for the resolution of the environmental problem linked to the dispersion of plastic wastes in nature. Indeed, plastic wastes collected in nature could be used for the preparation of polymer / vegetable oil mixtures. If the resulting mixtures show interest in attractive applications, a waste collection activity could be supported, leading to the rapid remediation of the environment. The obtained mixtures also open up new perspectives in the recovery of plastic wastes. Polymeric mixtures can have interesting applications in a wide variety of fields [2, 3, 4, 5].

This work has succeeded in obtaining laboratory polymeric mixtures from vegetable oils and polymers resulting from the most diverse plastic wastes. A knowledge has been acquired both in the preparation of vegetable oils solvents able to mix with polymers and in the preparation of polymeric mixtures. This expertise could be shared with services or companies interested in the polymeric mixtures industrial production.

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