Innovative Pipe Coating Material and Process for High Temperature Fields

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Résumé — **Nouveaux revêtements pour conduites pétrolières haute température** — L'intérêt porté de nos jours à l'exploitation offshore de champs pétroliers haute température (> 140 °C, par exemple en mer du Nord) impose le développement de technologies de revêtement innovantes. En réponse à cette problématique, un procédé original de mise en œuvre de polymères thermostables a été étudié comme voie nouvelle (extrusion réactive de thermoplastique amorphe de haute Tg en présence d'un solvant réactif de monomères époxyde et amine).

L'objectif est ici de présenter les avantages du procédé de mise en œuvre et des revêtements thermostables obtenus, en soulignant leur caractère non polluant. Les données de vieillissement sur de longues périodes sont discutées pour différentes compositions thermostables, dont certaines formulées. Des tests de durabilité en eau de mer à 160 °C ont été menés durant 12 000 heures, et les échantillons vieillis ont été désorbés puis testés par analyse dynamique mécanique, afin de détecter la présence de dégradation irréversible. En vue de l'application revêtement, des mesures d'adhérence sur acier au carbone ont été réalisées à température ambiante et l'effet plastifiant de l'eau a été étudié (mesure *in situ* de la Tg par spectroscopie d'impédance). Enfin, la spectroscopie d'impédance a également permis d'évaluer le caractère protecteur des revêtements anticorrosion exposés à des conditions de vieillissement accéléré.

Abstract — *Innovative Pipe Coating Material and Process for High Temperature Fields* — *To date, the high temperatures (above 140°C) met in some fields in,* e.g.*, the North Sea, impose the development of innovative corrosion protecting coatings. Thermostable products have been developed from combining a high-*Tg *thermoplastic and epoxyamine monomers (the latter reducing the viscosity of the former to allow processing) which, together with the associated coating process solve these services innovatively.*

Details of the subtleties of material choice and behavior, process engineering and how environmental issues are met are presented. Data from various long term ageing tests performed on these thermostable materials, including filled formulations, are discussed. Durability tests against sea water over 12 000 hours at 160°C are followed by desorption and dynamic mechanical analysis to assess whether any irreversible degradation has occurred. Carbon steel adhesion measurements are carried out in the view of coating applications as well as in situ Tg *values evaluated by impedance spectroscopy. Plasticization effect of water is discussed. In addition, impedance spectra also indicate the quality of corrosion resistance achieved under accelerated ageing conditions.*

INTRODUCTION

Offshore pipe lines devoted to oil transport are externally coated with organic material for several reasons. The main one is to protect the steel against corrosion to sea water. But pipe coatings also impart protection against mechanical damage or disruption occurring when a flow-line is being installed and also throughout its life on the sea-bed. Nowadays, offshore infrastructures are required to operate in extreme conditions, since they may be exposed to temperature above 140°C (for example high temperature fields in North Sea). Therefore, requirements on pipe coatings are more and more severe [1]. Indeed, external pipe coatings should provide continuous corrosion protection in service conditions, meaning that the coating material has to exhibit stability in sea water and adherence on steel beyond 140°C. In addition, organic coating material should be processed under 250°C in order to avoid changes in steel microstructure, while respecting environmental requirements. So far, classical three layers coating can provide continuous corrosion protection up to 120°C and a five layers coating to be submitted to 140°C is under test. FBE (resin powder melted on a preheated pipe) is prone to mechanical damage, polyolefin (processed easily under 250°C) have intermediate softening temperature up to 120°C and polyurethane (processed by moulding or directly poured on a pipe) has a maximum service temperature in water around 120°C due to hydrolysis. Very high *Tg* thermosets are already used as epoxy-phenolic or epoxy-novolak, but such polymers are very brittle and cannot be used for offshore pipelines. Thus, there is a need in organic coating material and process to overlay actual technical limitations.

Fundamental work [2-4] has recently highlighted the benefits related to reactive extrusion of a polymer blend including high-*Tg* thermoplastic *(TP)* as major component, and thermoset precursors *(TS)* as reactive solvent. At a given temperature, the latter reduces the viscosity of the so-called intractable high-*Tg* thermoplastic (*Tg* around 210°C) and allows extrusion around 180°C *(see Fig. 1)*. The reactive organic compound of low viscosity formulated with pigments and/or fillers specific to the application could be directly applied on a rotating pipe (continuous production line process) or micronised into powder for later projection on steel. An additional cure around 220°C induces a phase separation [5], leading to a biphasic material where the matrix (phase α) is the high-*Tg* thermoplastic and epoxy-amine are nodules (phase β) when the thermoplastic part is greater than 20% in weight. Therefore, the final material exhibits the thermostable and toughness properties of the thermoplastic matrix (*Tg* around 210°C). In particular, one should note that *TP/TS* blends exhibit higher tenacity values ($K_{1c} \sim 2.7$ MPa·m$^{1/2}$ at 21°C [5]) than pure highly cross-linked thermosets ($K_{1c} \sim 0.6$ MPa·m$^{1/2}$ at 21°C).

The aim of this paper is to highlight the benefits of such coating process and materials and to explain why they provide an innovative and suitable solution for the aforementioned needs of the offshore industry. Fillers and pigments are incorporated in order to firstly improve corrosion protection and secondly release internal stresses [6, 7]. Various tests performed on these innovative coatings —evaluation of durability, water-uptake, adhesion and protective performance in service conditions—are reported and discussed in this paper.

1 EXPERIMENTAL

1.1 Materials

The amorphous high-*Tg* thermoplastic under study is polyphenylenether, PPE, supplied by *General Electric* (Blendex 820, *Mn* = 12 000 g/mol). The epoxy prepolymer
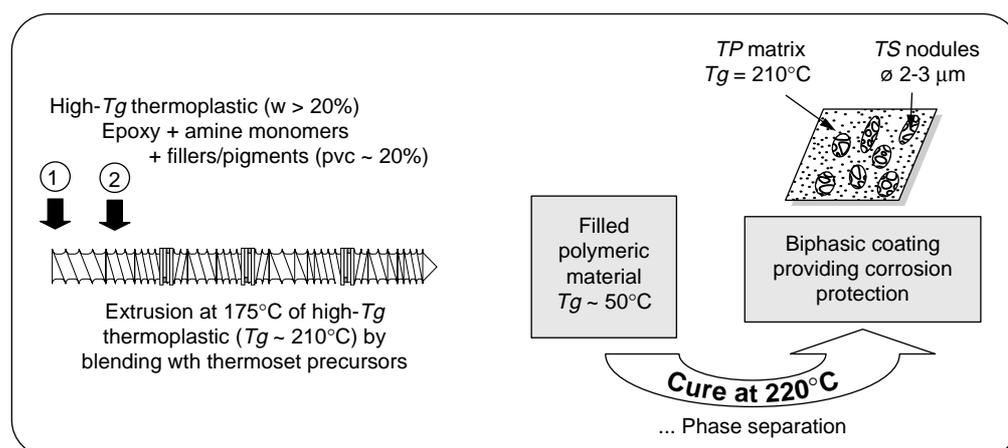

Figure 1

Schematic overview of high-*Tg* thermoplastic processing by reactive extrusion to produce a coating material.

under consideration is diglycidylether of bisphenol A (DGEBA), supplied by *Ciba Geigy* (LY 556, small polymerization degree $n = 0.15$, $Mn \approx 380$ g/mol). The hardener added in stoichiometric amount is the aromatic diamine 4,4'-methylenebis(3-chloro-2,6-diethylaniline), MCDEA, supplied by *Lonza* ($Mn = 380$ g/mol).

Three filler/pigment formulations A, B and C chosen among non toxic fillers/pigments are studied in this paper. A, B and C stand respectively for pure kaolin, a mixture of micaceous iron oxide (MIOX) and kaolin, and a mixture of zinc phosphate (Zn Ph) and kaolin.

1.1.1 Code Name

Unfilled formulations are designed by the thermoplastic name and proportion (in weight percent of the polymeric mixture without fillers). For example, PPE40 corresponds to a mixture of 40% by weight of PPE with 60% of DGEBA-MCDEA. In the case of filled material, the filler/pigment concentration is given in volume percent. For example, PPE40-A21 corresponds to PPE40 with a PVC (pigment volume concentration) of 21% of filler/pigment formulation "A".

1.1.2 Process and Cure Conditions

A double screw extruder *Clextral* BC21 including three mixing zones is used to perform homogeneous blending of thermoplastic with epoxy-amine precursors at 175°C. The uncured extruded material is cut into pellets for practical use. material sheets $100 \times 100 \times 2$ mm^3 are moulded and cured under pressure (220°C during 2 h, 10 MPa). Coatings (DFT around 600 μm-24 mils) are achieved under similar pressure/cure conditions on low carbon steel sheets (60×40 mm^2, sand blasted before use with corindon 400 μm to SA 2 1/2 according to ISO 8501-1; anchor profile $R_{ZD} \sim 30\text{-}35$ μm according to ISO 8503-2).

In order to take industrial requirements under considerations, one should notice that the cure cycle chosen in this work is voluntarily reduced in comparison to the one recommended in literature [8] to achieve extensive cure (2 h at 200°C followed by 2 h postcure at 220°C); this point will be discussed further in Section 2.

1.2 Characterization Means

Figure 2 presents the overall methodology of characterization.

Viscoelastic experiments were carried out at low deformation by means of dynamic mechanical thermal analyser DMTA-MARK III *(Polymer Laboratories)* on parallelepipedic samples of 8 mm width and 2 mm thickness. A single cantilever flexural mode was used at frequency 1 Hz from room temperature to 250°C at a heating rate of 2°C/min *(see Fig. 3)*. The glass transition temperatures of the two
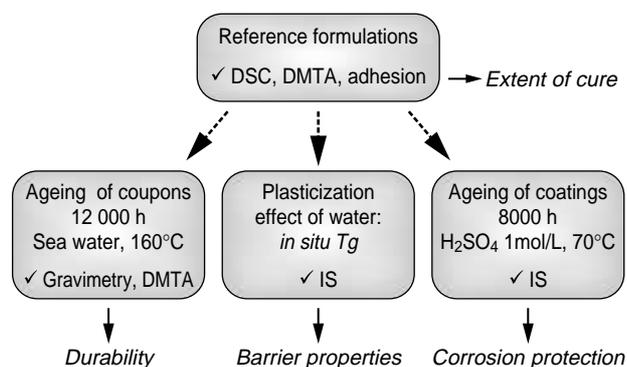

Figure 2
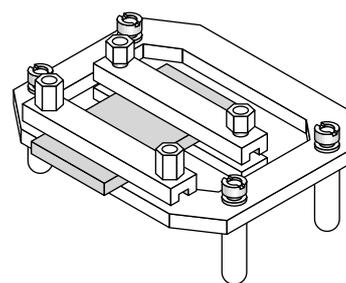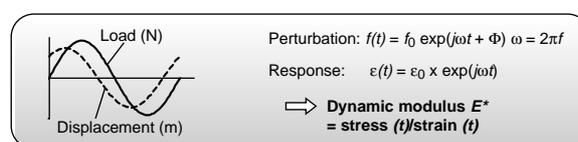
Methodology of characterization.

Figure 3

Principle and experimental set-up of DMTA.

material phases were conventionally taken at the maximum of the dissipation modulus E''.

Differential Scanning Calorimetric (DSC) measurements were performed on a *TA Instruments* 2920 spectrometer at a heating rate of 10°C/min. The DSC traces of all the thermoplastic/thermoset samples exhibit two well defined glass transitions associated to each phase. The glass transition temperatures *(Tg)* were taken at the onset of the transition. Modulated Differential Scanning Calorimetric (MDSC) measurements were also carried out to determine the increase of calorific capacity *(Cp)* at glass transition from the reversing *Cp* trace, using a ramp of 5°C/min modulated +/– 0.80°C every 60 s.

Ageing experiments were conducted in sea water at 160°C on coupons ($40 \times 40 \times 2$ mm^3) immersed in a pressurised vessel (under 2 MPa of N_2) over 12 000 h. Gravimetric measurements were first made on soaked samples to evaluate the water absorption, then on desorbed samples (80°C under vacuum during 56 h until constant mass) in order to control the reversibility of water-uptake.

Adhesion on low carbon steel is evaluated according to ASTM D1002. This method allows the determination of the shear strengths of adhesives for bonding metal panels ($80 \times 25.4 \times 2$ mm^3). Metal surfaces were submitted to similar surface cleaning and preparation than substrates used for coating application. An adhesive joint of about 300 μm thickness was prepared at 200°C under 0.5 MPa pressure and cured during 2 h at 220°C. The specific surface overlap is 25.4×12.7 mm^2. Lap shear tests were performed at room temperature on five specimens for each formulation using an *Instron* tensile machine at a displacement rate of 1 mm/min. Load versus displacement is recorded until failure.

Impedance Spectroscopy (IS) was used to evaluate the dielectric properties of organic formulations under study. IS is an AC (alternative current) technique for determining the components of an analog circuit that may represent an electrochemical process. Impedance is the ratio of the change in potential to the change in current ($\Delta E/\Delta I$), and is determined from the applied potential and the response current as a function of frequency in an electrochemical cell, when potential and current are linearly related. The impedance Z incorporates the magnitude value of $\Delta E/\Delta I$ and the phase shift between E and I. The frequency dependence of the impedance versus frequency enables the evaluation of coating resistance and capacitance [4]. Figure 4 presents the two-electrodes experimental set-up used here for IS
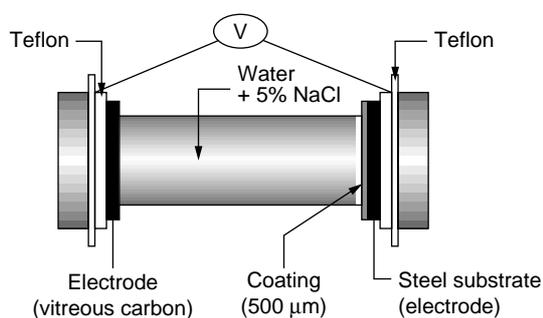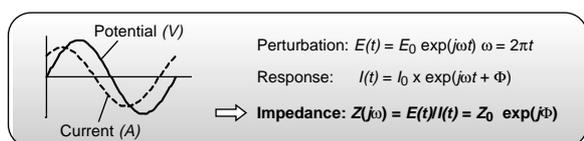

Figure 4

Principle and experimental set-up of IS.

measurements on coatings. Simple parallel planar configurations electrode/material/electrode were used for the characterization of dry and massive material (thickness about 1 mm). The frequency range was 105 Hz-10–1 Hz with an imposed voltage of 100 mV by using a Solartron 1260 impedance analyser equipped with the dielectric interface 1296 to measure large impedance values. Dielectric properties were evaluated by IS:

– on dry and soaked samples at a heating rate of 10°C/h from room temperature to, respectively, 190°C and 250°C;
– on coatings at a given temperature under accelerated ageing conditions (H_2SO_4 1 mol/L, 70°C) over 8000 h.

2 RESULTS AND DISCUSSION

2.1 Process

The processing of high-*Tg* thermoplastic with epoxy-amine precursors by reactive extrusion is well controlled, since extensive studies have been devoted to the blend kinetics and rheological behavior before and after phase separation [5, 9, 10]. Three main benefits should be underlined:

– the reactive extrusion process uses a classical twin-screw extruder allowing to blend thermoplastic and thermoset precursors at minimum cost, while respecting the requirement T < 250°C;
– blending and coating technologies are non polluting processes in respect with environmental requirements—Volume Organic Compounds (VOC) = 0%, and non toxic filler/pigment);
– the crude compound thermoplastic/thermoset can be cut into pellets after the first extrusion, then extruded a second time in band to coat a tube (in-line process). Indeed, the diamine hardener MCDEA is very latent and the viscosity of the blend remains low enough to be processed twice in a twin screw extruder before phase separation occurs. An alternative process of application is based on the micronisation of pellets for a final powder application.

2.2 Thermal Characterization after Cure

The glass transition temperature was used to characterize the cure state of the thermoplastic/thermoset blends under study. For comparison purpose throughout the article, *Tg* measurements performed on neat PPE and DGEBA-MCDEA are reported in Table 1. Note that DGEBA-MCDEA was cured during 2 h at 220°C to be a reference for the studied thermoplastic/thermoset blends. However, this is not an optimised cure cycle for this resin, since its optimized *Tg*∞ reaches 184°C according to DMTA and 177°C according to DSC experiments.

TABLE 1

Tg (°C) of neat PPE and *Tg* (°C) of DGEBA-MCDEA cured 2 h at 220°C (by DMTA, DSC and IS)

Code name	DMTA	DSC	IS
	Dry reference	Dry reference	Dry reference
PPE	222	210	224
DGEBA-MCDEA	177	160	175

2.2.1 Neat Thermoplastic/Thermoset Blends

Tg measurements performed by DMTA, DSC and IS on samples PPE40 and PPE60 after cure are reported in Table 2. The *Tg* of the matrix (phase α rich in thermoplastic) is about 10 degrees lower than the *Tg* of neat PPE, meaning that phase separation is not readily achieved. In addition, the low *Tg* values of the epoxy-amine nodules (phase β) show that the resin within the nodules is not fully cross-linked. The influence of this voluntary under-cure will be discussed in the Section 2.3.

TABLE 2

Tg (°C) of PPE40 and PPE60 cured 2 h at 220°C given by DMTA, DSC and IS

Code name		DMTA	DSC	IS
		Dry reference	Dry reference	Dry reference
PPE40	Phase α	213	195	
	Phase β	162	145	
PPE60	Phase α	214	198	210
	Phase β	167	147	140

2.2.2 Influence of Filler/Pigment Addition

Three filled formulations called PPE60-A21, PPE60-B21 and PPE60-C21 were characterized by DMTA after curing 2 h at 220°C in order to gain information about the filler/pigment distribution. The viscoelastic results are given in Figure 5 where the PPE60 curves are added for comparison purpose.

The plot relative to pure PPE60 shows two mechanically active relaxations located in the glass transition region of each phase, the *Tg* peak in the upper temperature range being associated to the PPE rich phase and the other to the epoxy riche phase. Filled samples exhibit also two relaxations. The presence of fillers strongly increases the storage modulus whatever the filler/pigment nature, illustrating the classical reinforcement effect of fillers. In addition, fillers affect both relaxation regions as revealed by the broadening of the *E''* peaks and the increased drop in the storage modulus *E'* while passing the relaxation. This observation reveals the occurring
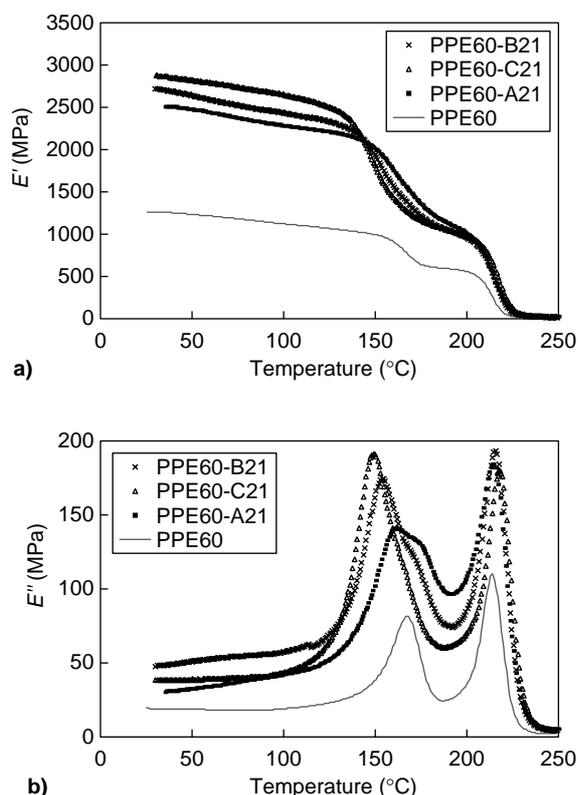
a)

b)

Figure 5

Temperature dependence of a) storage *(E')* and b) loss *(E'')* moduli at frequency 1 Hz for filled PPE60 and pure PPE60 samples after 2 h cure at 220°C.

of more heterogeneous molecular mobility in both glass transition regions due to filler/pigment dispersion. Therefore, fillers and pigments are expected to interact tightly with both the PPE rich matrix and the epoxy rich nodules. Interestingly, *Tg* values of PPE rich phase related to the filled samples are similar to *Tg* of PPE60, revealing that the incorporation of fillers and pigments did not disturb the phase separation. Moreover, *Tg* values of epoxy-amine rich phase related to the filled samples are shifted towards lower temperature in comparison to the *Tg* in PPE60. However, the *Tg* value of phase β is no more easily defined since *Tg* peaks observed on the dissipation modulus exhibit a splitting phenomenon. Since the incorporation of inert fillers is not expected to affect the network building, this observation was attributed to an interphase effect, revealing some segregation of the fillers entrapped in the epoxy-rich phase.

2.3 Durability in Seawater, 160°C

2.3.1 Water Uptake in Unfilled Thermoplastic/Thermoset Blends

PPE40 and PPE60 samples were immersed in seawater at 160°C over 12 000 h. Soaked samples were weighted twice

(after 2300 h and 12 000 h ageing), then desorbed and weighted dry. According to the gravimetric results given in Table 3, the relative stability of water-uptake with immersion time after 12 000 h ageing and the reversibility of mass gain with respect to initial mass suggest that PPE40 and PPE60 exhibit good durability properties in seawater at 160°C. These results will be assessed further by dynamic mechanical analysis and DSC measurements.

TABLE 3

Water uptake (gravimetric measurements in weight percent) of PPE40 and PPE60 aged in seawater at 160°C

| | Gravimetric measurement | |
Code name	Soaked samples 2300 h	Soaked samples 12 000 h
PPE	0.60	
DGEBA-MCDEA	2.20	
PPE40	1.45	1.45
PPE60	1.40	1.50

As expected, the water-uptake for the polymer alloy is between those of neat components *(Table 3).* Moreover, the matrix of thermoplastic/thermoset blends is expected to exhibit a water permeation behavior of similar magnitude to that of the thermoplastic under consideration, which is particularly interesting in terms of corrosion protection in the case of low hydrophilic PPE.

After extensive drying, aged samples were submitted to dynamic mechanical analysis in order to detect significant residual water and/or material degradation, inducing classically a broadening/depression effect on the glass transition peak, and/or a peak splitting. The comparison of the viscoelastic behavior of PPE40 before and after 12 000 h ageing is illustrated on Figure 6.
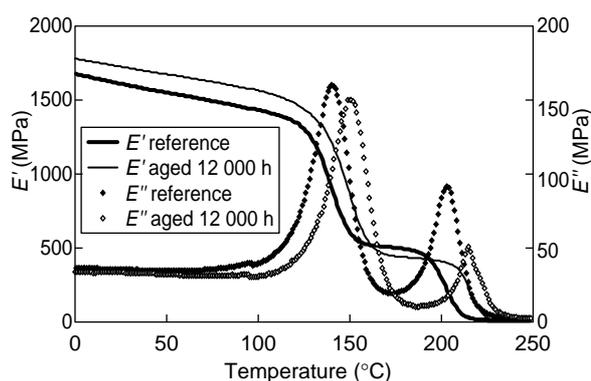

Figure 6

Temperature dependence of storage *(E')* and loss *(E'')* moduli at frequency 1 Hz for dried PPE40 samples before and after 12 000 h ageing in seawater at 160°C.

The viscoelastic behavior of aged PPE40 does not exhibit any sign of residual water or degradation. Neither do DMTA curves for 12 000 h aged PPE60 sample. On the contrary, one should notice that both Tg peaks developed on E'' curves were shifted towards higher temperature during ageing. This observation, supported by Tg values reported in Table 4, is made whatever the composition. After ageing, the Tg of the PPE rich phase is around the Tg of pure PPE *(Table 1),* revealing that extensive phase separation achieved during ageing. In addition, the Tg increase of epoxy rich phase indicates that further network building occurred during ageing. One can note that DSC measurements reflect the Tg increase less markedly since values are taken at the onset of the increase of the heat capacity *(Cp).*

TABLE 4

Tg (°C) of aged PPE40 and PPE60 given by DMTA and DSC measurements, and Tg discrepancies between reference and aged samples

Code name		DMTA		DSC	
		Aged sample	Tg_{aged} - Tg_{ref}	Aged sample	Tg_{aged} - Tg_{ref}
PPE40	Phase α	222	+9	214	+19
	Phase β	173	+11	148	+3
PPE60	Phase α	222	+8	220	+22
	Phase β	174	+7	148	+1

2.3.2 Water Uptake in Filled Formulations

Filled formulations PPE60-A21, PPE60-B21 and PPE60-C21 as coupons were immersed in seawater at 160°C over 3500 h in order to study the influence of pigment addition on water permeation. In order to avoid degradation phenomenon artefacts, soaked samples were weighted at saturation after a short immersion period (1500 h) then desorbed to control the reversibility of mass gain. Aged and desorbed materials were further investigated by dynamic mechanical thermal analysis.

The gravimetric results are given in Table 5. The water-uptake of neat PPE60 is also given after immersion in the same conditions in order to assess that saturation was reached within 1500 h. Formulations are shown to exhibit different mass gain at saturation and after extensive drying, underlying the specific influence of each pigment/filler nature on water-uptake behaviors with respect to neat PPE60. Indeed, formulation A (pure kaolin) lowers the final water-uptake, suggesting improved barrier properties, whereas B (kaolin + MIOX) does not change the water-uptake and C (kaolin + Zn Ph) rather increases it, which could favour corrosion processes. The inspection of the final

weight loss suggests that the water uptake is reversible in PPE60-B21 and PPE60-C21 and that a small amount of pigments had been released out during the experience. Dynamic mechanical analysis was necessary to validate this hypothesis. Desorbed PPE60-A21 exhibits on the contrary an outstanding weight gain after drying, suggesting the presence of residual water molecules sharing strong interactions with kaolin.

TABLE 5

Water uptake (in weight percent) of PPE60, PPE60-A21, PPE60-B21 and PPE60-C21 aged in seawater at 160°C during 1500 hours (gravimetric measurements)

	Gravimetric measurement	
Code name	Soaked samples 1500 h	Desorbed samples 1500 h
PPE60	1.40	+ 0.02
PPE60-A21	1.27	+ 0.29
PPE60-B21	1.40	− 0.24
PPE60-C21	1.97	− 0.30

Viscoelastic behaviors after ageing and drying are shown on Figure 7. Since the ageing period is shorter than for pure resin, the main trends reported previously are observed, namely the increase of both epoxy Tg values, but in a smaller extent. In addition, one should notice that the relaxation peak associated to the epoxy rich phase in PPE60-A21 distinguishes from other epoxy rich Tg peaks by occurring in a lower temperature range. This is attributed to the plasticization effect associated with the residual mass gain observed in "dried" sample after ageing.

2.3.3 Conclusion

Considering both gravimetric and viscoelastic results of PPE40 and PPE60, the water-uptake appears almost reversible at 160°C, which assesses the thermostable character of materials under study in the test conditions aforementioned. In addition, the evolution of the Tg values during service conditions is particularly interesting in view of final application.

In filled formulations, the water-uptake at 160°C appears very sensitive to the presence of the fillers/pigments, and also to their nature. Pigment formulations A and B rather reduce water-uptake, whereas pigment formulation C promotes water entrance, which could impair barrier properties. However, the sensitivity of barrier properties to pigment/filler nature will be discussed elsewhere since further work is in progress to optimise these formulations.

2.4 Adhesion of Thermoplastic/Thermoset Blends on Steel

Adhesion is very important to coating performance. Lap shear tests were performed at room temperature on low carbon steel specimens bonded with adhesive joints of PPE40 and PPE60. The load at failure and the mode of failure (adhesive if breakage occurs between the metal and the adhesive joint, cohesive if breakage occurs within the adhesive joint) are given in Table 6. The failure load measured reached quite high levels and appeared almost not sensitive to the composition. The failure mode was adhesive whatever the composition. In addition, one should note that those results were obtained on sand blasted steel exhibiting an intermediate roughness (R_{ZD} about 30 μm), whereas true pipe steel is prepared with an higher roughness with R_{ZD} typically around 70 μm.
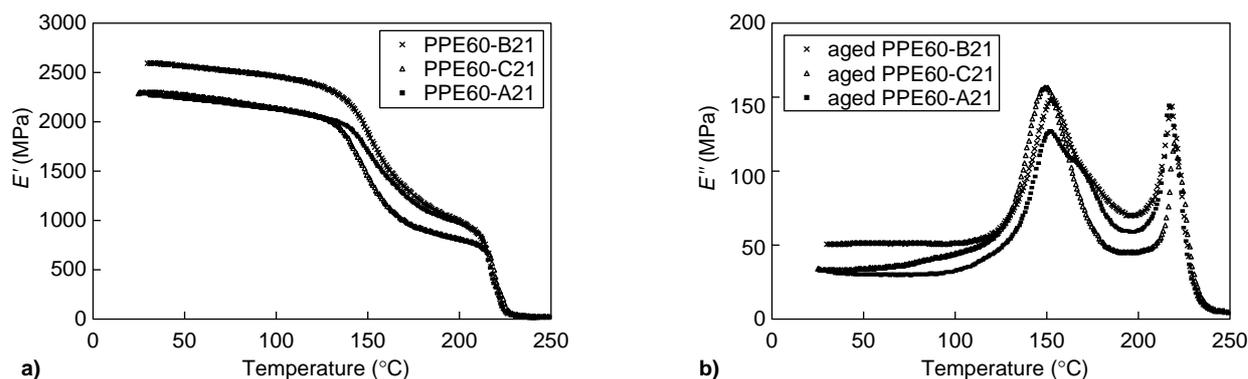

Figure 7

Temperature dependence of a) storage *(E')* and b) loss *(E'')* moduli at frequency 1 Hz for filled PPE60 samples after 3500 h ageing in seawater at 160°C.

TABLE 6

Adhesive properties of PPE40 and PPE60 to low carbon steel
evaluated by lap shear experiments according to ASTM D1002
at room temperature

| Adhesive joint	Load at failure (kN)		Stress at failure (MPa)	Nature of failure (proportion %)
	Mean value	Standard deviation	Mean value	
PPE40	6.5	0.8	20.1	Adhesive (100)
PPE60	7.4	0.5	22.8	Adhesive (100)

2.5 Plasticization Effect of Water on Saturated Materials

The plasticization of polymeric materials in contact with seawater is a key point since it induces a lowering of the *Tg*, which controls the barrier properties of an organic material. Indeed, generalised molecular mobility above glass transition allows ionic mobility through the polymer (it can be external ions that enter the polymer or enclosed ions of the polymer itself). This ionic mobility is a corrosion vector. Below glass transition on the contrary, it has been shown [11] that no significant ionic mobility can be measured through a good organic coating without defect (epoxy-resin film, 100 μm) in contact with an electrolyte. Therefore, an organic coating without defect (epoxy-amine or amorphous thermoplastic) will exhibit good barrier properties in given conditions if glassy.

2.5.1 Impedance Spectroscopy

In the case of our biphasic material, the determination of the *Tg* of the matrix at saturation is crucial since it will determine the upper limit use of those thermoplastic/thermoset coatings. Classical thermal analyses (DSC, DMTA) would not lead to reliable *Tg* measurements, since water diffuses out of the sample during the experiments [12]. IS was used to characterize the dielectric behavior of soaked PPE60 *in situ* versus temperature thank to an original measurement cell and a classical two electrodes set-up. Saturation was achieved by immersion in water at 120°C during one week with respect to the coupon thickness. In order to prevent any postcure phenomenon to proceed during water-uptake, the PPE60 under study are fully cured in this section (4 h 200°C + 2 h 220°C). Therefore, the comparison between dry and soaked material can be interpreted in terms of pure plasticization effect. Figure 8 shows the impedance data of dry and soaked PPE60 at 90°C, 130°C and 170°C. The wet coatings exhibited a capacitance relaxation easy to see on phase shift, which indicated a glass transition phenomenon.

According to [13], the representation of the material impedance modulus taken at low frequency towards
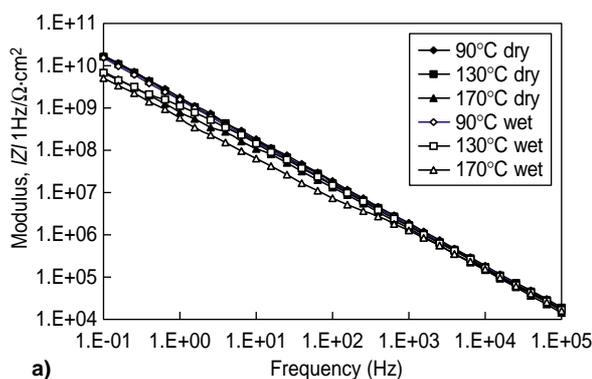
a)
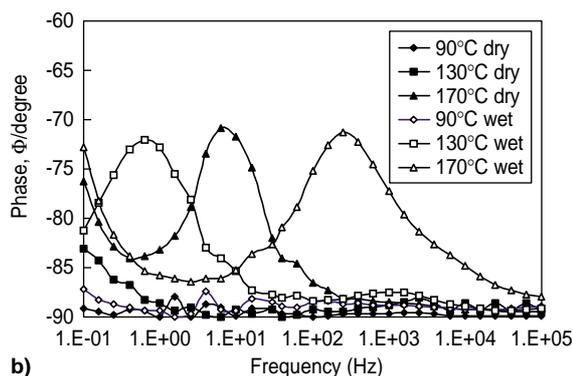
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Figure 8

Bode plot of IS results for dry and soaked PPE60 at various temperatures. a) impedance modulus; b) phase angle.
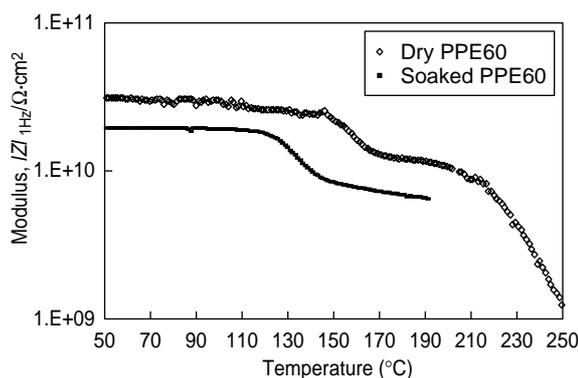
Figure 9

Evolution towards temperature of impedance modulus at 1 Hz in dry and soaked PPE60 cured 4 h at 220°C.

temperature is more convenient to determine *Tg* values, associated to impedance drop as illustrated on Figure 9. Note that IS measurements should be stopped at 185°C for soaked PPE60 due to the upper limit of pressure supported by the experimental set up. The curves associated to soaked PPE60 do not present any manifestation of glass transition in their upper part, suggesting that the matrix Tg remains higher than 185°C at saturation. Thus, the *Tg* shift towards lower temperature due to matrix plasticization is quite small thank to the low water uptake of PPE; this observation is very interesting in terms of barrier properties. On the contrary, the lowering of *Tg* due to epoxy-amine plasticization appears nicely, indicating a drop from 150°C to 125°C at saturation.

2.5.2 Discussion

Besides experimental approach, many theoretical approaches have been conducted to predict the *Tg* value of a polymeric material in presence of plasticizing molecules. In particular, the empirical relationship of Couchma and Karasz [14] is a convenient way to get a first estimation of the *Tg* associated to each phase plasticized by water, assuming that both behave as neat component. The soaked *Tg* of a polymer is calculated by the following Expression (1):

$$Tg_{soaked} = \frac{x_{polymer} \Delta Cp_{polymer} Tg_{polymer} + x_{water} \Delta Cp_{water} Tg_{water}}{x_{polymer} \Delta Cp_{polymer} + x_{water} \Delta Cp_{water}}$$

(1)

where:

- Tg_{soaked}, $Tg_{polymer}$ and Tg_{water} (134 K [12]) correspond to the glass transition temperatures of, respectively, polymer plasticized with water, dried polymer and water;
- $x_{polymer}$ and x_{water} are the mass fraction of, respectively, polymer and water at saturation (from neat components in Table 3);
- $\Delta Cp_{polymer}$ (ΔCp_{resin} = 0.20 J·g^{-1}·K^{-1}; ΔCp_{PPE} = 0.15 J·g^{-1}·K^{-1}) and ΔCp_{water} (1.94 J·g^{-1}·K^{-1} [12]) are the incremental change in specific heat at *Tg* for, respectively, dry polymer and water.

Numerical applications of Expression (1), reported in Table 7 as soaked values for PPE and DGEBA-MCDEA, were calculated on the basis of *Tg* values measured by DMTA, DSC and IS on neat components in the dry state. One should keep in mind that this *Tg* evaluation supposes that extensive phase separation and infinite cure have been achieved. However, the evaluation of Tg_{soaked} can be successfully compared to experimental measurement performed *in situ* by IS. Indeed, Tg_{soaked} evaluated for DGEBA-MCDEA by Relation (1) is in good agreement with the *in situ* IS measurement (125°C). Moreover, Tg_{soaked} for PPE is expected to be higher than 190°C according to *in situ* IS, which is in agreement with the value estimated by Relation (1) as well. This underlines that the *Tg* shift towards lower temperature due to the matrix plasticization in field conditions is less than 25°C thank to the low water uptake of PPE.

2.6 Protecting Performance under Accelerated Ageing Conditions (H$_2$SO$_4$ 1 mol/L, 70°C)

Organic formulated coatings were submitted to accelerated ageing over 8000 h in very aggressive conditions [15] (H$_2$SO$_4$ 1 mol/L, 70°C). Impedance measurements were performed regularly in order to evaluate the coating performance. High coating resistance, corresponding to no significant ionic mobility in the polymer, characterizes a coating with good barrier properties. On the contrary, low coating resistance is associated with high ionic mobility, which favours corrosion. Therefore, the evolution of the coating resistance with time reflects the evolution of its barrier properties, thus its protecting performance.

The protecting performance as the low frequency impedance modulus, $|Z|$, and phase angle, Φ, versus time exposure is given for PPE60-A21 in Figure 10 as example. The phase angle value (close to –90°) and the high impedance modulus remain almost constant over a 300 day immersion period, underlying the effective barrier properties of the coating. Indeed, the occurring of ionic pathways within the coating would induce a suddenly increase of the phase angle

TABLE 7

Tg (°C) of PPE and *Tg* (°C) of DGEBA-MCDEA (cured 2 h at 220°C) measured by DMTA, DSC and IS
for the dry stateand calculated at saturation (Couchman's relation)

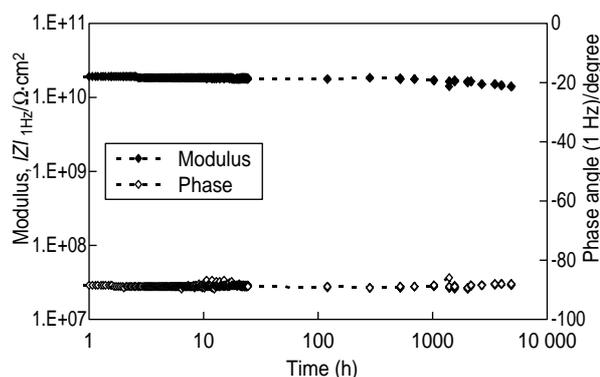| Code name	DMTA		DSC		IS	
	Dry (measure)	Soaked (Couchman)	Dry (measure)	Soaked (Couchman)	Dry (measure)	Soaked (Couchman)
PPE	222	195	210	184	224	198
DGEBA-MCDEA	177	129	160	115	175	128

Figure 10

Time dependence of impedance modulus and phase angle for PPE60-A21 coating exposed to H_2SO_4 1 mol/L at 70°C.

in parallel with an abrupt decrease of the modulus. PPE60-B21 and PPE60-C21 provided similar results, confirming that filled formulations provide effective protection against corrosion over considerable exposure time and show applicability as pipe coating systems.

CONCLUSIONS

New organic coating processes and materials were investigated at *IFP* in order to provide corrosion protection while answering high temperature requirements (120°C-160°C) and exhibiting both durability in aggressive media and impact resistance.

The material processing of high-*Tg* thermoplastic based on reactive extrusion at intermediate temperature range (T < 250°C) is respectful of environmental laws (VOC = 0%). In addition, it offers many advantages as being adaptable to either continuous coating deposit by side extrusion on a rotating pipe or adaptable to powder projection on a preheated pipe. One should note that such process and material could be dedicated to both external coatings (offshore fields, etc.) and internal coatings (geothermal fields, etc.).

Material properties as well as coating performance were inspected, including short and long term lab testing representative of field conditions. Raw materials exhibited good durability over 12 000 h in seawater at 160°C, in spite of their initial under-cured state. Barrier properties of organic coatings were characterized with respect to the formulation composition: the addition of fillers (PVC = 21%) influenced water sorption properties at 160°C and one filler formulation could even slightly reduce the water-uptake at saturation. Adhesion tests carried out at room temperature gave evidence of the outstanding adhesion on low carbon steel of materials under study. Finally, the anticorrosion properties of

formulations under study were assessed under accelerated ageing conditions (exposure to H_2SO_4 1 mol/L, 70°C during several months). The aforementioned results give good confidence in the potential use of filled formulations as pipe coatings in a wide range of applications.

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