Polymer Degradation and Stability 98 (2013) 809–817

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Durability of polydicyclopentadiene under high temperature, high pressure and seawater (offshore oil production conditions)

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ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form
6 December 2012
Accepted 7 December 2012
Available online 2 January 2013

Keywords:
Polydicyclopentadiene
Seawater
Accelerated ageing
Oxidation
Offshore
Field joint

ABSTRACT

In the offshore industry polymer coatings are widely used to ensure thermal insulation of steel pipes, and to avoid over-cooling of the hot oil inside. Because of very severe service conditions (i.e. high temperature, high pressure and presence of seawater) and an expected life time of 20 years, durability of these coatings is a major issue for this industry. Polypropylene and polyurethane are often used for this application, nevertheless these polymers have some limitations in terms of processing time for polypropylene and maximum service temperature for polyurethane. Polycyclopentadiene (pDCPD) shows good processing characteristics and low thermal conductivity, so this polymer could be a good alternative coating in the offshore industry, but the durability of this polymer under offshore conditions is unknown. This paper present results from an accelerated ageing study of pDCPD in seawater at temperatures from 90 °C to 180 °C for 18 months. Polymer evolution during ageing is characterized using both mechanical (tensile test and DMA) and chemical (FTIR, NMR) analyses. For ageing at temperatures below T_g (i.e. 155 °C) the only degradation mechanism is oxidation, whereas for ageing temperatures above T_g secondary polymerization process of the material is observed.

1. Introduction

Global increase in oil demand is extending the economic viability of oil fields to more severe conditions. This is especially true for the deep sea offshore industry where the water depths are increasing with oil increasingly difficult to extract, due to many factors such as oil composition, high temperature or distance from the floating production plant (Floating Production Storage and Offloading). When extracted, oil temperature can be up to 100 °C and has to be transported to the FPSO using steel pipes in seawater at low temperature (basically 4 °C). To ensure extraction it is absolutely mandatory to limit the over-cooling of the oil both to avoid gas hydrate formation and also to increase productivity. A multi-material passive insulation layer is placed between the hot steel pipe and the cold seawater to limit thermal transfer between oil and water (Fig. 1). During installation of a deep offshore field, coated steel pipes are joined together by welding. To ensure the continuity of the insulation along the flow line it is necessary to add an insulation layer over the weld (Fig. 1), this section is known as a Field Joint (FJ). Field joints are complex from a material point of view: First, the material has to be a good thermal insulation polymer. Second, this polymer requires good adhesion to the multi-material layer used on steel pipe, with appropriate mechanical properties. And finally, this material needs a good durability under severe conditions such as high temperature, high pressure and seawater. Currently there are two main solutions for this application, polyurethane is widely used but this polymer has some limitations in terms of durability under this conditions. In fact when PU's are used in hot water they undergoes hydrolysis even if they are based on polyether [1,2]. The second solution is polypropylene which presents better durability but has some process limitations.

DCPD (dicyclopentadiene) liquid engineered formulations designed for reaction injection moulding (RIM) have been commercially available since the end of the 1980s. DCPD is a readily available diolefin monomer found in the off streams of petrochemical refineries. It has been used as a chemical intermediate for both flame retardant and EPDM elastomers. DCPD monomers undergo polymerization via ring opening metathesis polymerization or an ROMP

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0141-3910/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.12.023

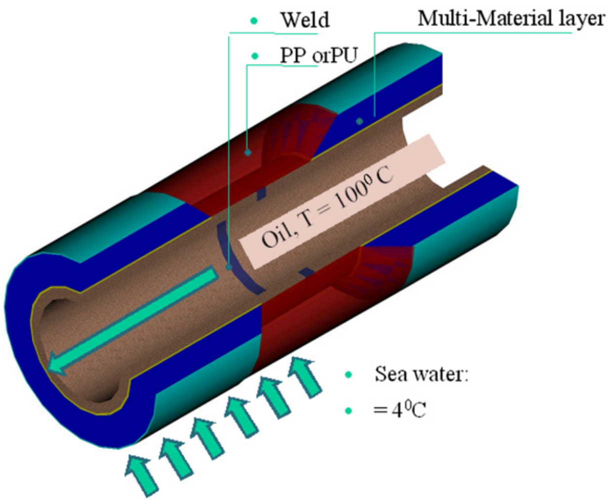

Fig. 1. Schematic representation of a field joint.

reaction, to give a tough, thermoset polymer. Typical commercially available DCPD formulations are formulated in 2 components, A and B. Component A contains DCPD monomer, norbornene based comonomer, cocatalyst and additives. Component B is almost identical to component A, apart from containing an organometallic catalyst instead of the cocatalyst. The catalyst is often a chloride or an ammonium salt of a transition metal such as tungsten or molybdenum. The cocatalyst is usually an alkyl aluminium chloride. The reaction mechanism is based on metathesis chemistry. The reaction starts when catalyst and cocatalyst are combined by mixing A and B components. The active initiator of the reaction is a coordination type catalyst formed by the reaction of the metal compound with the alkyl aluminium chloride. The resulting complex then opens the highly strained norbornene ring. Propagation is by a metathesis mechanism through the norbornene. The reaction mechanism of the DCPD ROMP has been described elsewhere [3]. The less strained cyclopentene ring can also react leading to the cross-linked network [4]. The actual process of polymerization mechanism is a complex process and still not fully understood. The DCPD liquid formulation offers several characteristics that make it suitable to be processed by reaction injection moulding:

- Similar and low viscosity of both components, adjustable gel time allowing the moulding of large and complicated parts.
- Fast curing time, no need for mould release, except for parts presenting mechanical locking possibilities.
- Less sensitivity to stoichiometric ratio control than other RIM polymers.

Typical properties of a non-reinforced pDCPD system are presented in Table 1. Due to its characteristics, it seems that pDCPD exhibits potential for the field joint application, but the question of the durability of this polymer in an offshore environment has to be assessed.

Table 1
Main properties of the pDCPD used in this study.

Properties	Value
T_g	155 °C
Tensile modulus	1.8 GPa
Elongation at yield	5%
Thermal conductivity	0.17 W/m K

When immersed in seawater, a polymer absorbs water due to the difference in water concentration between the material and the external medium. In the case of Fickian behaviour, the water diffusion in a polymer can be defined by the kinetics of diffusion (i.e. the water diffusion coefficient) and the content at saturation (i.e. solubility of water in the polymer) [5,6]. The presence of water will plasticize the polymer, this leads to a decrease of the T_g [6,7] but also a decrease of the material stiffness [8,9]. At the same time, large absorption of water in a polymer will increase the thermal conductivity significantly [10], and thus decrease the thermal insulation properties of the coating in service. Due to temperature gradients in the insulation layer, it is necessary to assess water absorption at different temperatures to be able to predict the water content in the coating as a function of time. Water may also cause irreversible damage in polymers due to hydrolysis, especially at high temperature [11–16], this point has to be addressed to evaluate the durability of this polymer under offshore conditions.

The aim of this study is to evaluate the durability of pDCPD for field joints in deep offshore applications. Because the service life required is 20 years, it is mandatory to performed accelerated ageing tests. Accelerated ageing was performed on polydicyclopentadiene in natural renewed seawater at temperatures from 90 °C to 180 °C under hydrostatic pressure for durations up to 18 months. The evolutions of chemical and mechanical properties have been investigated in order to assess the ageing mechanisms and consequences. Using these results it is possible to evaluate the durability of this polymer for field joint applications.

2. Methods

2.1. Material

The DCPD formulations consist of a stable two component's system :

- Component A comprises DCPD monomer and norbornene based co-monomers, co-catalyst and additives.
- Component B is more than 99% identical to component A apart from containing an organo-metallic catalyst instead of the co-catalyst.

The samples used in this study have been produced from Telene 1650 formulation by reaction injection moulding process (RIM) on a Cannon A40 RIM injection unit at 100 bars in the FPL 10 Mixhead with a 1 to 1 ratio. Raw material was injected at 25 °C in an aluminium alloy mould at 75 °C. The catalyst of the metathesis polymerization is a molybdenum base salt and the cocatalyst is diethyl aluminium chloride. Some elastomers (EPDM about 3%) are also included in the formulation in order to improve mouldability and flexibility of the formulation. The actual structure of the polymer is complex and represented in Fig. 2, overall cross-link density of this material is 0.7 mol kg^{-1}. This polymer does not have any ductile/brittle transition when tested at low temperature.

2.2. Accelerated ageing

Accelerated ageing was performed in natural renewed seawater at 5 different temperatures from 90 °C to 180 °C for up to 18 months. Accelerating factors are both temperature and water accessibility. In fact during these ageing tests, polymer is directly in contact with hot seawater whereas in service water has to diffuse from the cold external surface to the inside of the coating. For temperatures above 90 °C, ageing was also performed under