Science Arts & Métiers (SAM)

is an open access repository that collects the work of Arts et Métiers Institute of Technology researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: https://sam.ensam.eu
Handle ID: .http://hdl.handle.net/10985/19199

To cite this version :

Jing HUANG, Isabelle DERUE, Pierre YVES LE GAC, Emmanuel RICHAUD - Thermal oxidation of polydicyclopentadiene - Changes in water absorption - Polymer Degradation and Stability - Vol. 180, p.1-7 - 2020

Any correspondence concerning this service should be sent to the repository Administrator : scienceouverte@ensam.eu

Arts et Métiers Institute of Technology

Thermal oxidation of polydicyclopentadiene - Changes in water absorption

Jing Huang [a], Isabelle Derue [a], Pierre Yves Le Gac [b], Emmanuel Richaud [a, *]

[a] Laboratoire PIMM, Arts et Metiers Institute of Technology, CNRS, CNAM, HESAM Université, F-75013, Paris, France
[b] IFREMER, Service Matériaux et Structures, Centre de Brest BP70, 29280, Plouzané, France

A B S T R A C T

This paper describes water absorption in polydicyclopentadiene (PDCPD) and more specially the impact of thermal oxidation on its behavior. Unaged PDCPD is found to be almost hydrophobic consistently with its non-polar structure. During thermal oxidation, hydrophilicity progressively increases with ageing time. This increase is linked with the buildup of polar products (mainly ketones, carboxylic acids, hydroperoxides, alcohols). Moreover, it appears that water absorption in PDCPD obeys to Flory Huggins law for all conditions considered here. In the meantime, water diffusivity seems to decrease when oxidation level increases. Finally, a mastercurve that links carbonyl concentration, water diffusivity and water-polymer interaction parameter is proposed and allows changes of water resistance of PDCPD to be predicted.

Keywords:
Polydicycopentadiene
Water absorption
Thermal oxidation

1. Introduction

Polydicyclopentadiene (PDCPD) is a promising alternative for designing many large polymeric parts with the advantage of short processing time. The metathesis polymerization mechanisms are documented elsewhere: to summarize, stressed alkene rings are opened in presence of metallic catalysts, leading to an unsaturated glassy network with a relatively "high" concentration in metallic catalysts. Those characteristics were shown to induce a low thermal oxidative stability [1,2]. However, oxidized layer is significantly lower than for many other thermosets (from less than 20 μm at 150 °C [1] to 100 μm at 100 °C [3] vs 100 μm–200 μm in the same conditions for epoxies [4]) which makes PDCPD suitable for manufacturing truck body panels, pipes resistant to chlorinated, acidic or basic media. In many service conditions, PDCPD is not only subjected to thermal ageing but also possibly to humid environment [5–7]. Its non-polar structure is expected to guarantee an excellent resistance to water [6,7]. However, many recent results illustrate that thermal oxidation has a large effect on water properties of polymers, for example in EPDM [8] or in epoxies [9] where water uptake curve display a positive slope at long exposure times which is attributed to the "slow" oxidation generating polar species with greater water affinity. In the case of epoxies, a model was proposed to describe mass changes in the case of water + thermal ageing but a complex coupling phenomena was highlighted and possibly ascribed to the blocking effect of oxygen on water solubility [10].

The aim of this study is to investigate the water transport properties in virgin and oxidized PDCPD (in particular the maximum concentration of absorbed water and its diffusion coefficient). Firstly, results obtained by Dynamic Vapor Sorption (DVS) for unaged and oxidized PDCPD will be presented. The existing knowledge on the polymer-water interaction mechanisms will be briefly recalled and discussed in the case of PDCPD. Based on the mechanism chosen, the exploitation of experimental results will lead to diffusion coefficient and interaction parameters. Finally, a relationship between water uptake and polar groups concentration within the polymer will be proposed.

2. Materials and methods

2.1. Materials

The samples under investigation were supplied as stabilized bulk material prepared by reaction injection molding process (RIM) at about 40 °C. Films of 6–15 μm thickness were obtained by cutting the bulk material with a microtome (RM 2255 Leica), and then theses ones were purified by refluxing in CH_2Cl_2 (270997 Sigma-

* Corresponding author.
E-mail address: emmanuel.richaud@ensam.eu (E. Richaud).

Table 1
Concentration of polar groups during ageing.

Temperature (°C)	70	70	70	50	50	50	25
Ageing time (h)	2	2.67	3.33	9	12	15	100
Water volume ratio f_w at a = 0.9	0.04	0.043	0.051	0..037	0.052	0.070	0.075
[OH] (mol l^{-1})	2.86	3.74	4.24	3.99	5.14	5.63	3.54
[C=O] (mol l^{-1})	0.85	1.27	1.52	1.191	1.68	1.94	1.76
[hydroperoxides] (mol l^{-1})	0.97	1.20	1.1	1.4	1.55	1.59	1.5
[carboxylic acids] (mol l^{-1})	0.23	0.39	0.49	0.35	0.54	0.64	0.60
[alcohols]+[hydroperoxides] (mol l^{-1})	2.63	3.35	3.74	3.64	4.60	5	2.94
[ketones] (mol l^{-1})	0.61	0.88	1.03	0.84	1.14	1.30	1.16

Aldrich) overnight. Unstabilized samples were stored in fridge (−20 °C) for maximum 7 days before ageing.

2.2. Ageing

Samples were firstly aged at 50 °C and 70 °C in ventilated ovens (supplied by System Climatic Service). Ageing at 25 °C was performed in a temperature controlled room.

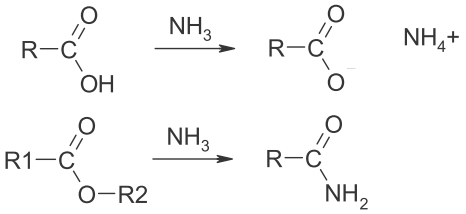
2.3. Characterization

2.3.1. FTIR

Samples were characterized by Fourier Transform InfraRed spectroscopy using a Frontier apparatus (PerkinElmer). The analyzes were conducted in a spectral range from 400 to 4000 cm^{-1} by averaging 4 scans and at a 4 cm^{-1} resolution. Spectra were then analyzed with Spectrum software. In particular, we focused on the carbonyl (1850-1650 cm^{-1}) and hydroxyl absorbances (3600-3100 cm^{-1}) which were converted into concentration using Bert lambert law using respectively 300 and 70 l mol^{-1} cm^{-1} as molar absorptivities [2].

2.3.2. NH_3 treatment

Oxidized samples were subjected to ammonia treatment so as to distinguish carbonyl compounds. Carboxylic acids and esters can be tracked back from changes in FTIR spectra since both species react with ammonia according to the following reaction [11]:



Gaseous ammonia was generated from an equimolar solution of NH_4Cl (ref A9434 from Sigma Aldrich - 13 g) and NaOH (ref CL00.1403.1000 from ChemLab - 10 g) in 40 ml of water. Differences in FTIR spectra were recorded after 24 h of treatment, this duration being chosen long enough so as to not observe changes in FTIR spectra anymore.

2.3.3. Dynamic vapor sorption (DVS)

The water absorption was measured in air at 0.1 MPa with fixed water partial pressures in a dynamic vapor sorption apparatus DVS-1000 (Surface Measurement Systems). The additive-free PDCPD thin samples were thermally aged at 25 °C, 50 °C and 70 °C during various exposure times. About 1.5 mg of virgin and aged samples were tested under varying water humidity (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90%) with 150 min steps at each humidity level. Mass changes in samples are continuously recorded, which makes possible to directly obtain the sorption and desorption curves.

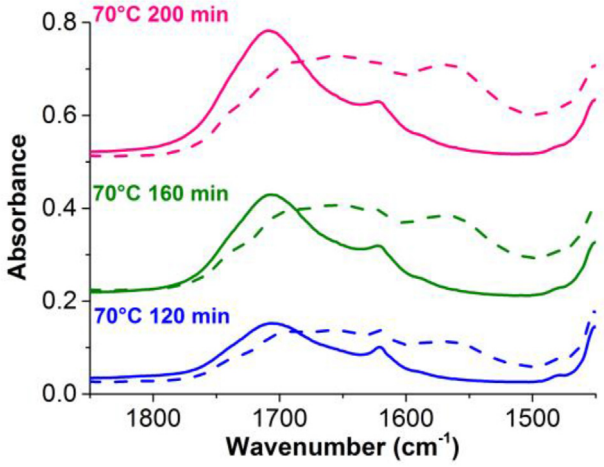


Fig. 1. Effect of NH_3 treatment (full lines: before, dashed lines: after) for PDCPD exposed at 70 °C under air.

3. Results

3.1. Chemical characterization of aged samples

Samples were thermally oxidized at several temperatures (25 °C, 50 °C and 70 °C). Ageing leads to the formation of carbonyl species involving the appearance of a broad absorption in FTIR spectroscopy with a maximum centered at 1710 cm^{-1}(Fig. 1). It is due to several species among which ketones, aldehydes and carboxylic acids. NH_3 treatments allowed the detection of carboxylic acids for each ageing temperature under investigation, in line with previous results suggesting that their formation is favored by the low mobility in glassy state favoring initiation reaction (likely to generate aldehydes and later carboxylic acids) compared to ketones (generated from termination steps) [2].

From a quantitative point of view, it can be stated that:

$$[OH] = [\text{alcohols}] + [\text{hydroperoxides}] + [\text{carboxylic acids}] \quad \text{Eq. 1}$$

$$[P{=}O] = [\text{ketones}] + [\text{carboxylic acids}] \quad \text{Eq. 2}$$

The concentration of carboxylic acids can be calculated by the difference of absorbance before and after NH_3 treatment. Using $\varepsilon_{\text{carboxylic acids}} = 660$ l mol^{-1} s^{-1} [12], $\varepsilon_{\text{ketones}} = 200$ l mol^{-1} s^{-1} [13] and $\varepsilon_{CO} = 300$ l mol^{-1} cm^{-1} as a mean value (as done in [2,14]) it can be seen that carboxylic acids represent almost 1/3 of overall carbonyl species. Using hydroperoxides concentrations measured

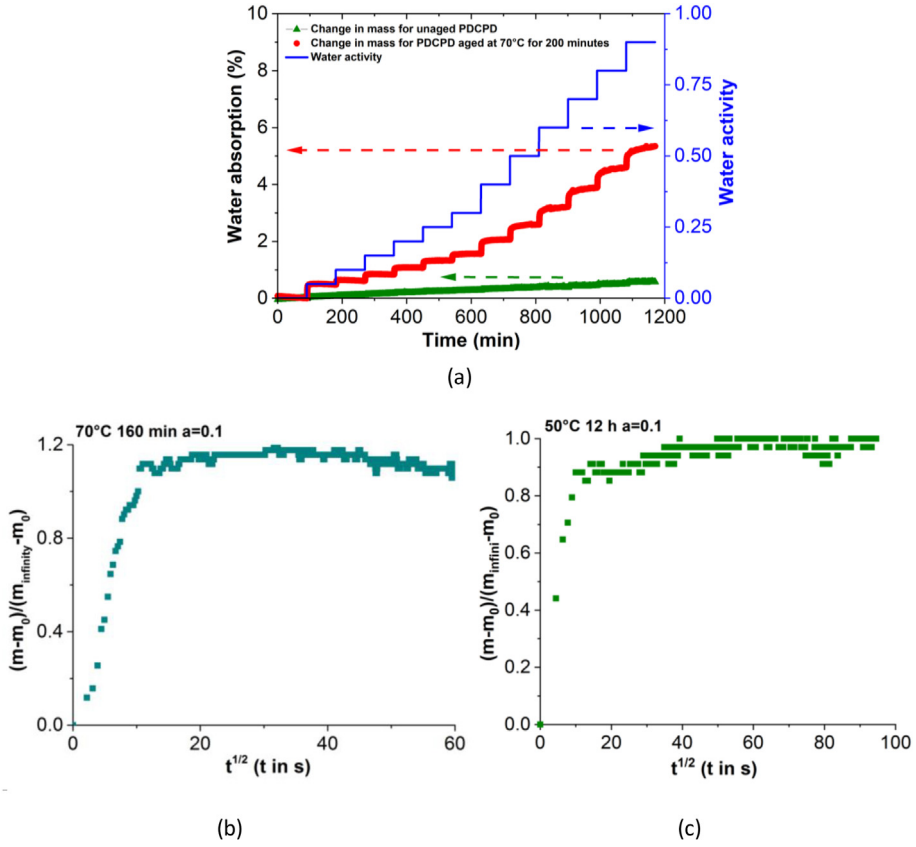


Fig. 2. Sorption isotherms recorded at 70 °C for unaged and aged PDCPD (70 °C - 160 min) (a) and zoom on the reduced water uptake in the early absorption times (b, c).

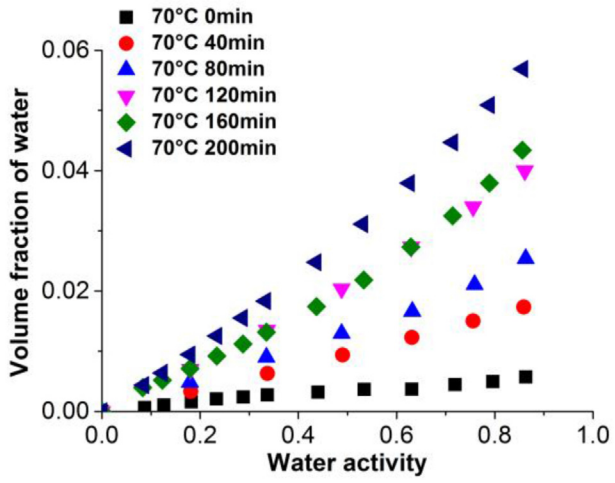


Fig. 3. Sorption isotherms recorded at 70 °C for PDCPD with various oxidation times at 70 °C.

in [14], a possible repartition of oxygenated species is proposed in Table 1.

3.2. DVS study of water absorption in virgin and oxidized PDCPD

Fig. 2a shows a typical sorption isotherm (water mass uptake vs water activity in environment) for unaged PDCPD . It clearly confirms that maximal water uptake in the unaged material is very low (typically below 0.3%) consistently with its non-polar structure [5–7]. For oxidized PCPCD (160 min at 70 °C in air), a different behavior is observed:

- maximal water absorption gets higher than 3% at high water activities,
- at short exposure times, the water uptake seems to linearly increase with square root of time (Fig. 2b and c) which will be discussed in terms of diffusion mechanism.

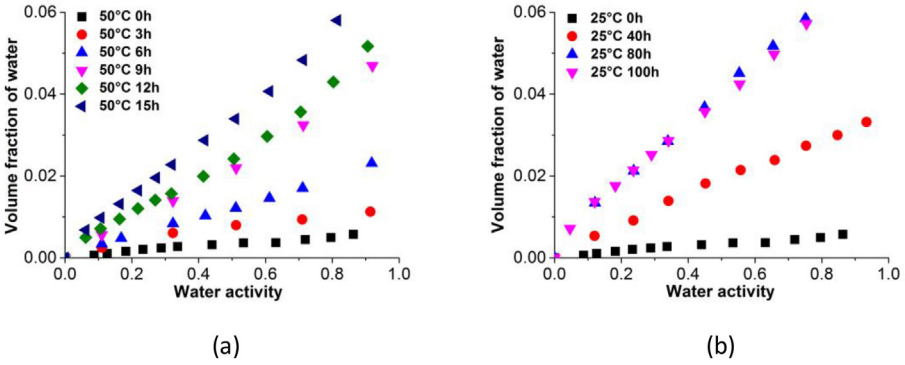
Thin films of oxidized PDCPD with various exposure times (at 70 °C) were tested in DVS at 70 °C. Corresponding sorption isotherms show that the water uptake of PDCPD largely increases with polymer oxidation level (Fig. 3). For example at a 0.8 water activity, water uptake is almost 9 times higher for the oxidized sample (200 min at 70 °C) than for the unaged one, which seems linked to the increase of the concentration in oxygenated species (Table 1).

For virgin PDCPD, sorption isotherm appears almost linear. This feature remains almost true for aged PDCPD at low water activity but a positive curvature seems to appear in the domain where water activities is typically higher than 0.5, indicating some changes in the polymer-water interaction mechanism.

Oxidation of PDCPD was also performed at 50 °C and 25 °C to check the temperature dependence of our results. The sorption isotherms (recorded at the same temperature than the temperature of oven ageing) are presented in Fig. 4 and confirm the increase in water uptake with oxidation time whatever the temperature of oxidation.

4. Discussion

The main aims of this section are:



(a) (b)

Fig. 4. Water sorption isotherms for PDCPD tested at 50 °C with different oxidation times at 50 °C (a) and at 25 °C (b).

Table 2
Mean cluster size for PDCPD tested at 70 °C for different oxidation times at 70 °C in oven.

Ageing time (h)	unaged	0.67	1.33	2	1.33	3.33
MCS at 0.9 activity	1.8	1.4	1.5	1.6	1.6	1.7

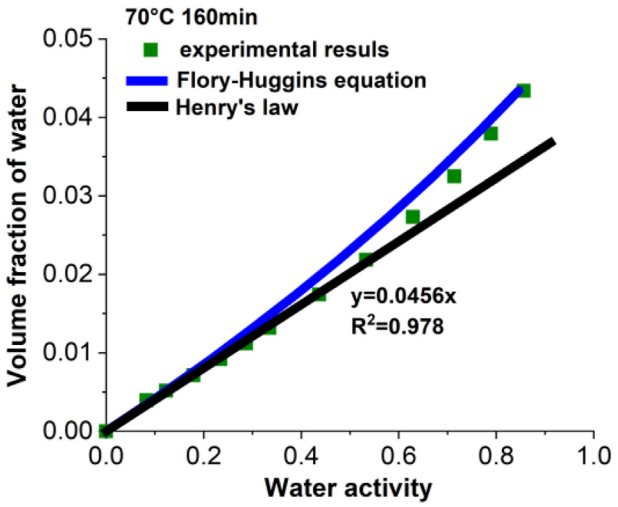


Fig. 5. Determination of Flory-Huggins parameters for PDCPD samples aged 160 min at 70 °C. Solid line: Simulation by Flory-Huggins equation.

- to discuss on the possible mechanism of water sorption in virgin and oxidized PDCPD,
- to propose a relationship between oxidation level and water affinity,
- to discuss on the possible water diffusion mechanism in PDCPD and the changes of diffusivity with oxidation level.

4.1. Water sorption in PDCPD

To our knowledge, there are three main mechanisms describing interaction between water and a polymer [15]:

① Water sorption isotherm is linear at every water activity. The water absorption obeys here to Henry's law (Equation (3)):

$$V = H.a \quad \text{Eq. 3}$$

where v is the volume fraction of water, H is Henry's coefficient and a is the water activity (i.e. partial pressure).

It seems here that Henry's law does not describe experimental results for oxidized samples and in particular the positive concavity in the domain of high water activities. Other mechanisms of polymer-water interaction must be investigated here.

② Water sorption isotherm can be described by the sum of Henry's law at low water activity and a supplementary contribution due to clusters at high water activity [16]:

$$V = a.H + B.a^n \quad \text{Eq. 4}$$

where B and n can be determined from experimental results.

The slight positive curvature in the DVS sorption isotherms (Fig. 4a) could be due to presence of water clusters (i.e. associated water molecules groups) in the oxidized PDCPD. This would mean that water-water interactions are stronger than interactions between polymer and water. In order to verify this assumption, the clustering function was calculated by the Zimm-Lundberg method [17,18]:

$$f_{ZL} = -(1 - v)\left[\frac{\partial a/v}{\partial a}\right]_{T,P} - 1 \quad \text{Eq. 5}$$

Clusters occur when $f_{ZL} > -1$ and the mean cluster size (MCS) is given by:

$$MCS = 1 + \upsilon.f_{ZL} \quad \text{Eq. 6}$$

The mean cluster size (MCS) at water activity equal to 0.9 was calculated for several aged samples (Table 2). It must be recalled that MCS = 1 represents an isolated water molecule whereas MCS = 2 represents a cluster made of two water molecules [19]. MCS always ranges from 1.4 to 1.8, which suggests that there is almost no water clusters (NB: values for example higher than 7 are for example reported in oxidized polychloroprene [20]).

Water absorption obeys Flory-Huggins law which actually describes linear increase of water sorption isotherm at low water activity and a positive concavity at high water activity:

$$\ln a = \ln v + (1 - v) + \chi(1 - v)^2 \quad \text{Eq. 7}$$

where χ is the polymer-water interaction defined by the following expression:

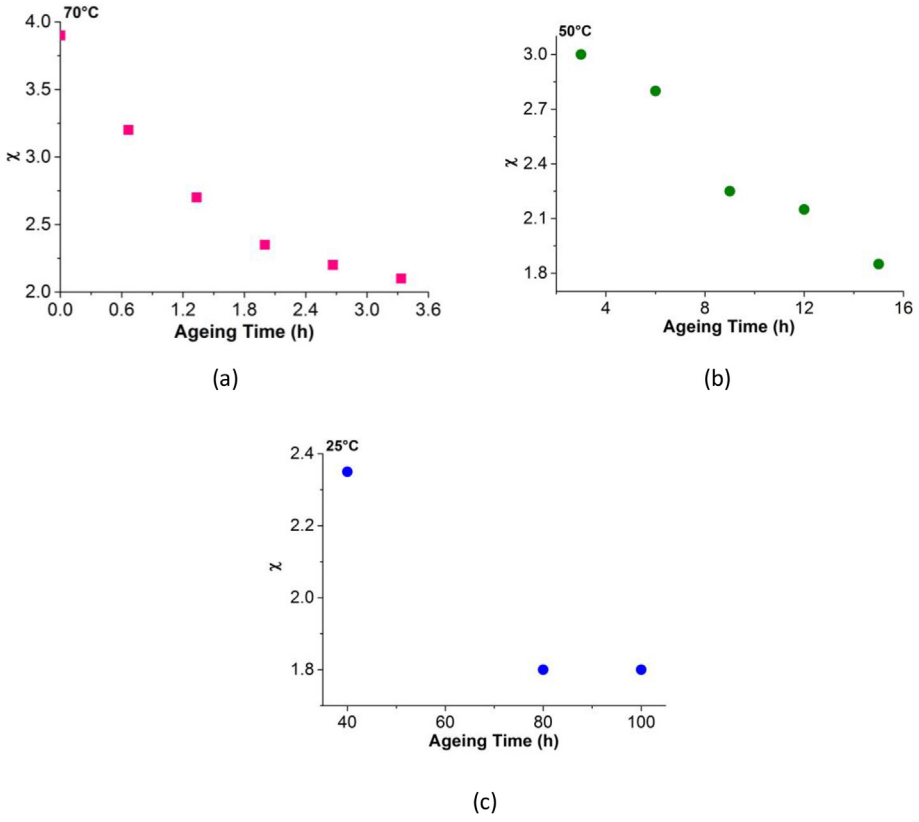


Fig. 6. Changes in interaction parameters with oxidation time for samples aged at 70 °C (a), 50 °C (b) 25 °C (c).

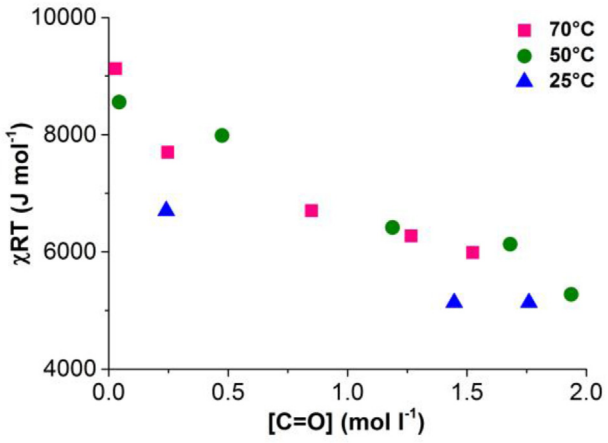


Fig. 7. Changes on interaction parameters as a function of carbonyls concentration.

$$\chi = \frac{V_m}{RT} \times \left(\delta_{polymer} - \delta_{water}\right)^2 \quad \text{Eq. 8}$$

where $\delta_{polymer}$ and δ_{water} are respectively the solubility parameters of polymer and water, V_m is the molar volume of water (18 $cm^3\ mol^{-1}$), R the gas constant and T the temperature. δ_{water} is close to 48 $MPa^{1/2}$ [21] and δ_{PDCPD} would be about 17 ± 1 $MPa^{1/2}$ consistently with other non-polar polymers [22]. Fig. 5 shows an example of experimental results obtained after 160 min of oxidation at 70 °C compared with the Flory-Huggins equation curve fitting, which illustrates that that water content in the polymer can be described by Flory-Huggins equation. For unaged PDCPD, χ value would be about 4.0, which is on the same order (but a little bit lower) than the estimation from Eq. (8). It can hence be concluded that Flory Hugging model can be used in a first approach for describing the water sorption in PDCPD.

Sorption isotherms were thus fitted using Flory-Huggins equation to assess the possible PDCPD-water interaction parameters. These latter are given in Fig. 6 showing that the interaction parameters decrease with ageing time. Thermal oxidation of PDCPD actually leads to the formation of oxidation products with polar groups (hydroxyls, carbonyls) increasing the solubility parameter of polymer thus decreasing interaction parameters. The more polar groups are generated, the smaller the value of the interaction parameter and the higher the affinity with water are.

4.2. Relationship between oxidation level and maximal water uptake

Based on results obtained after ageing at 25 °C, 50 °C and 70 °C, it is thus possible to relate Flory-Huggins interaction parameter with the carbonyl C=O content in the material (Fig. 7). The χ.RT parameter expressing the polarity difference between water and polymer (Eq. (8)) decreases with the carbonyl concentration (Fig. 7). It is possible to establish a mastercurve that link the water content in this material as a function of the oxidation level exists for all temperatures and ageing time considered here.

Using Eqs (1) and (2), the concentrations in oxygenated species was approximated so that a relationship between water volume fraction (for 0.9 water activity) and concentration of polar groups is proposed:

$$f_w = a.[\text{carboxylic acids}] + b.([\text{alcohols}] + [\text{hydroperoxides}]) + c.[\text{ketones}] \quad \text{Eq. 9}$$

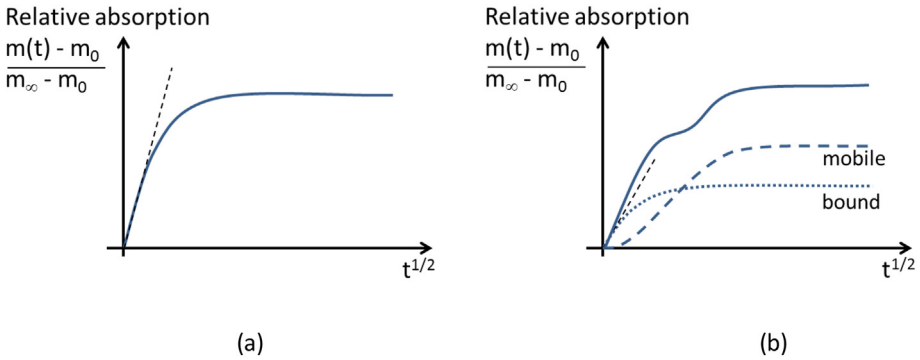


Fig. 8. Water diffusion obeying Fick's law (a); Water diffusion appearing Langmuir mechanism (b) with schematic diagram of changes of mobile and bound water according to Popineau et al. [23].

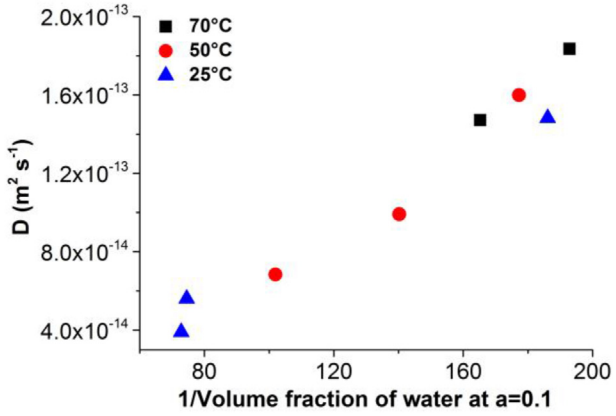


Fig. 9. The diffusion coefficient for 0.1 activity as a function of reciprocal of water volume fraction.

with for example a = 0.0889, b = 0.0028 and c = 0.001. Some other sets with slightly different parameters values could fit as well but all have in common that carboxylic acids are by far the main contributing species to the observed increase in water affinity.

4.3. On the mechanism of water diffusion

Based on DVS results, it is also possible to focus on water diffusion mechanisms. It is often considered that diffusion in polymers is given by Fick's diffusion (Fig. 8a). It is typical of diffusion of molecules at low concentration with weak or without interaction with polymer. In the case of Fickian diffusion, the equation for water transport is:

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial x^2} \qquad \text{Eq. 10}$$

where c is the concentration of water absorbed at time t at depth x and D is the diffusion coefficient in the polymer matrix.

Fick's law is characterized by a linear increase in water concentration as a function of the square root of time, and a plateau at long exposure time. The diffusion coefficient can be determined from the slope (Fig. 8):

$$D = \frac{\pi}{16}e^2 \times slope \qquad \text{Eq 11}$$

where e is the thickness of sample. Diffusivity would depend on free volume [24], polymer structure, testing temperature …. It seems clear here that D decreases with oxidation, in link with the appearance of crosslinking and possibly free volume decrease. But this hypothesis remains to be validated in the future.

Another explanation can be proposed from Carter and Kibler [25] who developed the so-called Langmuir-type model taking into account the presence of sites generating strong interactions of penetrant with the hosting polymer (Fig. 8b). Their model involves bound and mobile water, which corresponds well to the water diffusion behavior in a polymer with polar groups (e.g. epoxy resins [26], oxidized PEI and PEEK [27]) favoring polymer-water interaction. The existence of those two types of water was confirmed by NMR experiments [28]. In this second diffusion mode, two plateaus are expected even if Gilormini and Verdu [29] showed that many cases of "Langmuir" and "Fick" diffusion are hardly distinguishable. The principle of diffusion of bound water could be schematized by the following steps [30]:

(1) $[P1 \cdots W] \rightarrow P1 + W$
(2) $W \rightarrow \ldots$
(3) $W + P2 \rightarrow [P2 \cdots W]$

The initial slope of mass uptake curves (Fig. 8) is here related to the bound water diffusivity according to Eq. (12). Assessed diffusivity values were versus reciprocal of water volume fraction. There is a clear inverse correlation between diffusivity and the water volume fraction (Fig. 9). This trend can be explained as follows: the appearance of polar species increases water solubility in polymer, but water becomes more and more bonded with polymer oxidation products so that its diffusivity decreases during oxidation.

5. Conclusions

This paper deals with the water sorption behavior of virgin and aged PDCPD. According to DVS results, unaged PDCPD presents low water absorption level whereas higher water uptakes are observed for thermally oxidized samples. The study of water absorption mechanism showed that water sorption isotherm could not be described by Henry's law, and the mean cluster size is low enough to be neglected whatever the water activity. Results were thus described by the Flory-Huggins equation. The diffusion kinetics can be described by Langmuir-type model involving bound water and mobile water. The changes of these properties (volume fraction of water, interaction parameter and water diffusion coefficient) are closely related to polar groups (hydroxyls and carbonyls) created during thermal oxidation of PDCPD. The interaction parameter χ was shown to decrease i.e. the water uptake at low water activity is shown to increase and the maximal water uptake (i.e. in the case of

immersion in water) also increase with the carbonyl concentration (and especially the contribution of carboxylic acids). The clear existence of a positive concavity in sorption isotherms makes the oxidation effect are more pronounced at high water activity than at low ones which is crucial for under water applications [5]. If the effect of water on oxidation mechanism could be investigated (it is for example reported that water accelerates the decomposition of peroxides [31]), it seems that a kinetic model predicting the oxidation rate in PDCPD [2,14] will make possible to predict the change in water absorption in service conditions. It remains in particular to address the effect of water uptake on mechanical properties of aged PDCPD.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jing Huang: Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **Isabelle Derue:** Data curation, Methodology. **Pierre Yves Le Gac:** Conceptualization, Methodology, Supervision, Validation, Writing - original draft. **Emmanuel Richaud:** Conceptualization, Formal analysis, Methodology, Project administration, Supervision, Validation, Writing - original draft, Writing - review & editing.

Acknowledgements

Agence Nationale de la Recherche is gratefully acknowledged for having funded this study (Project VRPOM – Vieillissement des Réseaux Polymérisés par Métathèse – 2016-2019).

References

[1] V. Defauchy, P.Y. Le Gac, A. Guinault, J. Verdu, G. Recher, R. Drozdzak, E. Richaud, Kinetic analysis of polydicyclopentadiene oxidation, Polym. Degrad. Stabil. 142 (2017) 169–177.
[2] E. Richaud, P.Y. Le Gac, J. Verdu, Thermooxidative aging of polydicyclopentadiene in glassy state, Polym. Degrad. Stabil. 102 (2014) 95–104.
[3] Y. Hu, Y. Zhang, S. Nutt, Thermal oxidation aging of polydicyclopentadiene and composites, Polym. Compos. 39 (2018) 1742–1751.
[4] A. Quintana, M.C. Celina, Overview of DLO modeling and approaches to predict heterogeneous oxidative polymer degradation, Polym. Degrad. Stabil. 149 (2018) 173–191.
[5] P.Y. Le Gac, D. Choqueuse, M. Paris, G. Recher, C. Zimmer, D. Melot, Durability of polydicyclopentadiene under high temperature, high pressure and seawater (offshore oil production conditions), Polym. Degrad. Stabil. 98 (2013) 809–817.
[6] Y. Hu, A.W. Lang, X. Li, S.R. Nutt, Hygrothermal aging effects on fatigue of glass fiber/polydicyclopentadiene composites, Polym. Degrad. Stabil. 110 (2014) 464–472.
[7] Y. Hu, X. Li, A.W. Lang, Y. Zhang, S.R. Nutt, Water immersion aging of polydicyclopentadiene resin and glass fiber composites, Polym. Degrad. Stabil. 124 (2016) 35–42.
[8] M. Lacuve, Etude de la diffusion de l'eau dans les jonctions HTA, Thèse Arts et Métiers ParisTech, 2019.
[9] A. Simar, M. Gigliotti, J.C. Grandidier, I. Ammar-Khodja, Evidence of thermo-oxidation phenomena occurring during hygrothermal aging of thermosetting resins for RTM composite applications, Compos. Appl. Sci. Manuf. 66 (2014) 175–182.
[10] A. Simar, M. Gigliotti, J.C. Grandidier, I. Ammar-Khodja, Decoupling of water and oxygen diffusion phenomena in order to prove the occurrence of thermo-oxidation during hygrothermal aging of thermosetting resins for RTM composite applications, J. Mater. Sci. 53 (2018) 11855–11872.
[11] C. Wilhelm, J.-L. Gardette, Infrared identification of carboxylic acids formed in polymer photooxidation, J. Appl. Polym. Sci. 51 (1994) 1411–1420.
[12] F.M. Rugg, J.J. Smith, R.C. Bacon, Infrared spectrophotometric studies on polyethylene. II. Oxidation, J. Polymer Sci. 13 (1954) 535–547.
[13] J. Heacok, Determination of carboxyl groups in the presence of carbonyl groups in oxidized polyolefins by using sulfur tetrafluoride, J. Appl. Polym. Sci. 7 (1963) 2319–2322.
[14] J. Huang, A. David, P.-Y. Le Gac, C. Lorthioir, C. Coelho, E. Richaud, Thermal oxidation of poly(dicyclopentadiene)– kinetic modeling of double bond consumption, Polym. Degrad. Stabil. 166 (2019) 258–271.
[15] J.A. Barrie, in: J. Crank, G.S. Park (Eds.), Diffusion in Polymer, Academic Press, London, 1968 chap 8 p.p. 260.
[16] M. Lacuve, X. Colin, L. Perrin, L. Flandin, P. Notingher, C. Tourcher, M. Ben Hassine, H. Tanzeghti, Investigation and modelling of the water transport properties in unfilled EPDM elastomers, Polym. Degrad. Stabil. 168 (2019) 108949.
[17] B.H. Zimm, J.L. Lundberg, Sorption of vapors by high polymers, J. Phys. Chem. 60 (1966) 425–428.
[18] J. Lundberg, Clustering theory and vapor sorption by high polymers, J. Macromol. Sci. Part B: Physics 3 (1969) 693–710.
[19] E.M. Davis, Y.A. Elabd, Water clustering in glassy polymers, J. Phys. Chem. B117 (2013) 10629–10640.
[20] P.Y. Le Gac, G. Roux, P. Davies, B. Fayolle, J. Verdu. Water clustering in polychloroprene, Polymer 55 (2014) 2861–2866.
[21] J. Karl Fink, Reactive polymers: fundamentals and applications (third edition) A concise guide to industrial polymers plastics design library, React. Polym.: Fundamental App. (2018) 403–415. Chap 12 - Terpene Resins.
[22] D.W. Van Krevelen, K. Te Nijenhuis, in: D.W. Van Krevelen, K. Te Nijenhuis (Eds.), Chapter 7 - Cohesive Properties and Solubility," in Properties of Polymers, fourth ed., Elsevier, Amsterdam, 2009, pp. 189–227.
[23] S. Popineau, C. Rondeau-Mouro, C. Sulpice-Gaillet, M.E. Shanahan, Free/bound water absorption in an epoxy adhesive, Polymer (2005) 10733–10740.
[24] M. Jackson, M. Kaushik, S. Nazarenko, S. Ward, R. Maskell, J. Wiggins. Effect of free volume hole-size on fluid ingress of glassy epoxy networks, Polymer 52 (2011) 4528–4535.
[25] H.G. Carter, K.G. Kibler, Langmuir-type model for anomalous moisture diffusion in composite resins, J. Compos. Mater. 12 (1978) 118–131.
[26] A. Tcharkhtchi, P. Bronnec, J. Verdu, Water absorption characteristics of diglycidylether of butane diol–3, 5-diethyl-2, 4-diaminotoluene networks, Polymer 41 (2000) 5777–5785.
[27] E. Courvoisier, Analyse et modélisation cinétique du vieillissement thermique des matrices PEI et PEEK et ses conséquences sur l'absorption d'eau, Ecole nationale supérieure d'arts et métiers - ENSAM, 2017.
[28] S. Popineau, C. Rondeau-Mouro, C. Sulpice-Gaillet, M.E. Shanahan, Free/bound water absorption in an epoxy adhesive, Polymer 46 (2005) 10733–10740.
[29] P. Gilormini, J. Verdu, On the role of hydrogen bonding on water absorption in polymers, Polymer 142 (2018) 164–169.
[30] I. Merdas, F. Thominette, A. Tcharkhtchi, J. Verdu, Factors governing water absorption by composite matrices Composites, Sci. Technol. 62 (2002) 487–492.
[31] J.L. Henry, A.L. Ruaya, A. Garton, The kinetics of polyolefin oxidation in aqueous media, J. Polym. Sci. Polym. Chem. 30 (1992) 1693–1703.