

DEPARTMENT OF THE NAVY NAVAL UNDERSEA WARFARE CENTER DIVISION NEWPORT OFFICE OF COUNSEL PHONE: (401) 832-3653 FAX: (401) 832-4432 DSN: 432-3653



Attorney Docket No. 96813 Date: 4 February 2008

The below identified patent application is available for licensing. Requests for information should be addressed to:

TECHNOLOGY PARTNERSHIP ENTERPRISE OFFICE NAVAL UNDERSEA WARFARE CENTER 1176 HOWELL ST. CODE 07TP, BLDG. 990 NEWPORT, RI 02841

Serial Number12/022,415Filing Date30 January 2008

Inventor

Thomas S. Ramotowski

Address any questions concerning this matter to the Office of Technology Transfer at (401) 832-1511.

DISTRIBUTION STATEMENT Approved for Public Release Distribution is unlimited

ACTIVATION ENERGY MEASUREMENT METHOD

STATEMENT OF GOVERNMENT INTEREST

[0001] The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefore.

CROSS REFERENCE TO OTHER PATENT APPLICATIONS

[0002] None.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0003] The present invention relates to a material testing method for determining the activation energy for diffusion through polymers.

(2) Description of the Prior Art

[0004] Polymer coated material are frequently used in a marine environment. In these materials, a polymer such as a paint or a plastic is painted, coated or formed on a substrate. The polymer acts as a barrier preventing environmental fluids from affecting the substrate. Environmental fluid diffusing

through the polymer can result in corrosion or electrical shorting. Thickness of the polymer coating is also of concern for cost, weight and geometric considerations. Thus, there is a great interest in reducing the permeability of polymer . materials. This allows a thinner coating of polymer on the substrate to be protected.

[0005] Diffusion is also important for maintaining bonding of the polymer coating on the substrate. In cathodic delamination, the current model holds that water and oxygen diffuse through the polymer layer to trigger cathodic delamination. Delamination is begins by the build up of water in the space between the polymer and the substrate. This results in interfacial blisters which triggers the actual delamination or debonding.

[0006] Activation energy, E_a, is an important value for determining the rate of diffusion. Activation energy is akin to an energy barrier that must be surmounted by the reactants before a reaction can take place. The higher the activation energy, the slower the reaction proceeds at the measured temperature. Unfortunately, activation energy is often unknown for a given material or set of materials, and it requires experimental determination.

[0007] Activation energy, E_a , is typically calculated by first measuring water diffusion constants at three different

temperatures for the polymer in question, and then relating them to the Arrhenius equation. This tends to be a time consuming process because the polymer samples must fully saturate with water before calculations can be made. There are also several ways to calculate diffusion coefficients, and the different methods may not produce compatible results.

SUMMARY OF THE INVENTION

[0008] An object of this invention is to provide a method for determining the saturation activation energy for a material of interest.

[0009] Accordingly, the current invention provides a method for computing activation energy of diffusion for a material in a liquid. At least two identical samples of the material are submerged in the liquid at different temperatures. The time required for saturation of each sample is measured. A reaction acceleration factor is computed for the two samples from the saturation times and temperatures. Activation energy of diffusion is computed from the reaction acceleration factor and the temperatures. Additional samples can be used to give an error estimate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0010] This invention provides an improved method for measuring the activation energy for diffusion of water through a polymer. This method uses the reaction acceleration factor ("RAF") equation derived from the Arrhenius equation:

$$RAF = e^{\frac{-E_a(T_2 - T_1)}{R(T_2 T_1)}}$$
(1)

where: RAF is the reaction acceleration factor, E_A is the activation energy, R is the gas constant, and T_1 and T_2 are the absolute temperature in degrees Kelvin of the reactions.

[0011] The reaction acceleration factor equation (1) is used to calculate E_a for diffusion of water into the polymer of interest. Identical polymer samples are used. 1/16 in. thick, 2 to 3 in. diameter disks are preferred. The samples are divided into at least two groups. The first group is placed into a container filled with distilled water at a first temperature, T_1 . The other group is placed in distilled water at a different temperature, T_2 . The mass of each sample is monitored until it becomes saturated with water (i.e., the mass gain levels off). The time required to saturate two identical polymer disks at two different temperatures can be used to determine the RAF for the process by dividing the time t_1 required by the first temperature

 (T_1) experiment sample by the time t_2 required by the different temperature (T_2) experiment sample.

$$RAF = \frac{t_1}{t_2} \tag{2}$$

[0012] A third sample or group of samples can be tested at a third temperature or at one of the other temperatures. This sample serves as a control to ensure accuracy. The two temperatures involved are the T_1 and T_2 values in the RAF equation, which can then be solved for the only remaining variable, E_a . (Note, R is a constant.)

$$E_{a} = \frac{-RT_{2}T_{1}(\ln(RAF))}{T_{2} - T_{1}}$$
(3)

[0013] In an alternative embodiment, activation energy, E_a, can be calculated for diffusion of water into a polymer until the sample has reached a predetermined percentage weight gain. As an initial step, a predetermined percentage weight gain must be selected. One practicing this method should insure that the predetermined percentage weight gain is less than the percentage weight gain at saturation. Factors that can be used to determine this predetermined percentage weight gain include equipment accuracy, time available for the test, and accuracy required for the result.

[0014] After selecting the percentage weight gain, identical samples are divided into at least two groups. The first group is placed into a container filled with distilled water at a

.

first temperature, T_1 . The other group is placed in distilled water at a different temperature, T_2 . The mass of each sample is monitored until it reaches the predetermined percentage weight gain. As above, the time required to saturate two identical polymer disks at two different temperatures can be used to determine the RAF for the process by dividing the time t_1 required by the first temperature (T_1) experiment sample by the time t_2 required by the different temperature (T_2) experiment sample. A third group of samples can be tested as a control at either T_1 , T_2 , or a third temperature, T_3 , until it reaches the predetermined percentage weight gain. Activation energy, E_a , is calculated as given in Equation (3), above.

[0015] These embodiments provide a more direct way to calculate E_a for the diffusion through a polymer. This calculation does not depend on additional assumptions in the calculation of diffusion constants. This method can be used to determine the activation energy, E_a , when long-term effects of polymer immersion are of interest.

[0016] The method taught here can be varied in several respects. The size and shapes of the samples can be different as long as all of the samples tested for a given material are identical. The values of T_1 and T_2 can be varied. Different fluids can be used as the testing environment.

.

[0017] In light of the above, it is therefore understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

ABSTRACT

A method for computing activation energy of diffusion for a material in a liquid is provided. At least two identical samples of the material are submerged in the liquid at different temperatures. The time required for each sample to reach a goal weight percentage is measured. A reaction acceleration factor is computed for the two samples from the resulting times and temperatures. Activation energy of diffusion is computed from the reaction acceleration factor and the temperatures. Additional samples can be used to give an error estimate.