I.A.U. Karaj Branch

Journal of Applied Chemical Research, 10, 2, 107-115 (2016)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Aging Study of Oil Impregnated Repulped and Standard Cellulose through Measuring Viscometric Degree of Polymerization

Sohrab Rahmani[*1], **Rana Rahmati**[3,4], **Ali Ramazani**[2]

[1]*Department of Chemistry, Laboratory of Polymer Synthesis, University of Zanjan, Zanjan, Iran*

[2]*Department of Chemistry, University of Zanjan, Zanjan, Iran*

[3] *Iran Transfo group, Materials Laboratory, Zanjan, Iran*

[4] *Department of Chemistry, Payame Noor University, Tehran, Iran*

(Received 14 Jan. 2016; Final version received 24 Mar. 2016)

Abstract

This paper describes the aging behavior of the oil impregnated repulped cellulose and compares it with the aging behavior of the oil impregnated standard cellulose. In order to evaluate the reliability of using repulped cellulose in transformers, the accelerated aging process was applied to both types of cellulose by increasing the temperature to 150 °C and their aging behavior was studied and compared through measuring their viscometric degree of polymerization (DP) in consecutive aging periods. Results were fitted to estimate an aging relation respect to the initial DP and this was yield that the accelerated pyrolysis behavior of two survived types of cellulose are completely similar and obeys the same damping model. From the obtained results, it can be concluded that the moulded insulating parts made of repulped cellulose can be used in the insulation system of power transformers with a good and acceptable reliability. The reduction of DP to 30% of its initial value was estimated as a criterion for the end of life time of these celluloses.

Keywords: *Repulped cellulose, Oil impregnated cellulose, Accelerated pyrolysis, Viscometric degree of polymerization, Insulation system life time.*

Introduction

Oil transformers, especially power transformers that are the main part of electrical networks, are extra expensive equipments that should provide permanent access to the electrical energy with the most reliability [1]. The

***Corresponding author:** *Dr. Sohrab Rahmani, Department of Chemistry,Laboratory of Polymer Synthesis, University of Zanjan, Zanjan,Iran. E-mail: rahmani.sohrab@znu.ac.ir, Tel: 024-33052589.*

performance of these transformers and their life time depends on the condition of their cellulosic insulation impregnated with oil. Cellulose insulation is the most effective and economic solid insulation for oil cooled power transformers, despite some disadvantages which cannot be neglected. Aging is one of them; another common fact that the dielectric strength of oil paper systems is dependent on the thermal, oxidative, hydrolytic, electrical and mechanical condition, which the transformer experiences during its lifetime. The most important character of cellulose is the powerful bonds between its fibers and the physicochemical interaction between them in the form of intermolecular hydrogen bonds [2-4]. Cellulose is a linear polymer of glucose; consisting D-anhydroglucopyranose units joined together by glycosidic bonds. The number of such units per chain is called the degree of polymerization (DP). A single cellulose fiber is formed from a number of these chains held together by hydrogen bonds. The aging process is essentially one of depolymerization, brought about by acid hydrolysis, pyrolysis, and oxidation. The aging mechanism affects the electrical and mechanical properties of the dielectrics [5]. The manufacturers and specialists of this industry have determined a life time of more than 40 years for these equipments. In fact their life time is the life time of their insulation system i.e. the combination of oil/cellulose and actually some of them are permanently used in power networks even more than 50 years. Standard cellulose impregnated with oil, has a determined life time in normal condition, which expires under aging mechanisms. But some parts of transformer's insulation system are not made of standard cellulose sheets. They are moulded in special shapes from waste of these sheets that are repulped using dewatering process under vacuum and then are dried in ovens (figures 1 and 2).

(A) (B)

Figure 1. Cellulose pulp (A), pressboard waste (B).

Figure 2. Moulded insulating parts made from repulped cellulose.

These parts will not have the same life time of standard cellulose, particularly if their production process doesn't include the fiber refining station. The performance of fiber refining system has an effective role in regular formation of cellulose fibers and its structure and it has been macroscopically found that lack of this system significantly weakens the mechanical properties of the repulped cellulose. Shaped insulating parts produced from moulding the repulped cellulose, during their performance in the structure of power transformers are not exposed to considerable mechanical stresses while are permanently subject to thermal stresses with the temperatures of 60-90º C. So study of the thermal aging behavior of repulped cellulose based on reduction of its DP in defined sampling periods during accelerated thermal aging process is an appropriate method for characterizing the aging behavior of this type of cellulose comparing with the aging behavior of standard cellulose. In a previous study, we reported the aging behavior of these two types of cellulose based on determination of 2-furfural content of oil. The obtained results showed that the aging behavior of two types of cellulose is the same according to the contents of released 2-Fufural in oil during the accelerated pyrolysis [6]. For further confirmation of this behavior, in continuation of this work, we now investigate the accelerated thermal aging process of these two types of cellulose through measuring viscometric degree of polymerization. To our knowledge, thermal aging behavior of repulped cellulose based on DP measurement has not been reported so far.

Experimental

Materials

Acetone (99%), dicholomethane (99.9%), and Cupper ethylenediamine hydroxide (1 M, Molar ratio or ethylenediamin concentration to the cupper concentration, C_{EN}/C_{Cu}= 2± 0.04) were from Merck and used as received. The oil used in this modeling was mineral transformer oil according to IEC 60296 standard that produced by Nynas Company. Standard pressboard samples were prepared from Weidmann production pressboard sheet, type B.4.1 and repulped cellulose samples were prepared from repulping the Waste of the same type of sheet.

Preparing the samples of accelerated pyrolysis

Regarding the rate of aging, the number of measurements and the time intervals between them are determined. After drying and impregnation with oil, the specimens are transferred to special containers and located in oven under heat. The temperature of the oven in order to apply the accelerated aging process has been determined according to the previous researches [7-9] as described below.

During the life time of transformer, oil impregnated cellulose is subject to electrical stresses under the temperature of maximum 90º C and remains in this condition until 40 years. Since a laboratory model in order to study the aging behavior actually necessitates shorter time intervals, so higher temperatures can be considered in a laboratory model to accelerate the aging procedure. As the result of studying the researches done in this regard, the permanent and constant temperature of 150º C according to the following calculations is considered to create accelerated aging mechanism in this paper. Arrhenius model is a neperian model that based on it an increase in temperature from 7 to 10º C makes the rate of pyrolysis twice according to the following relation [10]:

$$V = 2^{\frac{\theta - 98}{6}} \quad (1)$$

In equation (1), θ (°C) is the hot spot temperature and *V* is the relative loss of life or relative aging. Every 6ºC increase in the temperatures upper than 100º C increases the rate of pyrolysis of oil impregnated cellulose by a factor of 2[11]. According to relation (1), pyrolysis in the temperature of 150º C, increases the rate of aging by a factor $2^{8.6}$. If the life time of oil impregnated cellulose in 100º C is supposed about 40 years, increasing the temperature of pyrolysis to 150º C will decrease its life time to about 36 days. So, measuring periods, considering two measurements in the first week and one measurement in the other weeks totally will produce 6 results. Before preparing the samples and impregnating the cellulose with oil, the DP of both repulped and standard cellulose were measured. Each DP result has been obtained from two measurements on two separated samples. Attention to the volume of used containers (24 containers of 250 ml) and considering a weight ratio of about 11.5% according to IEC 60763-2 standard [12], 30 gr cellulose was determined for each container. Each set of standard and repulped cellulose samples were weighed and classified as shown in figure 3.

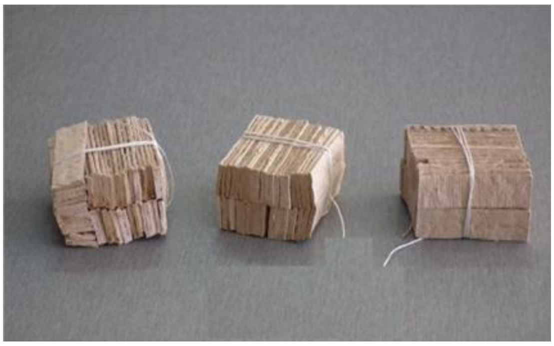

Figure 3. Classified and weighed cellulose samples.

The sets of each group were separately put in a special drying container according to the method described in IEC 60641-2 standard as follows [13]: Samples were dried inside this container using a vacuum oven with the temperature of 105º C and the pressure of less than 1 mbar for 24 hours. The impregnating process of samples was performed in oil under 90º C and vacuum condition for 2 hours. Then impregnated samples were removed from oven and transferred to the containers of Fig.4 as well as the impregnating oil. After labeling the containers, they were put in another oven with the temperature of 150° C.

Figure 4. Containers including the samples ready to spend the accelerated pyrolysis in the 150°C.

In the determined times, each of them was removed from the oven and the DP of the aged cellulose were measured.

Measuring the DP of cellulose

DP of standard and repulped cellulose have been measured using the viscometric method described in IEC 60450 standard [14]. The principle of this method is based on dissolving cellulose in cupper ethylenediamine hydroxide and measuring the specific viscosity of the obtained solution. Intrinsic viscosity and then the degree of polymerization are calculated using the specific viscosity. According to the standard method, oil impregnated cellulose samples were fluffed after degreasing and then dissolved in cupper ethylenediamine (Cuen) under Nytrogen using a magnetic stirrer. Then the specific viscosity of the obtained solution is measured using a capillary viscometer in constant temperature and finally the degree of polymerization of cellulose is calculated based on the specific viscosity of cellulose/Cuen solution and its concentration. After removing each samples from the oven in the determined periods, about 10-15g of their cellulose were took out of them, cut into pieces of about 1 cm^2 and each one separately were degreased in an appropriate soxhelt extractor using dichloromethane as solvent. It is needed to separate the cellulose fibers through a suitable method in order to facilitate dissolution in Cuen. Here, the dry fluffing method is used and degreased cellulose samples were fluffed using a blender, and turned to the form shown in Figure 5.

Figure 5. Degreased and fluffed cellulose.

The mass of cellulose needed to dissolve depends on the expected concentration of cellulose/Cuen solution and the moisture content of the samples. Concentration of the solution was determined according to the expected degree of polymerization [15]. According to Fig.6, dissolving process was carried out under nitrogen atmosphere that help complete dissolution of cellulose in Cuen.

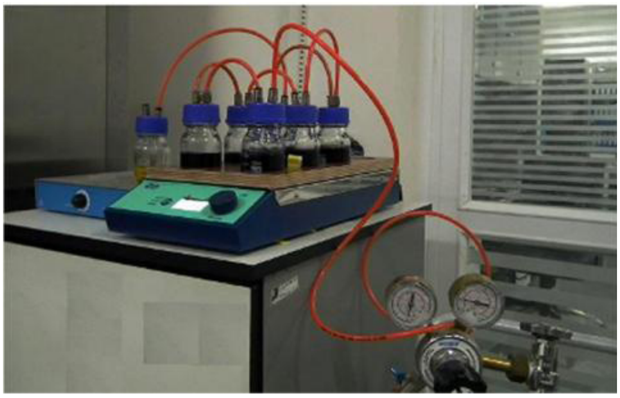

Figure 6. Dissolving cellulose in Cuen using magnetic stirrer under flushing with nitrogen.

Determining the viscosity of Cellulose/CUen solution

To determine the specific viscosity of cellulose/Cuen solution, the viscosityof the solvent (distilled water and Cuen) and the cellulose/Cuen solution were separately measured by using of Ubbelohde viscometer. All measurement was performed in the controlled temperature range of 20±0.2º C.

Results and discussion

The results of seven periodic DP measurements for each type of oil impregnated cellulose are presented in table 1 and are plotted as a curve in Fig.7 each as a point. Mathematical relation describing the aging behavior of each type has been obtained from fitting these points. The DP of both standard and repulped cellulose samples before aging was over 1000 and so both of them were categorized as new cellulose according to standard. DP reduction behavior for both types during pyrolysis as shown in figure 7 was completely the same and at the end of fifth week both of them was converged to the same value of 340±4. Fitting the resulted points according to the damping exponential model was led to relations (2) for standard cellulose and relation (3) for repulped cellulose. In these relations t is the pyrolysis period in terms of day and DP is the degree of polymerization

$$DP = 378 + 965\ e^{\frac{-t}{4}} \quad (2)$$

$$DP = 353 + 775\ e^{\frac{-t}{4}} \quad (3)$$

With a good approximation the aging behavior of two types on the basis of initial DP can be described by relation 4:

$$DP = DP_0(0.3 + 0.7\ e^{\frac{-t}{4}})$$

Table 1. DP results of the oil impregnated samples after successive pyrolysis periods for both types of standard and repulped celluloses.

Pyrolysis duration (day)	DP of Repulped cellulose		DP of standard cellulose	
	Each result	Average of two results	Each result	Average of two results
0	1134	1135	1356	1357
	1136		1358	
3	633	599	746	755
	564		763	
7	485	492	604	593
	498		582	
14	429	406	462	491
	383		519	
21	326	329	367	396
	332		425	
28	343	337	335	343
	332		351	
35	380	344	329	337

In this relation, DP_0 is initial cellulose DP before aging, t is pyrolysis period in terms of day and DP is cellulose DP after aging period. This relation states that in the pyrolysis process the value of DP at the end of the cellulose life time decreases to the 30% of its initial value that has been reported in the previous researches [6- 8] and 70% is depreciated during this process in 5 weeks. The results show that the aging behavior of two types of cellulose during accelerated pyrolysis in 150 °C follows the same aging model and so using repulped cellulose for manufacturing transformer moulded insulating parts does not menace its reliability during the life time. Therefore the production of moulded insulating parts using repulped cellulose further to making this industry domestic saves more than 20 billion Rials foreign exchange.

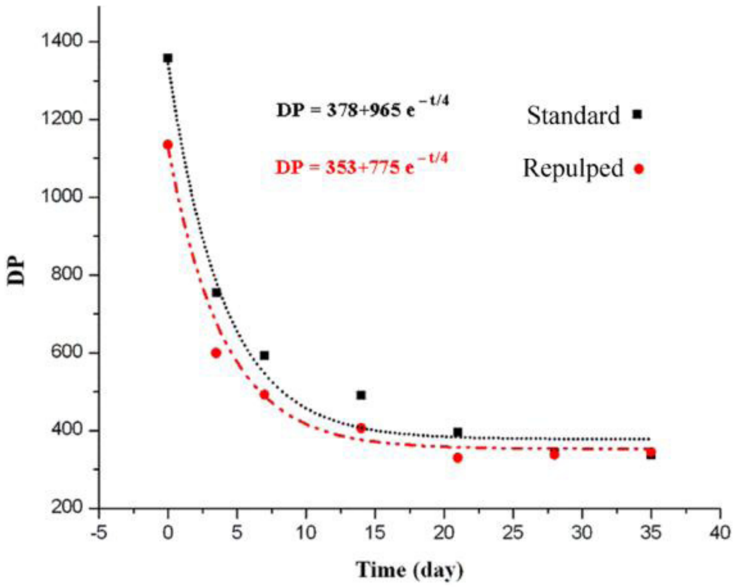

Figure 7. Comparative graphs of DP versus time for standard and repulped celluloses.

Conclusion

In this study an accelerated laboratory model has been utilized to investigate and compare the pyrolysis behavior of two types of standard and repulped cellulose. Measuring the DP of two types of oil impregnated cellulose aged in 150 0 C in the consecutive aging periods indicated that DP reduction trend in both types follows the same damping model. So it can be said that using repulped cellulose obtained from cellulose sheet's waste residues for manufacturing transformer moulded insulating parts does not menace its reliability during the life time. Also, production of moulded insulating parts using repulped cellulose could be effective and economical.

References

[1] Y. Li, M.J. Tang, F.J. Wu, G.J. Zhang, S.H. Wang, *IJEEI*, 5, 34 (2013).

[2] P. Verma, D.S. Chauhan, P.Singh, Effects on Tensile Strength of Transformer Insulation Paper under Accelerated Thermal and Electrical Stress, *Annual Report Conference on Electrical Insulation and Dielectric Phenomena*, 619, (2007).

[3] Ch. Krause , P. Brupbacher, A. Fehlmann , B. Heinrich, Moisture Effects on the Electric Strength of Oil/Pressboard Insulation used in Power Transformers, *IEEE International Conference on Dielectric Liquids*, 369 (2005).

[4] K. Gandhi, Y.R. Sood, R.K. Jarial, *IJECSE*, 1, 896 (2012).

[5] M. Arshad, S. M. Islam, A. Khaliq, Power Transformer Aging and Life Extension, *SL International Conference on Probabilistic Methods Applied to Power Systems, Iowa State University, Ames, Iowa* (2004).

[6] A. Ramazani, R. Rahmati, S. Bigdeli, S. Rahmani, M. Hamidi, JACR, accepted paper, (2015).

[7] J. Faber, A. Pichon, Deteriorating processes and products of paper in oil, application to transformers, CIGRE paper, Paris, 137 (1960).

[8] A. M. Emsley, G.C. Stevens, *IEE Proc.Sci. Meas. Technol,* 141, 324, (1994).

[9] D.H. Shroff , A.W. Stannett, A review of paper aging in power transformers, *Generation, Transmission and Distribution, IEE Proceedings C,* 132, 312, (1985).

[10] M. Mamdouh Abd El Aziz, *OJEEE*, 2, 269, (2011).

[11] IEC 60505, Evaluation and Qualification of Electrical Insulation Systems (2004).

[12] IEC 60076-7, Loading Guid for Oil Immersed Power Transformers (2005).

[13] IEC 60641, Part 1, 2, 3, Specification for pressboard and presspaper for electrical purposes (2008).

[14] IEC 60450, Measurement of the Average Viscometric Degree of Polymerization of New and Aged Cellulosic Electrically Insulating Materials (2007).

[15] IEC 60763-2, Specification for Laminated Pressboard-Part 2: Methods of tests (2007).