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*A.A. Ostapenko, M.D. Gomelya, O.M. Movchaniuk, V.V. Halysh***DETERMINATION OF THE AZETIDE GROUPS RELATIVE CONTENT IN THE COMPOSITION OF AMPHOTERIC POLYMER RESINS****National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine**

The work is devoted to the determination of the relative content of azetidine groups included in amphoteric polymer resins. The use of such resins for gluing cardboard from wastepaper ensures its strength in both dry and wet conditions. However, when choosing a resin from a fairly wide range of these reagents on the market, the content of azetidine groups is not included in the list of main characteristics. In this research work, the methods of ^1H and ^{13}C NMR spectroscopy were used which allowed carrying out the qualitative and quantitative analysis of the azetidine groups in polyamidamine-epichlorohydrin resins according to their structural and functional characteristics. In order to obtain quantitative information about individual groups of studied polyamidamine-epichlorohydrin resins a new technique was proposed for calculating the relative content of azetidine groups in resins with respect to the theoretically possible content. The essence of the technique was that the ^{13}C NMR spectra of the investigated amphoteric polymer resins were divided into integration intervals corresponding to the nuclei of carbon atoms in the same type of structural fragments of polyamidamine-epichlorohydrin resin molecules. To determine the relative content of azetidine groups, the corresponding values of spectroscopic parameters of carbon atoms (integral line intensities and their ratio) of carboxyl and carbonyl groups, as well as carbon atoms of azetidine groups, were used. In this work, the effect of the researched resins on the main quality indicators of laboratory paper samples of different composition was studied. The research results proved the dependence of paper parameters on the relative content of azetidine groups in the resin.

Keywords: amphoteric polymer resin, azetidine groups, relative content, ^1H and ^{13}C NMR spectroscopy, cellulose, wastepaper, physical-mechanical properties of paper.

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Introduction

The highest competition in the market of corrugated cardboard products is observed in the segment of corrugated boxes. One of the significant disadvantages of corrugated cardboard is a low indicator of moisture resistance. This significantly narrows the scope of its application in cases where it is necessary to ensure the preservation of the strength of the package under conditions of high humidity. Meanwhile, the international experience shows that it is the use of containers made of moisture-resistant corrugated cardboard and cardboard with protective properties that is the most effective, as it significantly expands

the scope of application and ensures the economical use of resources for containers [1,2].

Depending on the requirements for cardboard containers and the scope of its application, various types of adhesives are used to increase moisture resistance [3,4]. Low moisture strength (without moisture-resistant additives) is explained, first of all, by the rapid destruction of inter-fiber bonds during the swelling of the cardboard in water and the subsequent stretching of the fibers after applying a mechanical load. When immersed in water and wet environment, ordinary cardboard loses up to 97–98% of its original strength.

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Methods of providing moisture resistance to cardboard can be divided into two main groups. The first includes the methods associated with the introduction of various chemical auxiliary substances into the cardboard. The advantages of moisture-resistant cardboard include its resistance to high levels of humidity (85–95%), freezing-thawing cycles, and direct contact with water [5].

Polyamidamine-epichlorohydrin resins for providing moisture resistance are an important group of chemical auxiliary substances for cardboard and paper production. Their action is unusual in that they cause changes in such physical properties of cardboard and paper products as dry strength and water resistance [3–5].

Due to the fact that polyamidamine-epichlorohydrin resins have a positive charge and cellulose molecules have a negative charge [6], the cellulose molecule interacts with the resin molecules. At the same time, the strength of the paper increases both in the dry and in the wet states. Polyamidamine-epichlorohydrin resins are synthesized in the following three steps: condensation between adipic acid and diethylenetriamine to form polyamidamine, attachment of epichlorohydrin to the secondary amino group of polyamidamine to form N-(3-chloro-2-hydroxypropyl) polyamidamine, and a four-membered azetidinium ring from 3-chloro-2-hydroxypropyl group [7,8]. Here, azetidinium rings play a key role in improving the strength of paper and cardboard in the case of using polyamidamine-epichlorohydrin resins [8].

It should be noted that currently the market offers a wide range of such resins for the use in paper and cardboard technology. However, despite the importance of the content of functional groups, the available technical characteristics do not allow considering this parameter when choosing a resin for a specific technological flow. Commonly, the characteristics of these resins are represented by such indicators as the content of dry substances, pH of the medium and density. Therefore, the purpose of this work was to study the content of azetidinium groups in polyamidamine-epichlorohydrin resins of different manufacturers for the possibility of determining the most effective reagents for the application in paper and cardboard production.

Experimental

Polyamidamine-epichlorohydrin resins of various manufacturers with such trade names as UltraRes 200, Fennostrength PA 21, Kymene 25X- Cel, Eka WS 325, and LURESIN KS [9] were selected for the study.

In this work, the methods of ^1H and ^{13}C NMR spectroscopy were used. The choice of ^1H and ^{13}C

NMR-spectroscopy methods is due to the fact that they allow carrying out qualitative and quantitative analysis of the azetidinium groups in polyamidamine-epichlorohydrin resins according to their structural and functional characteristics. The general structural formula of polyamidamine-epichlorohydrin resins is shown in Fig. 1 [7].

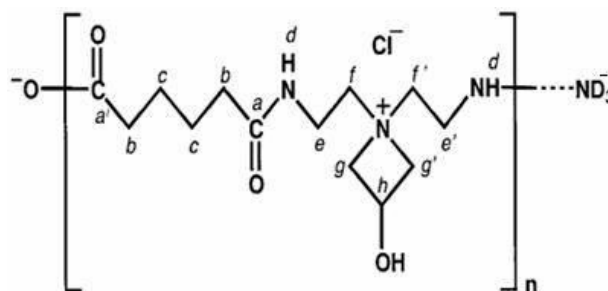


Fig. 1. The general structural formula of polyamidamine-epichlorohydrin resins: a, a', b, c, e, e', f, f' – carbon atoms of the linear chain of amphoteric polymer resins and g, g', h – carbon atoms of the azetidinium group

In the process of recording the ^1H NMR spectrum of the investigated polyamidamine-epichlorohydrin resins, the method proposed elsewhere was used [10]. In order to ensure the necessary quality of paper and cardboard, studies of the effect of polyamidamine-epichlorohydrin resins on the physical and mechanical parameters of laboratory samples of paper with mass of 125 g/m² were conducted. The consumption of polyamidamine-epichlorohydrin resins was 4; 6; and 8 kg/t. For the production of laboratory samples of paper, both primary fiber (unbleached cellulose from coniferous wood of the HC-2 grade) in accordance with the current regulatory document, and waste paper of the MC-8B-1 grade in accordance with EN 643 «Paper and board – European list of standard grades of paper and board for recycling» were used. Obtained paper samples were tested for mechanical strength parameters such as breaking force during ring compression (according to the Ukrainian state standard DSTU ISO 12192) and absolute compression resistance (according to the Ukrainian state standard DSTU ISO 2759), which are important for packaging types of paper and board.

Results and discussion

Table 1 shows the values of ^1H NMR chemical shifts and the relative integral intensity of signals of hydrogen atoms in polyamidamine-epichlorohydrin resins. As can be seen from the data, the ^1H NMR spectra of the studied resins have a noticeable difference in the values of the chemical shifts (δ) of the characteristic lines and their broadening, which occurs

due to the rapid proton exchange between the functional groups of polyamidamine-epichlorohydrin resins with labile hydrogen atoms ($-\text{OH}$, $-\text{NH}$) and solvent (H_2O).

The analysis of the obtained ^1H NMR spectrum for the studied polyamidamine-epichlorohydrin resins (Table 1) shows that the signals in the regions $\delta=8.23$ – 8.31 ppm, $\delta=4.70$ – 4.83 ppm, and $\delta=4.10$ – 4.28 ppm belong to the protons of the amino group *d*, the methine protons *h* of the azetidine group of N-(3-chloro-2-hydroxypropyl) polyaminoamide, and the protons of the methylene groups *g*, *g'* of the azetidine group, respectively. Signals at $\delta=3.57$ – 3.70 ppm, $\delta=3.18$ – 3.40 ppm, $\delta=3.42$ – 3.56 ppm, $\delta=2.25$ – 2.30 ppm, and $\delta=1.54$ – 1.58 ppm belong to the protons of methylene groups (*f*), the protons of methylene groups (*f'*), the protons of methylene groups *e*, *e'*, the protons of methylene groups *b*, and the protons of methylene groups *c*, respectively.

As can be seen from the ^1H NMR spectrum shown in Fig. 2, the signal of the methine proton *h* in N-(3-chloro-2-hydroxypropyl) polyamine amide is practically overlapped by the signal of the methylene protons *g* and *g'* of the azetidine group, which complicates the quantitative assessment of the relative content of azetidine groups in the studied polyamidamine-epichlorohydrin resins. Therefore, it is advisable to use ^1H NMR spectra only for a qualitative assessment of the azetidine groups of polyamidamine-epichlorohydrin resins. Thus, for a clearer idea of the course of interactions involving polyamidamine-epichlorohydrin resins, a study of the structure of their macromolecules was carried out using ^{13}C NMR spectroscopy (Fig. 3). Since the scale of chemical shifts of carbon atoms of different functional affiliations is known to be longer compared to the range of values of chemical shifts for protons of ^1H

nuclei, the ^{13}C NMR spectroscopy method allows reducing the overlap of the signals of individual NMR groups, which is especially important for the quantitative determination of the content of functional groups in molecules of polyamidamine-epichlorohydrin resins.

Analysis of the ^{13}C NMR spectrum (Fig. 3) shows that the signals of carbon atoms belonging to different homo- and heteroatomic chains of polyamidamine-epichlorohydrin resins imply different values of chemical shifts, and they differ in integral intensity in the case of their homogeneity in the series of polyamidamine-epichlorohydrin resins (Table 2).

The specified difference in the spectrum (Table 2) of the investigated polyamidamine-epichlorohydrin resins made it possible to use the values of integral signal intensities of carbon atoms for quantitative assessment of the contribution of various fragments of macromolecules of polyamidamine-epichlorohydrin resins.

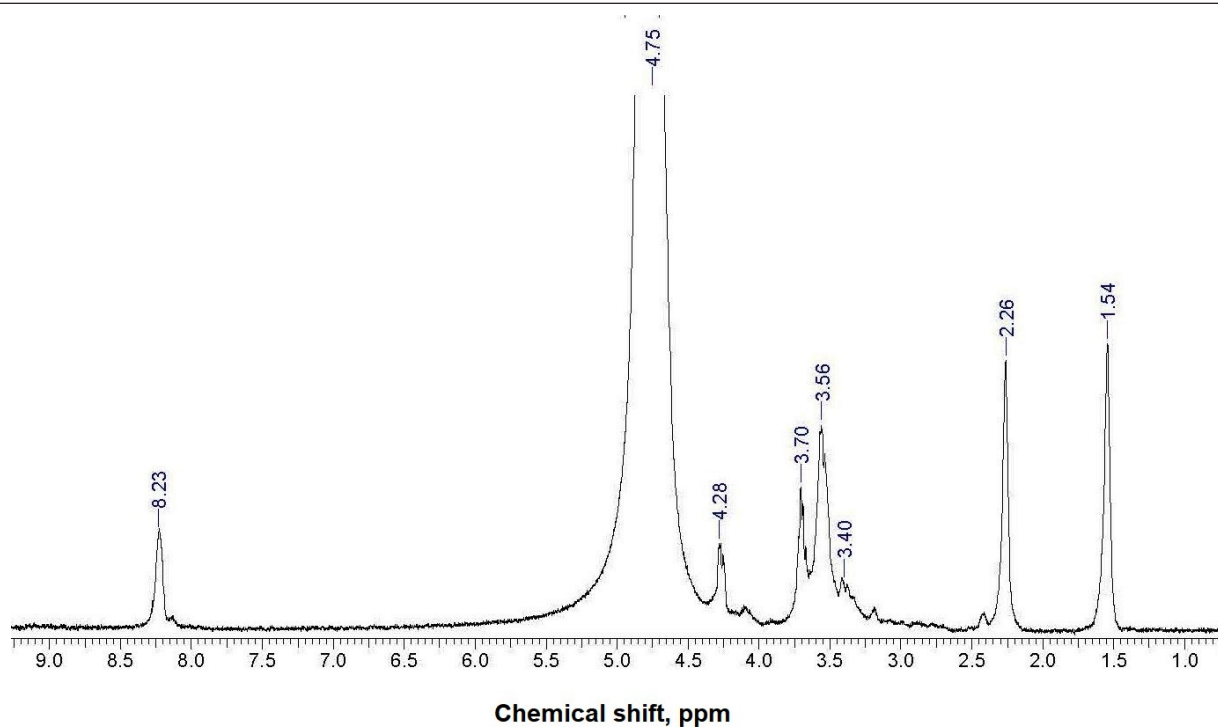
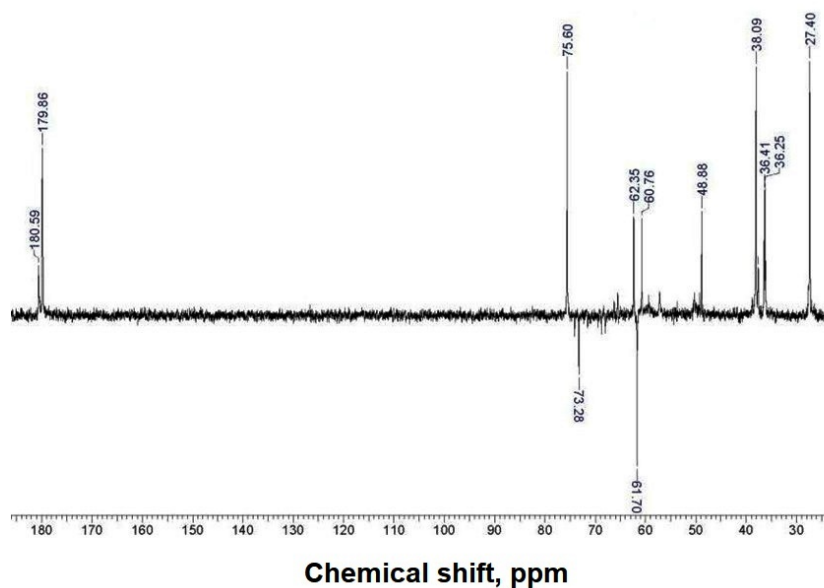
As can be seen from the data given in Table 2, the differences are observed in the ratios of relative integral intensities, which are characteristic of certain types of signals of groups in a number of polyamidamine-epichlorohydrin resins selected for research. Thus indicates that the producers of polyamidamine-epichlorohydrin resins used raw materials for synthesis, which in terms of reactivity belong to the same class of organic compounds, but in origin differ in the fragment composition (hydrocarbon chain length, specificity of its modification).

From the obtained data (Table 2), it can also be concluded that the identified structural features of the investigated polyamidamine-epichlorohydrin resins can affect the probability of the formation of azetidine

Table 1

Values of chemical shifts (I) of ^1H NMR (ppm) and relative integral intensity (II) (%) of signals of hydrogen atoms in polyamidamine-epichlorohydrin resins

Type of polyamidamine-epichlorohydrin resin		Hydrogen atoms								
		d	h	g/(g')	f	e	e'	f	b	c
UltraRes 200	I	8.23	4.75	4.28	3.70	3.56	3.56	3.40	2.26	1.54
	II	6.20	30.00	4.80	8.50	11.60	3.40	3.40	16.00	16.30
Fennostrength PA 21	I	8.28	4.79	4.26	3.71	3.56	3.53	3.42	2.26	1.55
	II	6.00	33.00	4.70	6.40	10.00	7.00	3.00	13.40	14.40
Kymene 25X-Cel	I	8.31	4.79	4.27	3.70	3.56	3.40	3.18	2.25	1.53
	II	5.90	36.40	3.80	5.20	9.60	6.50	2.80	13.90	15.90
Eka WS 325	I	8.28	4.83	4.29	3.57	3.42	3.39	3.34	2.27	1.55
	II	5.60	46.20	2.60	8.60	5.60	4.10	3.70	11.20	12.00
LURESIN KS	I	8.30	4.83	4.10	3.61	3.52	3.44	3.36	2.30	1.58
	II	4.80	40.80	2.80	8.50	5.80	4.40	4.90	12.10	13.30

Fig. 2. NMR ¹H spectrum of water solution of polyamidamine-epichlorohydrin resinFig. 3. NMR ¹³C spectrum of water solution of polyamidamine-epichlorohydrin resin

cycles and, as a result, the physical and mechanical parameters of paper and cardboard due to the steric factor.

Therefore, the following technique was used in order to obtain quantitative information about individual groups of studied polyamidamine-epichlorohydrin resins when calculating the relative content of azetidine groups in them with respect to

the theoretically possible value. The essence of the proposed technique is that the ¹³C NMR spectra of the studied amphoteric polymer resins were divided into integration intervals corresponding to the nuclei of carbon atoms in the same type of structural fragments of polyamidamine-epichlorohydrin resin molecules. The calculation of the relative content of azetidine groups with respect to the theoretically possible value

was carried out using the standard program SpecManager ACD Labs.

To determine the relative content of azetidine groups with respect to the theoretically possible one, the corresponding values of spectroscopic parameters of carbon atoms (integral line intensities and their ratio) of both carboxyl (a') and carbonyl (a) groups, and carbon atoms of azetidine groups (g, g') were used [10,11]. To calculate the relative content of azetidine groups with respect to the theoretically possible, the integral intensities of the lines of carbon atoms of azetidine groups (g, g') were taken equal to 1.

Integral intensities of atoms of carboxyl (a') and carbonyl (a) groups and the results of calculations of the relative content of azetidine groups with respect to the theoretically possible one are given in Table 3.

As can be seen from the data in Table 3, the samples of the investigated polymers (polyamidamine-epichlorohydrin resins) contain different numbers of azetidine groups, depending on the conditions of the polymerization reaction (temperature, concentration, and stoichiometry of reagents) and the structural and functional characteristics of the starting reagents.

This indicates that we can expect the implementation of various methods of spatial

organization of paper and cardboard in the process of interaction of cellulose fibers with the participation of chains of polyamidamine-epichlorohydrin resins with different degrees of their fragment reactivity. That means that the ability to form both the covalent (esterification process) and intermolecular and interfragmentary bonding is through hydrogen bonds which are established between water and the hydroxyl groups of the cellulose.

It is noticeable that according to the content of azetidine groups (in order of their increase), amphoteric polymer resins are located in the following sequence: Luresin KS < Eka WS 325 < Kymene 25X-Cel < UltraRez 200 < Fennostrength PA 21. This can be used to choose a resin to improve the paper-making properties of paper and cardboard.

We also studied the effect of the researched resins on the main quality indicators of laboratory paper samples of different composition. The research results proved the dependence of paper parameters on the relative content of azetidine groups in the resin.

The paper indicators increase with an increase in the relative content of azetidine groups. The effect of polyamidamine-epichlorohydrin resin Fennostrength PA21, which contains the maximum

Table 2

Values of chemical shifts (I) of ^{13}C NMR (ppm) and relative integral intensity (II) (%) of signals of carbon atoms in the composition of the investigated polyamidamine-epichlorohydrin resins

The type of polyamidamine-epichlorohydrin resin	Hydrogen atoms											
		a'	a	b	c	e	e'	f	f'	g	h	i
UltraRes 200	I	180.59	179.86	38.09	27.40	36.41	36.25	62.35	60.76	75.60	61.70	48.88
	II	3.80	11.70	18.10	18.90	10.20	9.80	6.70	6.90	17.50	9.60	7.00
Fennostrength PA 21	I	180.39	179.88	38.07	27.39	36.41	36.25	62.35	60.75	75.60	61.69	50.28
	II	1.90	9.60	19.20	18.10	8.00	7.70	6.90	6.90	17.30	11.50	6.90
Kymene 25X- Cel	I	180.56	179.89	38.07	27.39	36.42	36.25	62.35	60.75	75.60	61.69	49.35
	II	3.30	8.40	7.10	21.30	7.50	7.10	5.80	5.00	14.20	10.00	2.90
Eka WS 325	I	180.57	179.85	38.06	27.40	36.88	36.23	62.29	60.70	75.60	61.69	49.29
	II	3.00	33.00	11.80	19.80	1.40	0.90	6.10	6.60	3.30	5.60	4.70
LURESIN KS	I	180.82	176.94	–	26.38	–	–	64.17	62.79	75.60	–	–
	II	1.80	7.50	–	1.25	–	–	60.60	6.20	12.50	–	–

Table 3

Integrated intensities of lines of carbon atoms in ^{13}C NMR spectra and relative content of azetidine groups of studied polyamidamine-epichlorohydrin resins

The type of polyamidamine-epichlorohydrin resin	Fennostrength PA21	UltraRes 200	Kymene 25X-Cel	Eka WS 325	Luresin KS
Integrated intensities of lines of carbon atoms (a'+a) in ^{13}C NMR spectra	1.22	1.31	1.89	2.50	14.73
The relative content of azetidine groups in comparison with carboxyl and carbonyl groups g/(a'+a), %	81	76	53	40	7

number of azetidine groups among the listed resins under study, on the main indicator of paper strength is shown in Fig. 4,a.

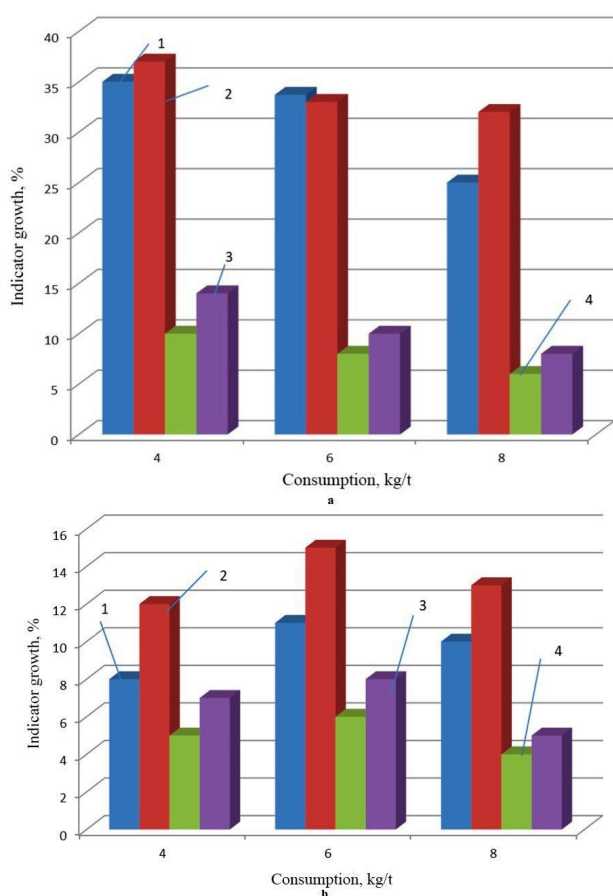


Fig. 4. Diagrams of the influence of polyamidamine-epichlorohydrin resin Fennostrength PA21 (a) and Luresin KS (b) on the burst resistance (1, 2) and the crushing strain during the compression of the ring (3, 4) of paper made of unbleached cellulose of HC-2 grade (1, 4) and paper from wastepaper of MC-8B-1 grade (2, 3)

It is noticeable that the addition of resin in the amount from 4 kg/t to 8 kg/t has a significant effect on the increase of the absolute burst resistance to compression. For paper made from unbleached cellulose of the NS-2 grade from coniferous wood, this indicator increased by 34% and 24% at consumption of 4 kg/t, and 8 kg/t, respectively. When using MS-8B-1 waste paper, the increase in absolute resistance to crushing for the same amount of resin was 36% and 32%, respectively. The increase of the crushing strain during the compression of the ring for a resin consumption of 4 kg/t amounted to about 14% for paper from wastepaper and 9% for cellulose paper. A greater increase in indicators for paper from wastepaper is observed at almost all values of the resin

consumption. This can probably be explained by the highly developed specific surface of the secondary cellulose fiber, which leads to an increase in the concentration of hydrogen bonds between the groups of cellulose and polyamidamine-epichlorohydrin resin and, as a result, to an increase in the mechanical strength of the paper.

The effect of polyamidamine-epichlorohydrin resin Luresin KS, with a minimum amount of azetidine groups, on the main strength indicators of laboratory paper samples was also studied. The results are shown in Fig. 4,b. As can be seen from this diagram, the use of polyamidamine-epichlorohydrin resin Luresin KS makes it possible to prepare the paper samples with lower physical and mechanical parameters than the corresponding parameters of paper made using Fennostrength PA21 resin. An increase in the investigated indicators for the variant with Luresin KS resin (compared to the corresponding paper samples without resin) was 5–15% and 4–11% for waste paper and cellulose samples, respectively.

Conclusions

Thus, based on the studies carried out by using the ^{13}C NMR spectroscopy, we showed that the signals of carbon atoms belonging to different homo- and heteroatomic chains of amphoteric polymer resins are characterized by different values of chemical shifts and integral intensities in the ^{13}C NMR spectrum, which made it possible to calculate the relative content of azetidine groups for polyamidamine-epichlorohydrin resins of various manufacturers.

According to the content of azetidine groups (in order of their increase), the studied amphoteric polymer resins are located in the following sequence: Luresin KS < Eka WS 325 < Kymene 25X-Cel < UltraRes 200 < Fennostrength PA 21.

With an increase in the relative content of azetidine groups in macromolecules of polyamidamine-epichlorohydrin resin, its positive impact on the mechanical strength of paper observed with the addition of this resin is increased. Therefore, the relative content of azetidine groups is an important indicator of resin quality, which should be included in the list of its main characteristics and used for effective resin selection to increase not only the moisture resistance of paper and cardboard, but also the strength of waste paper.

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ВИЗНАЧЕННЯ ВІДНОСНОГО ВМІСТУ
АЗЕТИДИНОВИХ ГРУП У СКЛАДІ АМФОТЕРНИХ
ПОЛІМЕРНИХ СМОЛ

А.А. Остапенко, М.Д. Гомеля, О.М. Мовчаниук, В.В. Галиш

Робота присвячена визначенню відносного вмісту азетидинових груп, що входять до складу амфотерних полімерних смол. Використання таких смол для проклеювання макулатурної картонної тари забезпечує її міцність як в сухому, так і у вологому стані. Однак при виборі смоли з доволі широкого асортименту даних реагентів на ринку показник вмісту азетидинових груп відсутній в переліку основних характеристик. У роботі застосовували методи ^1H і ^{13}C ЯМР спектроскопії, що дозволяють проводити якісний і кількісний аналіз азетидинових груп поліамідамін-епіхлоргідринних смол за їх структурно-функціональними характеристиками. Для отримання кількісної інформації про окремі групи досліджуваних поліамідамін-епіхлоргідринних смол під час розрахунку відносного вмісту в них азетидинових груп від теоретично можливого, запропоновано нову методику. Суть методики полягає в тому, що спектри ЯМР ^{13}C досліджуваних амфотерних полімерних смол розділялися на інтервали інтегрування за відповідністю ядрам атомів вуглецю у складі однотипних структурних фрагментів молекул поліамідамін-епіхлоргідринних смол. Для визначення відносного вмісту азетидинових груп використано відповідні значення спектроскопічних параметрів атомів вуглецю (інтегральних інтенсивностей ліній та їх співвідношення) карбоксильних і карбонільних груп, а також атомів вуглецю азетидинових груп. У роботі було вивчено вплив досліджуваних смол на основні показники якості лабораторних зразків паперу різної композиції. Результати досліджень довели залежність показників паперу від відносного вмісту азетидинових груп у смолі.

Ключові слова: амфотерна полімерна смола; азетидинові групи; відносний вміст; ^1H і ^{13}C ЯМР-спектроскопія; целюлоза; макулатура; фізико-механічні показники паперу.

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The work is devoted to the determination of the relative content of azetidine groups included in amphoteric polymer resins. The use of such resins for gluing cardboard from wastepaper ensures its strength in both dry and wet conditions. However, when choosing a resin from a fairly wide range of these reagents on the market, the content of azetidine groups is not included in the list of main characteristics. In this research work, the methods of ^1H and ^{13}C NMR spectroscopy were used which allowed carrying out the qualitative and quantitative analysis of the azetidine groups in polyamidamine-epichlorohydrin resins according to their structural and functional characteristics. In order to obtain quantitative information about individual groups of studied polyamidamine-epichlorohydrin resins a new technique was proposed for calculating the relative content of azetidine groups in resins with respect to the theoretically possible content. The essence of the technique was that the ^{13}C NMR spectra of the investigated amphoteric polymer resins were divided into integration intervals corresponding to the nuclei of carbon atoms in the same type of structural fragments of polyamidamine-epichlorohydrin resin molecules. To determine the relative content of azetidine groups, the corresponding values of spectroscopic parameters of carbon atoms (integral line intensities and their ratio) of carboxyl and carbonyl groups, as well as carbon atoms of azetidine groups, were used. In this work, the effect of the researched resins on the main quality indicators of laboratory paper samples of different composition was studied. The research results proved the dependence of paper parameters on the relative content of azetidine groups in the resin.

Keywords: amphoteric polymer resin; azetidine groups; relative content; ^1H and ^{13}C NMR spectroscopy; cellulose; wastepaper; physical-mechanical properties of paper.

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