

Effect of Addition of Glycolysis Products of Poly(ethyleneterephthalate) Wastes to Urea-Formaldehyde Resin on Its Adhesion Performance to Wood Substrates and Formaldehyde Emission

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ABSTRACT: Recycling of poly(ethyleneterephthalate) waste was achieved through glycolysis using diethyleneglycol (DEG) and poly(ethyleneglycol) (PEG 400), which yielded different fractions that exhibited hydroxyl numbers of 174.41 and 54.86 mg of KOH/g, respectively, whereas GPC profiles revealed bimodality in both cases corresponding to M_n values equivalent to 534 and 1648. The products of glycolysis from both cases were individually incorporated as modifiers during the synthesis of urea-formaldehyde resins from both the basic as well as acidic stages, respectively. It was found that the free formaldehyde level was remarkably decreased for the modified resins while the gel time was slightly affected indicating some activation of the resins. In addition, the adhesion strength of wood joints bonded with the modified resins improved markedly in the

dry state while the moisture resistance was significantly fortified with respect to the comparable joints formulated from unmodified resins where instant failure took place within few hours after immersion in water. The shelf life of the resins did not prolong and lasted maximum for about 2 months which was ascribed to the presence of reasonable amount of carboxyl terminal groups at the ends of a minor portion of the glycolyzed products that could actively act to self-catalyze the polycondensation and crosslinking reactions during storage leading eventually to vitrification of the resin and shortening of shelf life. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2377–2383, 2012

Key words: glycolysis; PET; degradation; urea-formaldehyde; adhesives

INTRODUCTION

Several routes have been of particular interest as modifiers to improve the performance of urea-formaldehyde (UF) bonded wood particleboard. These routes involved the coreaction of UF resins with small amounts of isocyanates,¹ propionaldehyde,² and aliphatic long chain diamines and triamines,³ which was originally proposed to introduce better flexibility, hence better stress distribution in a hardened plywood glue-line. In a similar study, a short chain aliphatic dialdehyde (succinaldehyde) was used as coreactant to UF system and found to improve the water resistance, which was attributed to the formation of a linear butyl chain, being inserted between the ureas upon the reaction of the aldehyde with urea, thus contributed efficiently to decrease the density of crosslinking.⁴

Polyethylene terephthalate (PET) is one of the versatile engineering plastics that are widely used in

diverse applications: textiles, manufacture of high strength fibers, photographic films, disposable soft drinks and others. It is also one of the largest components of the postconsumer plastics in landfills. With increasing applications and decreasing prices, PET became the symbol of high disposable in consumer, and hence, a noxious material of concern in the relatively recent environmental protection issues as it is in addition highly resistive to atmospheric and biological agents. Therefore, the necessity of finding a simple economic route for recycling of PET waste is an important practice for sustainable recycling and contributes to conservation of raw materials and energy.^{5,6}

Chemical depolymerization of PET wastes and conversion into reusable chemical products of added value is one of the most important recycling strategies for this material.^{5–7} This task can be achieved by glycolysis in excess diols or polyols which has been studied for many years⁸ The produced glycolyzed products could be divided into water soluble and insoluble oligomers. Most of the glycolyzed products precipitate out because of limitation in their solubility in water-based systems.⁷ The water soluble fractions are mainly hydroxyl-terminated while the main chains, either aliphatic or bearing

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aromatic ring, may be promising in improving the water resistance of the resin and in providing space between the ureas which allows decreasing the crosslinking density of UF resin providing that the hydroxyl terminals are the sources of reactivity during reaction with UF resin. In this work, we employ the degradation products (including the water insoluble fractions) as coreactants to UF resin, to investigate if they can be promising as cheap modifiers that can upgrade any of the UF properties that show poor performance.

We will pay attention to the critical chain length of the glycolized products, as too long chains would in turn lead to very low solubility of the compounds which would severely limit or even completely inhibit their reaction with such a water-based system.

EXPERIMENTAL

Materials

Urea was obtained from El-Delta Company for fertilizers and chemical industries, Talkha-Egypt. Formaldehyde (37% solution) was supplied from El-Mansoura for Resins & Chemical Industries, Egypt. Anhydrous aluminium chloride was a product of Merck-Schuchart chemical company, Germany. Ammonium chloride was provided from Veblabor Chemie, Apolda. Diethylene glycol (DEG), Aldrich; polyethylene glycol 400 (PEG 400), Fluka; lead acetate, Laboratory Rasyan were laboratory grade and used without further purification.

Methods

Glycolysis of PET

Clear postconsumer bottles of PET wastes were collected from local market. Samples were first conditioned with 1 wt % aqueous solution of sodium hydroxide for about 1 h to remove any surface impurities and subsequently washed with water and dried in an oven at 80°C. PET scraps were cut in a particle size between 3 and 5 mm and then subjected to glycolysis process. PET wastes were depolymerized in this study using two different glycols (DEG and PEG 400) in the presence of lead acetate as a transesterification catalyst. The PET waste to glycol ratio in each case (1 : 1 wt %) was calculated considering a molecular weight of one PET monomeric unit is 192 Da, thus relating each one to its molecular weight will correspond to relative molar ratios of 1 : 1.84 for PET/DEG and 1 : 0.484 for PET/PEG 400, respectively. The mixture was charged to a four-necked round bottom flask of 500 mL capacity, connected to a reflux condenser, thermometer, and stirrer. The reaction was carried out under reflux at 190–200°C for 8 h. The glycolized products were

analyzed for hydroxyl (HN) and acid (AN) numbers according to a procedure described elsewhere.⁹

Preparation of UF resins

A traditional two-step procedure was followed for the synthesis of UF resins at F/U = 1.5. Initially, formaldehyde (37–40%) was placed in the reactor then the solution pH was adjusted to 7.5 with sodium hydroxide (10 wt %). Subsequently, urea was added to the system and after ensuring complete dissolution the mixture was refluxed for 45 min. Then, the pH was changed to 5 with acidic solution of anhydrous AlCl₃: ethanol (1 : 1) and the polycondensation reaction was resumed for additional 15 min, the pH was finally readjusted to 8 and the mixture was left to cool.

Preparation of modified UF resins

The modification method of preparation was very similar to that of the general preparation of UF resins. It involved prior neutralization of formaldehyde using sodium hydroxide solution then appropriate amount of urea was added so that the F/U ratio was set at 1.5, whereas predetermined amounts (0.5, 1, 3) g of each glycolized product was either charged during the basic or acidic stage then the process was completed as above.

Characterizations

The solid content of the UF resins was determined in triplicates by taking the difference of the weight before and after drying of 1 g of UF resin into a disposable aluminum dish in air oven at 120°C for 3 h. The viscosity of the UF resins was measured from aqueous solutions at 25°C with a cone plate viscometer (DV-III, Brookfield, Middleboro, MA) with no. 2 spindle at 60 rpm. The free-formaldehyde content of the prepared resins was determined by the sodium sulfite method.¹⁰ The gel time was measured in 3 replicates for each resin at 100°C using a stop-watch. The IR spectra were recorded on a JASCO FT/IR 6100E Fourier transform infrared spectrometer, Japan. The molecular weights of the glycolized products were measured against polystyrene standard on Waters gel permeation chromatography. Samples were dissolved in tetrahydrofuran of HPLC grade at a constant concentration of 0.1 wt %. After filtration of samples, 200 µL of each sample was injected into ultrastyrogel columns. The flow rate of the eluent was 1 mL/min.

Wood samples (2 × 0.5 × 10 cm) for adhesion measurements were cleaned, smoothed then the hardener was added to the resin, based on the solid content of the resin, and mixed well just prior to

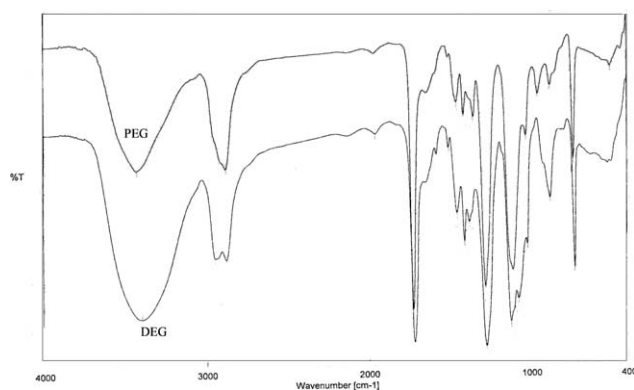


Figure 1 FTIR spectra of the glycolyzed products of PET wastes with DEG and PEG 400.

application. The resin was spread over $2 \times 2 \text{ cm}^2$ of the wood species and the joint was pressed using a hydraulic press of two plates, both heated to 150°C for 5 min. under pressure of 50 kg/cm^2 . The shear strength of the glued joints was evaluated using Lloyd universal testing machine Type LR/OK, Lloyd, England, operated at a minimum cross-head speed of 2 mm/min .

RESULTS AND DISCUSSION

Characterization of the glycolyzed product

The glycolysis consists of the transesterification of PET and the destruction of its polymer chains, resulting in the decrease of its molecular weight. Destruction of PET can take place at elevated temperatures. When glycols are used in the depolymerization of PET, the oligoesters obtained have two hydroxyl end groups, i.e. oligoester diols are formed.¹¹ In this study, the depolymerization of PET was carried out with DEG at molar ratio 1.84 and at 0.484 for PEG 400.

FTIR spectra of the glycolyzed products of DEG and PEG 400 were quite similar (Fig. 1) and showed the following bands:

An intense broad band at 3400 cm^{-1} characteristic to the stretching frequency of the hydroxyl groups.

The stretching band at 2950 cm^{-1} may be assigned to olefinic and aromatic CH.

The bands at $2878\text{--}1450 \text{ cm}^{-1}$ may be stand for stretching and bending frequencies of CH_2 groups.

A strong band at 1720 cm^{-1} due to the stretching frequency of the carbonyl groups.

The band at 1580 cm^{-1} is quite characteristic to the aromatic $\text{C}=\text{C}$ stretching.

The bending frequencies at $730\text{--}880 \text{ cm}^{-1}$ strongly suggest the presence of aromatic residue of the glycolyzed products.

It may be argued from the IR Spectra that the glycolyzed products are hydroxyl terminated oligomers.

The hydroxyl and acid values of the glycolyzed products were determined and the results are summarized in Table I. It was found that the glycolyzed products have low acid values, 17.44 and 15.62 mg KOH/g for DEG and PEG 400, respectively, although the glycolysis of PET should yield oligomers with hydroxyl end groups. This low acid value indicates that parallel hydrolysis may be occurring during the reaction and some products with carboxyl end groups can also be formed.¹² Table I illustrates the number average molecular weight (M_n) of oligomers calculated from hydroxyl number and obtained by GPC analysis as well. The fractions obtained as a result of glycolysis induced by DEG and PEG 400 were bimodal and exhibited different retention times, 32.71 and 28.78 minutes, respectively, which is thought to be a reflection of that the glycolyzed products composed mainly of two main components,¹³ (Fig. 2).

Dealing more generally with the GPC profiles, neglecting that there is more than one fraction, while taking the molecular weight to be representative to the sample as a whole gave rise to 534 and 1648 g mol^{-1} , respectively (Fig. 3) which are in close conformity to the comparable data obtained by the hydroxyl number method (Table I). These fractions can be represented by: {DEG-TPA-EG-TPA-DEG, molecular weight 534 g mol^{-1} } and {PEG 400-TPA-(EG-TPA-EG)₂-TPA-PEG 400, molecular weight 1648 g mol^{-1} } where TPA refers to terephthalic acid. We calculated the percentages of the high molecular weight fractions and low molecular weight ones as well so simply by taking the area under peak and relating to the total peak area for each case thus it

TABLE I
Characterization of Glycolyzed PET Wastes

Samples	Molar ratio	AN, mg of KOH/g	HN, mg of KOH/g	Mn (HN)	Data from GPC		
					M_n	M_w	Polydispersity
PET/DEG	1:1.84	17.44	174.41	585	534	734	1.33
PET/PEG ₄₀₀	1:0.484	15.62	54.86	1592	1648	2456	1.49

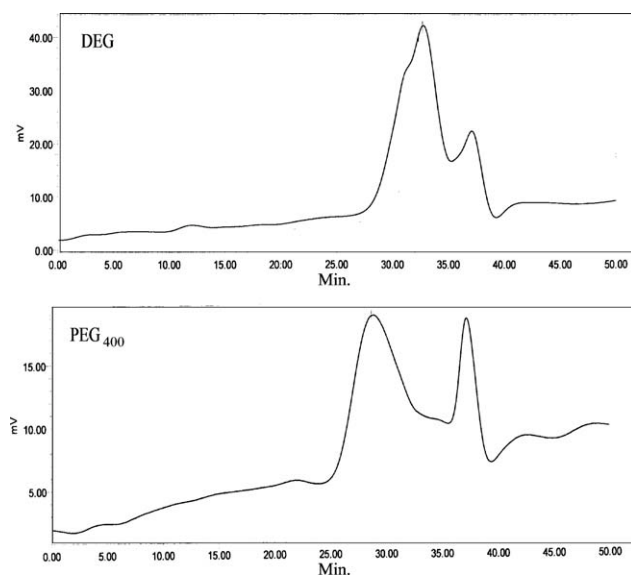


Figure 2 Plot of retention time data for the glycolyzed fractions.

was equivalent to 79.5 and 20.5% in case of DEG and 75.5 and 24.5% in case of PEG 400, respectively.

The produced glycolyzed fractions were employed as modifiers for UF resins from both the basic and acidic stages for each type (PEG 400 and DEG). It is worthy to mention that some insoluble parts still existing in case of PEG 400. However, we did not remove these parts hoping that they may convert to soluble fractions during the course of reaction which was not the case.

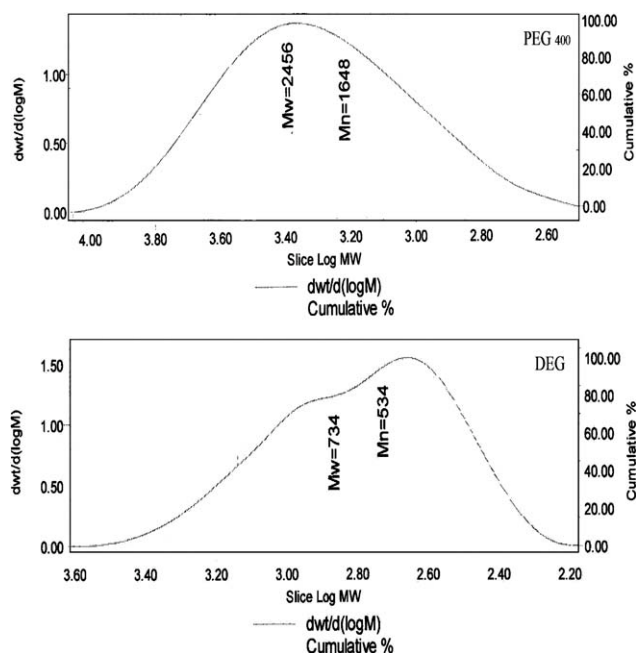


Figure 3 Cumulative GPC profiles of the glycolyzed products.

TABLE II
Physical Properties of UF Resins After Modification During the Basic Stage of Polycondensation with Different Amounts of Glycolysis Products of PET Using DEG

Properties	Unmodified UF resin	Modified UF resins with different additions during basic stage		
		0.5 g	1 g	3 g
Solid content, %	47.8	47.9	47.8	48.1
F.F., %	1	0.65	0.6	0.53
Viscosity, P.	0.8	0.7	0.65	0.55
Gel time (Sec.)	60	56	62	60

The physical properties of the modified UF resins with different additives of glycolyzed products of PET using DEG, from both, basic as well as acidic stages, are shown in Tables II and III, respectively. In both cases, the change in the solid content along with amount of modifier (0.5–3 g) is practically insignificant in comparison with the unmodified UF resin. The same trend can be observed for the free formaldehyde levels (remarkably lower level of free formaldehyde with respect to unmodified resin) while a slight decrease in the viscosity was noticed upon increasing the modifying agent either from the basic or the acidic stage during synthesis. Further, the gel time was not very much affected by the addition of the modifier. Initially some activation to the resin was noticed, represented by a decrease in the gel time from 60 s for the unmodified resin to about 54–56 s for 0.5 g of additive (either from the basic or acidic stage) which goes up again upon further increase of the additive to the common gel time of unmodified UF resin. The corresponding shear strength values of wood joints glued with the modified UF resin in the presence of 3 wt % of NH_4Cl as an accelerator (curing agent) before (dry state) and after immersion in cold water for 24 h (wet state), to induce hydrolytic degradation or better to express as a measure of moisture resistance of the glue after modification with glycolysis products of PET, are

TABLE III
Physical Properties of UF Resins After Modification During the Acidic Stage of Polycondensation With Different Amounts of Glycolysis Products of PET Using DEG

Properties	Unmodified UF resin	Modified UF resins with different additions during acidic stage		
		0.5 g	1 g	3 g
Solid content, %	47.8	47.2	48.1	48.9
F.F., %	1	0.8	0.6	0.6
Viscosity, P.	0.8	0.7	0.65	0.55
Gel time (Sec.)	60	54	59	60

TABLE IV
Shear Strength Values of Wood Joints Glued With Modified as well as Unmodified UF Resins in Presence of 3 wt % NH₄CL as a Curing Agent

Properties	Unmodified UF resin	Modified UF resins with different amounts of DEG induced glycolysis products during basic stage		
		0.5 g	1 g	3 g
Dry shear strength, Kg/cm ²	40	58	52	65
Wet shear strength, Kg/cm ²		17.2	21.3	35
		after 24 h immersion in cold water		
		Modified UF resins with Different amounts of DEG induced glycolysis products during acidic stage		
		0.5 g	1 g	3 g
Dry shear strength, Kg/cm ²		55	62	62
Wet shear strength, Kg/cm ²		36	48	38
		after 24 h immersion in cold water		

shown in Table IV. The shear strength of the joints formulated from unmodified resin (40 Kg/cm²) increased about 50% up to 0.5 g of addition of the modifier in the basic stage, this ratio further elevated to 57% for 3 g of an additive. A significant drop can be induced after immersion of the joints in cold water for 24 h, the drop is almost two-third for 0.5 g of the additive, more than half for 1 g addition while almost half for 3 g of additive (which can be considered the most resistive sample to moisture). In all cases, the modification results in better moisture resistance when compared with the unmodified resins, whose corresponding joints collapsed entirely after the immersion in water.

The situation is more or less the same for the comparable treatment using the same amounts from the acidic stage. However, the samples in this case showed much better resistance to moisture or induced hydrolytic degradation which can be accounted for by the glycolysis products of PET acting effectively as distancing agents that could facilitate semielastic three-dimensional network formation that can deal reversibly to the increased internal pressure associated with severe crosslinking thus help to dilute the crosslink density while providing some elasticity to their fracture mode upon being mechanically stressed. The increased resistance to moisture reflects the hydrophobic nature or relatively long-chained species comprised in the structure of the fractions of glycolyzed PET ($M_n = 584.9 \text{ g mol}^{-1}$ according to hydroxyl number method and 534 g mol^{-1} as determined by GPC). These fractions showed acid value up to 17.44 mg KOH/g while about 10-folds of equivalent hydroxyl number (174.41 mg KOH/g). The existence of such high hydroxyl number gives rise to their capability to incorporate in the network formation during gelation or crosslinking while the extremely shorter shelf-life (maximum 2 months for most of the samples) relative to our previous studies based on

modification of UF resins with dendritic poly(amidoamines) (PAMAM)^(14–17) is ascribed to availability of –COOH groups in reasonable amount that can self-catalyze the condensation reactions during storage and therefore shorten the shelf life.

In a very similar way, we repeated the same sequence of experiments for another set of samples while employing the glycolysis products of PET, but with using PEG 400 instead of its dimeric form as a glycolytic agent, as modifiers for UF resins using the same amounts (0.5–3 g) for comparison, the results of this series are shown in Tables V–VII.

It should be kept in mind that the main difference between the glycolysis products in this case with respect to the former case where DEG was employed, exhibited a comparable acid value (15.62 mg of KOH/g) while about one-third of the hydroxyl content that was obtained in case of DEG (54.86 mg of KOH/g). In a predictable way, it may be emphasized that less hydroxyl content means less reactivity of the resins. On the contrary, it was not the case and the reactivity of the resins remained the same as represented by the gel time data (Tables V and VI) except for the sample modified with 3 g from the basic stage (45 s), which may be actually

TABLE V
Physical Properties of UF Resins After Modification During the Basic Stage of Polycondensation with Different Amounts of Glycolysis Products of PET Using PEG₄₀₀

Properties	Unmodified UF resin	Modified UF resins with different additions during basic stage		
		0.5 g	1 g	3 g
Solid content, %	47.8	47.6	47.6	48.1
F.F., %	1	0.6	0.55	0.55
Viscosity, P.	0.8	0.65	1.4	0.6
Gel time (sec.)	60	55	60	45

TABLE VI
Physical Properties of UF Resins After Modification During the Acidic Stage of Polycondensation With Different Amounts of Glycolysis Products of PET Using PEG₄₀₀

Properties	Unmodified UF resin	Modified UF resins with different additions during acidic stage		
		0.5 g	1 g	3 g
Solid content, %	47.8	48.4	47.9	48.2
F.F., %	1	1	0.65	0.7
Viscosity, P.	0.8	1.3	0.55	0.6
Gel time (Sec.)	60	52	53	56

an artifact. The rest of the physical properties did not exhibit much difference relative to their counterparts modified with DEG (with few exceptions that can be observed from the tables). More importantly, the impact of these modifiers on these resins when applied as glues for binding cellulosic joints or what so ever, (Table VII).

From Table VII, the shear strength values from the resins modified from the basic stage improved strongly up to 1 g of additive then a deleterious drop was observed upon higher amounts of additives were used. Also, the resin modified with the least amount of additive (0.5 g) survived strongly after immersion in cold water for 24 h while the higher amounts caused surprisingly strong failing to the joints after immersion in water despite of their more hydrophobicity (hydroxyl content = 54.84) and longer chain length so less hydroxyl content per chain length means less reactivity or may refer to inappropriate compatibility with the reaction mixture that is based on water.

The improvement of the shear strength values was more pronounced for the modification achieved during the acidic stage of condensation which seems

to be more favored with these species. However, the molecular weight data determined by GPC for the produced species from the glycolysis of PET revealed it as a three times as much as that of the series that belong to the modification with glycolysis products using DEG ($M_n = 1592$, determined by hydroxyl number and 1648 determined by GPC).

This may not be very much surprising and can be explained by the bimodality of the GPC profiles (Fig. 2), which means that two types of fractions with a big difference in polarity, solubility, and molecular weight while the introduced overall value obtained by GPC represents the entire sample with no differentiation between the two fractions, one of these fractions precipitated out of the medium during reaction for the modifiers based on glycolyzed products by PEG 400. Generally, the shear strength remained almost of the same moisture resistance to the comparable series modified with DEG glycolysis products under the same reaction conditions (refer to Table IV).

Glycolysis products by PEG 400 seem in general to preponderate the DEG products in their performance especially if we consider the resistance of joints to hydrolytic degradation (up to 1 g of modifier) beyond which there may be some contradiction if we believe that this may be ascribed to their longer chains being inserted between the urea units upon the reaction between the aldehyde with urea, similar results were found by others.⁴

We will focus in a future study on isolating each fraction before involvement as modifier to UF resin to investigate the difference in performance and properties of the produced resins.

In the mean time, an intensive thermal study on the curing behavior of the resins after modification will be performed on the way to profound understanding of the role of these modifiers.

TABLE VII
Shear Strength Values of Wood Joints Glued With Modified as well as Unmodified UF Resins in Presence of 3 wt % NH₄CL as a Curing Agent

Properties	Unmodified UF resin	Modified UF resins with different amounts of PEG ₄₀₀ induced glycolysis products during basic stage		
		0.5 g	1 g	3 g
Dry shear strength, Kg/cm ²	40	65	70	25
Wet shear strength, Kg/cm ²		59	18	11
		Modified UF resins with Different amounts of PEG ₄₀₀ induced glycolysis products during acidic stage		
		0.5 g	1 g	3 g
Dry shear strength, Kg/cm ²		62	74	45
Wet shear strength, Kg/cm ²		41	45	20

CONCLUSIONS

Glycolysis products of PET wastes can be used to improve the properties of UF resins through participation in the polycondensation and crosslinking reactions with their hydroxyl end groups, whereas the existence of some carboxyl terminals was found to be involved in self-catalyzing these reactions. The resin activation, revealed by gel time data, lead to the conclusion that these glycolysis fractions were involved effectively in the network structure of the resin which could further be confirmed by the improvement in adhesion strength in the dry state and their moisture resistance after immersion in water in addition to the remarkable drop in the level of free formaldehyde. It could also be concluded that the shelf life shortening of the resins after modification was presumably a result of the carboxyl ends of a portion of these fractions.

References

1. Wieland, S.; Pizzi, A.; Hill, S.; Grigsby, W.; Pichelin, F. *J Appl Polym Sci* 2006, 100, 1624.
2. Mansouri, H. R.; Pizzi, A. *J Appl Polym Sci* 2006, 102, 5131.
3. Simon, C.; George, B.; Pizzi, A. *J Appl Polym Sci* 2002, 86, 3681.
4. Wang, S.; Pizzi, A. *Holz Roh Werkstoff* 1997, 55, 9.
5. Tawfik, M. E.; Ahmed, N. M.; Eskander, S. B. *J. Appl Polym Sci* 2011, 120, 2842.
6. Tawfik, M. E.; Eskander, S.B. *J Elast Plast* 2006, 38, 65.
7. Tawfik, M. E. *J Appl Polym Sci* 2003, 89, 3693.
8. Baliga, S.; Wong, W. T. *J Polym Sci Part A: Polym Chem* 1989, 27, 2071.
9. Boiko, V. P.; Grishenko V. K. *Rev Acta Polym* 1985, 36, 459.
10. Bleidt, R. A. In *Encyclopedia of Industrial Chemical Analysis*; Shell, F. D., Etre L. S., Eds.; Interscience Publishers: New York, 1971; p 13.
11. Halacheva, N.; Novakov, P. *Polymer* 1995, 36, 867.
12. Güclü, G.; Kasgöz, A.; Özbudak, S.; Özgümüş, S.; Orbay, M. *J Appl Polym Sci* 1998, 69, 2311.
13. Suh, D. J.; Park, O. O.; Yoon, K. Z. H. *Polymer* 2000, 41, 461.
14. Essawy, H. A.; Moustafa, A. B.; El-Sayed, N. H. *J Appl Polym Sci* 2009, 114, 1348.
15. Essawy, H. A.; Moustafa, A. B.; El-Sayed, N. H. *J Appl Polym Sci* 2010, 115, 370.
16. Essawy, H. A.; Moustafa, A. B., Abdel-Bary, E. M.; El-Sayed, N. H. *Egypt J Text Polym Sci Technol* 2010, 14, 1.
17. Essawy, H. A.; Mohamed, H. *J Appl Polym Sci* 2011, 119, 760.