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Investigation of the liquid tar product from the pyrolysis of yak-milk casein and its application in curing of epoxy resin

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The liquid tar product, obtained by pyrolysis of yak-milk casein was investigated and was applied for curing of epoxy resin. Physico-chemical and thermal characteristics, IR and ^{1}H NMR spectra were recorded and compared with the data obtained with the most often used hardener diethylenetriamine. The absorbancies of the liquid tar product were determined by quantitative IR analysis. The curing of epoxy resin was performed at room temperature for 24 h and at 105^{o}C for 150 min. The optimal quantity of the liquid tar product for providing maximal degree of cure at 105^{o}C is 22.22%; at room temperature it is a 20% mixture with diethylenetriamine 50:50 g/g. From the physico-mechanical characteristics of the cured bars and coatings it was concluded that the investigated product is a good hardener of epoxy resins.

Key words: liquid tar product, pyrolysis, casein, epoxy resin, hardener

INTRODUCTION

At the Institute of Chemistry and Chemical Technology of the Mongolian Academy of Sciences different kinds of Mongolian raw material were studied. The results of the characterization of the products obtained by pyrolysis of animal bones were published in [1, 2]. The data from the thermal analysis of yak-milk casein were given in [3]. Its pyrolysis was described in [4]. The obtaining and characterization of biochar from pyrolysed yak-milk casein was published in [5]. The characterization of liquid tar product (LTP) from pyrolysed yak-milk casein was made in [6]. In this article the yields of biochar (28.3%) and LTP (37.5%) are given. The amounts of gas and water were 20.9% and 13.3%, respectively. The elemental composition of the LTP was: C 66.7%, H 8.3%, N 12.1% and O 12.9% (by difference). The sample was characterized by mass spectrometry, gas chromatography (GC)/MS and heated-probe MS, to give molecular weight distributions for comparison with molecular weight ranges indicated by analytical-scale size-exclusion chromatography (SEC). It appeared to consist mostly of moderate molecular weight fractions with elution times of 18–26 min. The components of these fractions were probably 3-dimensional. GC/MS analysis showed the presence of both aliphatic and aromatic nitrogen-containing components. Neither GC/MS nor heated-probe MS were able to detect more than about half of the tar components. The aim of our studies was to continue with the characterization of LTP and its application as a hardener of epoxy resins.

EXPERIMENTAL

The investigations were made with technical grade low-molecular bisphenol A based epoxy resin DER 331 of Dow Chemicals (USA) and laboratory made LTP by pyrolysis of yak-milk casein, prepared in the Mongolian Academy of Sciences. The curing agent used for comparison was technical grade diethylenetriamine (DETA), product of Alpha Chemical (India). Spectroscopy-grade carbon tetrachloride of Merck (Germany) was applied for preparation of LTP solutions for IR analysis. The amine numbers of LTP and DETA were determined with hydrochloric acid for analysis (Merck) by the method described in [7]. The ^{1}H NMR spectra of a solution of LTP in toluene – D8 (Merck) were recorded on a JEOL instrument (Japan). IR spectra were obtained from thin layers of LTP and from its 1% and 20% solutions in carbon tetrachloride on a Perkin Elmer apparatus (USA). The thermal analyses were made on an OD 102 MOM apparatus (Hungary). The curing of the mixtures of epoxy resin and hardeners (DETA or LTP) was made in polyethylene containers. The degree of curing was determined after grinding the cured samples, measuring their

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weights at an accuracy of 0.0001 g before and after Neftochim (Bulgaria) for 4 h on a Soxhlet apparatus, subsequent 10 min extracting with acetone and heating at 105ºC to constant weight. The 4 h extraction was made with toluene because of the limited solubility of LTP in acetone; 10 min extraction with acetone was further performed to facilitate the drying of the samples. Physico-mechanical characteristics: density, Brinell hardness, impact resistance, adhesion on steel, wood and polystyrene (PS) surfaces, elasticity and pendulum hardness of the cured samples (bars or coatings) were determined by standard methods [9–14].

RESULTS AND DISCUSSION

It was shown in our previous investigation that yak-milk casein is a good hardener of epoxy resins [8]. However, it was difficult to prepare a mixture because of its poor solubility. The product from the pyrolysis of yak-milk casein is a liquid and its solubility in epoxy resins is very good. On the other hand, LTP has nitrogen containing groups capable to react with epoxy groups. It is well known that polyamines are applied as hardeners of epoxy resins at room temperature because of their high boiling pressure. It is of interest to compare the physico-chemical and thermal data of LTP with those of the most used polyamine DETA. The results are given in Tables 1 and 2.

Table 1. Characteristics of LTP and DETA.

Compound	pH	n_d^{20}	Amine number %	Specific density, g/cm^3
LTP	10.2	1.6735	4.47	1.02
DETA	8.7	1.4742	24.07	0.95

It is evident, that the amine number of LTP is 5.4 times lower than that of DETA. Therefore, larger quantities of LTP will be necessary for curing of epoxy resins. For comparison, the data of DETA, Merck, for synthesis, are: pH 12, refractive index 1.4826, specific density 0.949 – 0.952 g /cm^3. The differences with the data of technical grade DETA can be explained with the content of impurities in it. The values of the thermal index of technical grade DETA confirm this assumption, extracting with technical grade toluene, product of because the boiling point of DETA for synthesis is 206-209ºC. Probably, the high thermal stability of LTP is due not only to its molecular weight and the shape of its molecules, given in [6], but to the new products obtained at the higher temperatures. The values obtained by TG analysis show that LTP can be applied for curing of epoxy resins at high temperatures. The content of groups in LTP, available to cure epoxy resin is evident from their ^{1}H NMR and IR spectra. In the ^{1}H NMR spectra of the solution of LTP in toluene-D8 the following signals are registered: multiplate δ = 6.86 ppM for protons in aromatic rings and nitrogen containing groups; dublet δ = 0.9 ppM, singlet δ = 1.15 ppM and dublet δ = 2.15 ppM for protons in =CH- and =CH_2 groups. In the IR spectra there are peaks for groups described in [6]: -OH, aromatic rings, aliphatic groups. At 3220, 3200 and 1140 cm^{-1} there are peaks for –NH- , at 2980, 1460 and 815 cm^{-1} - for – CH_2 -. The absorbancies for –NH- and –CH_2– (internal standard) were determined and from their ratio the values of A* = $A_{NH}/A_{int.st}$ were calculated. On the base of the values of amine numbers of LTP in carbon tetrachloride solution (axis x) and the values of A* from their IR spectra (axis y), the most appropriate absorbancies for quantitative IR analysis were determined. The equations of the relationships A*/amine numbers were found for every absorbance and the coefficients *a* and *b* were determined. From the dispersion of the data the coefficients of correlation R were calculated. From these results the most appropriate absorbancies for quantitative IR analysis of LTP were determined: 3220 cm^{-1} for –NH- group and internal standard at 2980 cm^{-1} (minimal values of the coefficients: R = 0.01 and b = 0.75).

The determination of the optimal quantity of LTP for curing of epoxy resin was made using several experiments (series 1). The degree of cure was determined from the ratios of the weights of the samples cured at 105ºC 150 min (w_1) and the weights of the not cured part after extraction with toluene and acetone (w_2).

Table 2. TG data for LTP and DETA

Compound	E_{act} KJ/mol	n	I_{100}	I_{150}	I_{200}	I_{250}	I_{300}	I_{350}	I_{400}	I_{450}	I_{500}
LTP	9.51	0.53	6.44	12.63	18.82	31.9	43.56	48.64	52.01	72.58	89.97

Table 3. Determination of optimal quantity of LTP for curing epoxy resin DER 331

LTP, %	11.11	13.89	16.67	19.44	22.22	25	27.78	30.55
Degree of cure, %	93.35	95.85	97. 71	97.90	99.93	92.00	93.38	92.50

Table 4. Physico-mechanical characteristics of cured bars and 60 μm thick coatings

Series	Degree of cure, %	Density, g/cm^3	Brinell hardness, N/mm^2	Impact resistance, mm	Adhesion, knife test			Elasticity, mm	Pendulum hardness
					Steel	Wood	PS		
1	99.92	1.1481	34.43	230	2	2	2	20	0.88
2	92.92	1.0810	20.78	380	2	1	3	20	0.40
3	95.10	1.2112	29.06	150	2	1	2	20	0.73

It is evident that the influence of the quantity of LTP is not essential. The optimal quantity of LTP is 22.2% - two times larger than the optimal quantity of DETA for curing of this epoxy resin. If only nitrogen containing groups participate in the curing reaction, the optimal quantity should be about 50%. Probably other groups from LTP, eventually -OH participate in the curing reaction as well. It is known that this group is active at temperatures above 140ºC. Probably the –NH- groups lower both the temperature and the time of the curing reaction. The second series was made at 20ºC and 24 h curing with a LTP-DETA ratio from 80:20 g/g to 20:80 g/g to verify this hypothesis and to cure epoxy resin at room temperature. The obtained results confirmed that increasing of the quantity of DETA increases the degree of cure of the samples. With the optimal quantity of hardener 20% mixture of LTP: DETA = 50:50 g/g 93% degree of cure was achieved.

The physico-mechanical characteristics of the cured bars and coatings obtained with the optimal quantities of hardeners: 22.22% LTP, heating at 105ºC 150 min (series 1); 20% mixture of LTP:DETA = 50:50 g/g, at 20ºC 24 h (series 2) and 11% DETA at 20ºC 24 h (series 3) were determined (Table 4).

It is evident that the characteristics of the cured bars and coatings obtained with LTP are equal to or higher than those of samples, obtained with DETA. It may be, hence, concluded that LTP is a good hardener of epoxy resin.

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ИЗСЛЕДВАНЕ НА ТЕЧНИЯТ КАТРАНЕН ПРОДУКТ ОТ ПИРОЛИЗ НА КАЗЕИН ОТ МЛЯКО НА ЯК И НЕГОВОТО ПРИЛОЖЕНИЕ ПРИ ВТВЪРДЯВАНЕ НА ЕПОКСИДНА СМОЛА

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(Резюме)

Течният катранен продукт, получен при пиролиз на казеин от мляко на як беше изследван и бе използван при втвърдяване на епоксидна смола. Физико-химичните и топлинни характеристики, ИЧ и ^{1}Н ЯМР спектри бяха получени и сравнени със данните, получени от най-често използваният втвърдител диетилентриамин. Абсорбциите на течният катранен продукт бяха определени със количествен ИЧ-анализ. Втвърдяването на епоксидна смола беше правено при стайна температура за 24 ч. и при 105^{o}C за 150 мин. Оптималното количество на течният катранен продукт за достигане на максимална степен на омрежване при 105^{o}C е 22.22%; при стайна температура това е 20% смес със диетилентриамин 50:50 гр./гр. От физико-механичните характеристики на втвърдените пръти и покрития е установено, че изследваният продукт е добър втвърдител на епоксидни смоли.