Copolymerization of Turkish Tall Oil Specimens with Indene–Coumarone. I. Studies on Copolymerization of Tall Oil and Indene–Coumarone

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SYNOPSIS

In this study copolymerization of Turkish tall oil specimens with technical grade indene–coumarone fraction of coal-tar oils (bp 150–230°C) was investigated. The effects of temperature, the reaction time and reactant ratio on the reaction rate, and the composition of the resulting copolymer were determined. Based on these studies the optimal reaction conditions were established. Some main characteristics of these new type of tall oil/indene–coumarone copolymers were determined.

INTRODUCTION

Tall oil, consisting mainly of a mixture of C_{18} unsaturated fatty acids, resin acids and relatively small amounts of saturated fatty acids, and unsaponifiables, is one of the world's cheapest source of organic acids. It is obtained as a by-product in the manufacture of pulp by the sulfate or kraft process. With increasing production of sulfate pulp in the world, there is a corresponding increase in the availability of tall oil.

Indene and coumarone are also important unsaturated monomeric hydrocarbons present in the carbolic oil (bp 150–230°C) fraction of coal-tar oils.

Due to their chemical structures both tall oil and indene–coumarone are extremely reactive unsaturated substances, and they readily give diene addition reactions. Indeed, there are many literature references concerning the copolymerization of both tall oil and indene–coumarone, separately, with many of the olefinic monomers such as styrene, methyl styrene, cyclopentadiene, dicyclopentadiene, maleic anhydride, etc.[1] In the field of drying oils, only Kaufmann and Brünning[2] have studied the direct copolymerization of indene with some vegetable oils such as linseed, cottonseed, and soybean oils at 280°C.

In the scientific literature there is no record concerning the copolymerization of tall oil with indene–coumarone. Taking this into consideration, tall oil samples from SEKA Dalaman and Çaycuma Pulp and Paper Mills and indene–coumarone from Karabük Iron-Steel and Coal Coking Plants were obtained, and experiments on the copolymerization of these valuable by-products of Turkish origin were conducted.

The new copolymer products were developed and it was shown that these could be used in the field of organic surface coating.

EXPERIMENTAL

Materials

The general characteristics and compositions of these crude tall oil samples and their fatty and resin

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acid contents have been the subjects of a previous publication.[3] The experimental results are given in Table I. Here it may only be remarked that 7.7 and 16.1% of the fatty acid contents of Dalaman and Çaycuma tall oil specimens are of conjugated nature, respectively; a similar situation is also valid for their resin acid contents, being 73.4 and 65.0%, respectively.

In order to obtain light-colored and odorless refined tall oils, an acid-refining procedure was applied for tall oil samples.[4,5] Refined tall oils were used in all experiments of this study. Main characteristics of both refined tall oil samples are given in Table II.

For the preparation of indene–coumarone of technical purity, a standard refining process[6] was applied to carbolic oil fraction (bp 150–230°C), which was obtained from Karabük Coal-Tar Distillation Plants. Carbolic oil was washed first with caustic soda to remove the tar acids (phenols) and then with dilute sulfuric acid to remove tar bases such as pyridine. The carbolic oil was purified in a further stage by cooling and by crystallization in order to remove the dissolved naphthalene and the refined oil, called "neutral oil," was thus obtained.

In order to prepare indene–coumarone of technical purity in a high yield, several distillation treatments on this neutral oil were carried out under 15 mm Hg at atmospheric pressure at different temperature ranges. As a result of these preliminary experiments,[1] optimal distillation pressure and temperature range were found to be 15 mm Hg and 37–79°C, respectively. This fraction of neutral oil consisted of approximately 80% monomers of indene, and coumarone was used as a technical grade indene–coumarone throughout in this investigation.

Table I General Characteristics of Dalaman and Çaycuma Crude Tall Oil Samples

	Dalaman Tall Oil	Çaycuma Tall Oil
Acid value	169.3	140.7
Saponification value	173.3	160.0
Iodine value (Kaufmann)	179.1	175.8
Unsaponifiables (%)	6.8	13.2
Fatty acids content (%)	20.2	31.4
Resin acids content (%)	73.0	55.4
Ash content (%)	0.14	0.23
Moisture content (%)	0.81	0.31

Table II Main Characteristics of Refined Dalaman and Çaycuma Tall Oils

	Dalaman Refined Tall Oil	Çaycuma Refined Tall Oil
Acid number	165.1	148.5
Saponification number	169.3	161.4
Unsaponifiables (%)	1.8	5.0
Content of fatty acids (%)	24.8	37.0
Content of resin acids (%)	73.4	58.0

Synthesis and Analyses

The copolymerization reactions between tall oil and indene–coumarone have been conducted in Schott 24 788 type glass autoclave having 200 mL volume. The calculated amount of tall oil and indene–coumarone were placed in autoclave, and the autoclave was heated in a Heraeus FT 400 model oven for runs conducted with the range of temperature 185–260°C. At above 260°C, the autoclave was heated to desired temperature by electrical mantel. The heating was continued for the desired length of time; then the autoclave was allowed to cool.

At the end of the reaction, the final solution present in the autoclave is designed as a reaction product throughout this text.

Samples were withdrawn from the reaction product and the excess of (unreacted) indene–coumarone was removed from each sample using vacuum distillation at 135°C under 3–5 mm Hg pressure. The residue is also considered as the indene–coumarone copolymer of tall oil, briefly designed as copolymer throughout this investigation.

In order to evaluate the copolymerization experiments, density, refractive index, viscosity, acid,[7] and dien[8] values were experimentally determined, and the percent indene–coumarone in the copolymer and the ratio of decarboxylation were calculated for each run.

The amount of indene–coumarone that reacted with tall oil was calculated according to the known methods by both acid value and vacuum distillation methods.[9]

Establishing the Reactant Ratio

Assuming that the combination of tall oil with indene–coumarone takes place according to the Diels–Alder addition mechanism, one mole of indene–coumarone joins to the double bonds of one mole tall

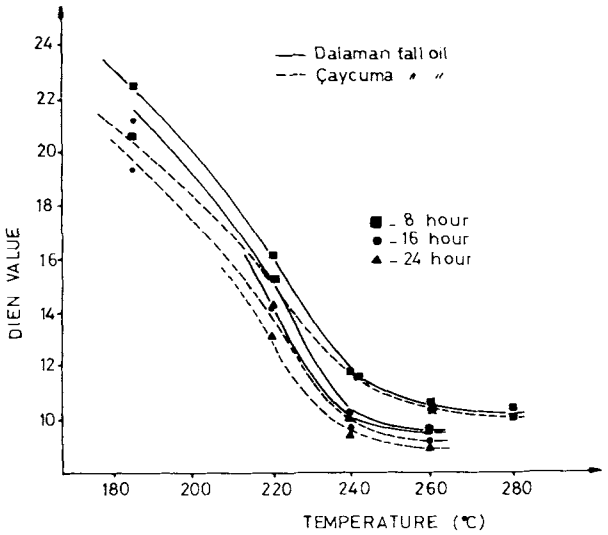

Figure 1 Variation of dien values of reaction products with temperature.

oil. Thus the reactant ratios were based on the dien values of tall oil specimens.

Results of preliminary experiments concerning the determination of tall oils' dien values by Ellis–Jones conventional method[8] were not accurate enough and showed no reproducibility. As it is known, in the Ellis–Jones method toluen (bp 110°C) is used as a common solvent, therefore, the reaction temperature cannot practically be raised above 110°C. In spite of this, a mixture of different resin acids with conjugated double bonds do not react with maleic anhydride below 150°C.[10] For this reason another solvent with some definite properties was needed; thus cyclohexanone (bp 155°C) as a neutral solvent immiscible with water, able to dissolve all the reactants, and having a boiling point higher than 150°C has been selected.

By modifying the Ellis–Jones method with the application of this new solvent, the dien values of Dalaman and Çaycuma specimens were found and theoretical amounts of indene–coumarone were calculated for each tall oil specimen and then applied in 100% excess for the preparation of reaction mixture. Thus, reactant ratio was established as 73 : 27 (tall oil/indene–coumarone) by mass for Dalaman and 74 : 26 for Çaycuma specimens, respectively.

Determination of Optimal Reaction Conditions

Because of the conjugated nature of tall oil samples, unlike the Kaufmann study,[2] the copolymerization reaction between tall oil and indene–coumarone might begin at temperatures lower than 280°C. Taking into consideration this fact, experiments on the copolymerization of our cited materials were conducted at large intervals of temperatures and heating periods.

In order to determine the suitable copolymerization temperature, two sets of experiments were conducted separately at 185, 220, 240, and 280°C for 8 h taking reactant ratios 73 : 27 for Dalaman and 74 : 26 for Çaycuma tall oil specimens, respectively.

The graphical representation of the results related to these experiments are shown in Figures 1–4. Owing to the similarity of the curves for the physical

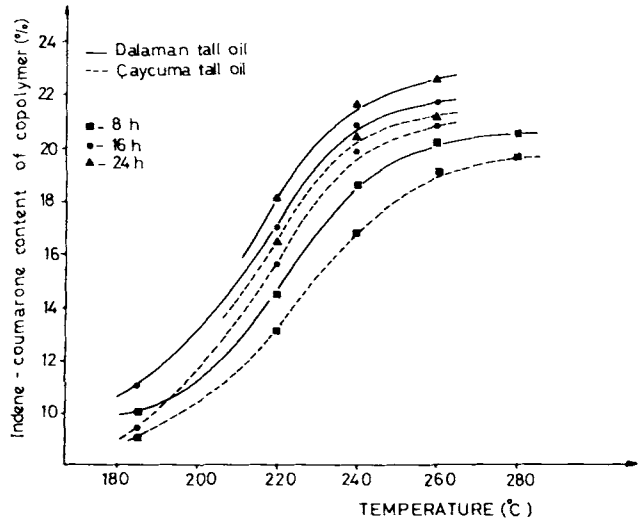

Figure 2 Variation of indene–coumarone content of copolymer with temperature.

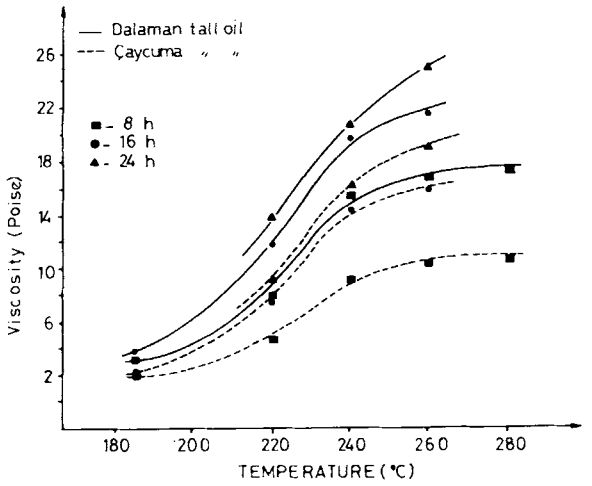

Figure 3 Variation of viscosity of reaction products with temperature.

properties (viscosity, density, refractive index), only the results for viscosity are shown in Figure 3, as a representative example.

In order to establish the suitable heating time, another two series of copolymerization experiments were run separately at 185, 220, 240, and 260°C for 16 and 24 h taking the same reactant ratios for each Dalaman and Çaycuma tall oil specimens. The results are also plotted in Figures 1–4.

Both tall oil specimens were then checked to see if thermal side reactions such as decarboxylation and homopolymerization occurred simultaneously. For this reason these tall oil specimens were heated

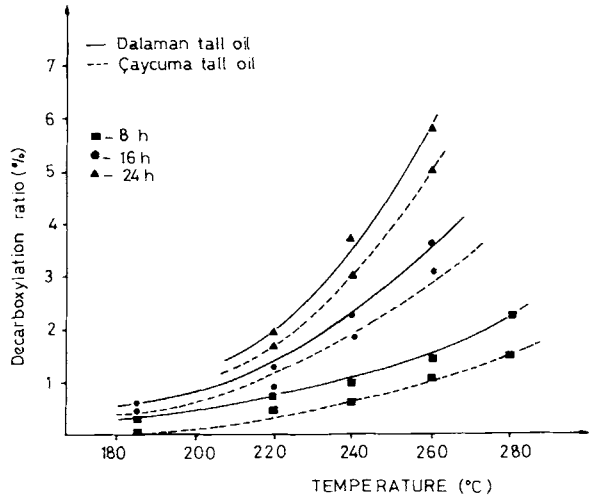

Figure 4 Variation of the ratio of decarboxylation with temperature.

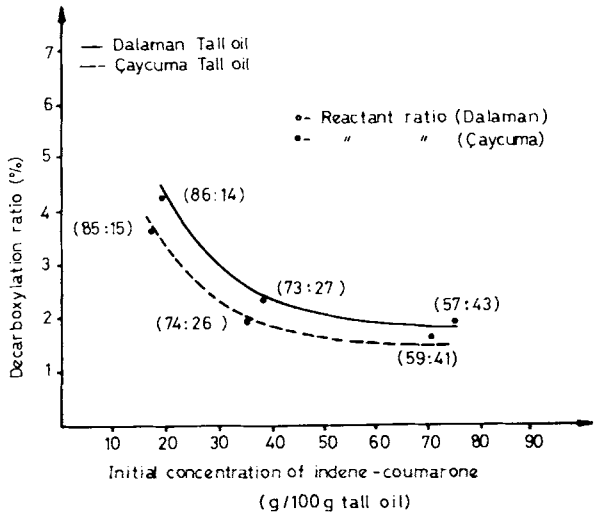

Figure 5 Variation of the ratio of decarboxylation with reactant ratio.

alone, without adding any component, in autoclave at 260°C for 24 h. After heat treatment, the obtained bulks were dissolved by adding the required amount of indene–coumarone to adjust the reactant ratio to 73 : 27 for Dalaman and to 74 : 26 for Çaycuma specimens, respectively. The properties of these resulting mixtures and of original initial mixtures are compared in Table III.

After establishing the optimal reaction conditions, in view of investigating the effect of the reactant ratio on the composition of resulting copolymer, two extra sets of experiments were conducted at these optimal conditions taking new reactant ratios 86 : 14 and 57 : 43 for Dalaman and 85 : 15 and 59 : 41 for Çaycuma tall oil specimens, respectively.

The final appropriate reactant ratios were established by the aid of curves shown in Figures 5 through 7.

Table III Total and Partial Iodine Values of Dalaman and Çaycuma Tall Oil Specimens

	Dalaman Tall Oil	Çaycuma Tall Oil
Iodine value (Woburn)	215.26	205.79
Partial iodine value (Kaufmann)	179.10	175.80
Calculated dien value	35.16	29.99
Experimental dien value by modified Ellis–Jones method	33.10	30.85

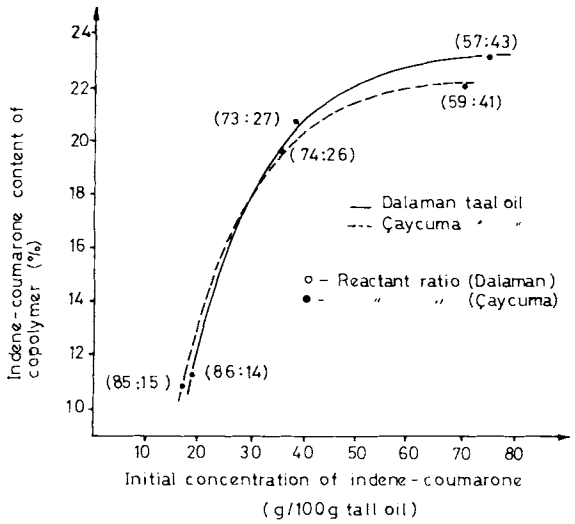

Figure 6 Variation of indene–coumarone content of copolymer with reactant ratio.

RESULTS AND DISCUSSION

It will be appropriate if we first start to discuss the successful adaptation of the Ellis–Jones method to substances like tall oil.

As stated earlier, the dien values by standard Ellis–Jones method[8] for tall oil specimens were not found to be accurate and reproducible; however, a reproducible value of 33.10 for Dalaman and 30.85 for Çaycuma specimens was obtained by means of cyclohexanone-modified Ellis–Jones method.

According to Mikusch and Frazier,[11,12] the Woburn iodine method can be used to determine total unsaturation of conjugated oils and fatty acids. And they also experimentally proved that the differential iodine value, in other words the difference between total and partial iodine values, is identical with the dien value of the substance.

Based on their studies, in order to verify our results, both total and partial iodine values of tall oil specimens were determined in accordance with the Woburn and Kaufmann methods, respectively. These experimental and calculated results are compared in Table IV.

From this comparison it is concluded that experimental results are in good agreement with calculated results within the error limits.

At first, the effects of temperature and heating period on the course of reaction and on the composition of the resulting copolymers were investigated.

All the curves in Figures 1–3 indicated that the temperature and heating period influenced considerably the course of copolymerization. The dien values of reaction products decreased rapidly for each sets of run with the range of temperature 185–240°C and then slowly approached almost the same value for each sample. The sharp decrease of dien values might be significant sign of reaction between indene–coumarone and conjugated double bonds of tall oil (see Fig. 1).

Indeed, the great increases in the indene–coumarone content of the copolymer would be also an indication of copolymerization reaction (see Fig. 2). The temperature had a remarkable effect on the progression of the reaction between 185 and 240°C for all heating periods.

At above 240°C, prolonging the heating period from 16 to 24 h did not change the chemical constitution of copolymers appreciably, however, as seen in Figure 3 the physical properties of these corresponding reaction products continued to rise. These continued increases might be due to the occurrence of side reactions of reactants.

As observed in Figure 4, both tall oil specimens decarboxylated rapidly at elevated temperatures as a function of reaction time. As is well-known, pure tall oil fatty and resin acids undergo decarboxylation and thermal polymerization particularly at high temperatures above 250°C.[12,13] In our study it was experimentally proved that these sorts of reactions also took place in tall oil even at temperatures lower than 250°C. This fact may be explained by the relatively high resin acid content of Turkish tall oil specimens. In fact, in the literature there is no record of tall oil with resin acid content as high as Dalaman tall oil.[3]

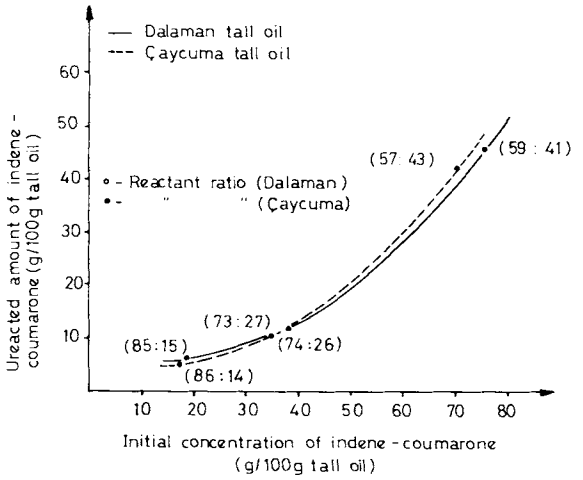

Figure 7 Variation of unreacted amount of indene–coumarone with reactant ratio.

Table IV Properties of the Mixtures Prepared with Tall Oil Heated at 260°C for 24 h and with Original Tall Oil

	Dalaman		Çaycuma	
	Mixture Prepared with Heat-treated Tall Oil	Mixture Prepared with Original Tall Oil	Mixture Prepared with Heat-treated Tall Oil	Mixture Prepared with Original Tall Oil
Dien value	22.89	24.8	20.70	22.21
Viscosity (20°C, cP)	387.7	289.9	234.4	130.1
Density (20°C, g/mL)	0.9842	0.9817	0.9821	0.9806
Refraction index [n_D(20°C)]	1.5384	1.5370	1.5371	1.5357
Acid value	109.74	119.96	101.82	109.01
The ratio of decarboxylation (%)	10.65	—	8.72	—

Both tall oil specimens were then checked to see whether side reactions such as decarboxylation and homopolymerization really occurred or not. From the examination of the results presented in Table IV, it was concluded that the quite noticeable changes, especially in viscosity and acid value, would be caused by thermal reactions of tall oil itself.[13,14]

In the literature it is stated that on being heated under pressure without catalyst, pure indene polymerizes very slowly up to 175°C; then the reaction becomes explosive.[15] For this reason the formation of polyindene and polycoumarone was not investigated under similar conditions.

Because of the tendency of tall oils to decarboxylate, which results in a poor product of drying oils,[16] it was necessary to find optimal conditions that would promote copolymerization as much as possible and at the same time cause minimum decarboxylation of the tall oils. Taking these criteria into consideration, 240°C and 16 h were admitted as optimal temperature and heating time.

According to our experimental results, it was noticed that although great differences were present between Dalaman and Çaycuma specimens in respect to their fatty and resin acids compositions mentioned in previous publication,[3] the individual experimental curves obtained from these specimens have been found to be almost similar to each other (see Figs. 1–7). Due to similar behaviors of Dalaman and Çaycuma specimens, optimal reaction conditions of cited specimens possessed practically the same value.

After establishing optimal conditions, in order to get a clear picture of how reactant ratios influence decarboxylation and copolymer composition, Figures 5 and 6 were plotted.

From the shapes of the curves in Figure 6, the amount of indene–coumarone present in reaction medium necessary for a significant effect, particularly at low concentrations is up to 30–35 g indene–coumarone per 100 g tall oil. After this certain concentration interval, further increases in concentration caused considerably less changes in the composition of the copolymers than that expected. On the other hand, it was also observed that the initial concentration of indene–coumarone had an inhibitory effect on the formation of decarboxylated products (see Fig. 5).

For choosing the optimal reactant ratios, in addition to the two criteria mentioned, the amount of unreacted indene–coumarone was also taken into consideration, and consequently the variation of unreacted amount of indene–coumarone with reactant ratio was investigated (see Fig. 7).

In order to minimize the unreacted amount of indene–coumarone, the final appropriate reactant ratios were established as 73 : 27 for Dalaman and 74 : 26 for Çaycuma tall oil specimens, respectively.

The copolymerization reaction most probably proceeds through the addition of indene–coumarone to the conjugated double bonds of tall oil. Although in this process the reaction temperature, heating period, and initial concentration of indene–coumarone are critical parameters, it is certain that at elevated temperatures above 240°C it was not possible to change the composition of copolymers to any great extents either by prolonging the reaction time (Fig. 2) or by increasing the initial concentration of in-

dene–coumarone (Fig. 6). Relatively small increases in percentage of indene–coumarone in copolymers might result by ordinary substitution reaction at these extreme conditions.[17]

CONCLUSION

In this investigation new types of tall oil copolymers containing indene–coumarone in their polymer structure were synthesized for the first time.

It is very important to point out that these optimal conditions are very moderate compared to the Kaufmann conditions.[2] The reaction between tall oil and indene–coumarone could begin readily at temperatures lower than 280°C. This can be explained in some degree with the conjugated nature of tall oil.[18,19]

These new types of copolymer-based products and their film properties showed that they could be used successfully in the field of organic surface coating. This section will be discussed in the following publication.

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