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## SYNTHETIC LUBRICANTS BASED ON COPOLYMERS OF *n*-BUTYL METHACRYLATE AND $\alpha$ -OLEFINS

*Synthetic fluids obtained by the copolymerization of  $\alpha$ -olefins with alkyl esters of unsaturated carboxylic acids have a unique combination of properties of non-polar poly- $\alpha$ -olefins (PAOs) and polar esters in a single molecule. These compounds are characterized by superior thermal, oxidative and hydrolytic stability, miscibility with mineral and synthetic base oils, solubility of additives and neutral elastomer behavior. Depending on the molar masses and comonomer ratios in the copolymer molecule, synthetic fluids with a wide range of properties are obtained. These compounds are valuable components in lubricating oil formulations for different applications.*

Synthetic lubricating oils have been used for more than 60 years due to severe requirements for the higher efficiency of internal combustion engines and machine tools, higher velocities and the serious need for saving fuel and energy, lubrication under extreme operating and weather conditions and growing environmental awareness.

The consumption of synthetic lubricants in Western Europe attains about 8% of the total lubricant production, while the global consumption is only about 3%, with the rate increasing 10–20% annually.

The properties of mineral base oils (obtained by classical solvent extraction technology) depend on the properties of the crude oil used. On the other hand, the properties of synthetic base fluids may be tailored according to needs.

Synthetic base fluids allow higher temperatures than the mineral ones, since they are characterized by higher thermal and oxidative stability and lower volatility. The consequences are prolonged oil drain intervals meaning lower oil consumption.

Compounds of different types have the properties mentioned above, but poly( $\alpha$ -olefins) and ester-based fluids (diesters – DE and neopolyoesters – NPE) are predominantly used [1,2,3].

Both product classes have significant advantages, but also some disadvantages resulting from their chemical composition. The main one is the poor solubility of additives PAOs and the low hydrolytic stability and interactions with sealing materials in the case of ester compounds. Therefore, PAO and ester oils are often blended in order to combine their properties. This need to combine the properties of both materials led to the idea for the synthesis of fluids with the properties of non-polar PAO and polar esters in a single

molecule. Such compounds are copolymers of  $\alpha$ -olefins and unsaturated acid esters [1,4,5] with mean molar masses usually lower than  $10^4$  g/mol. Depending on the comonomer ratio in the initial monomer mixtures, fluids of a wide viscosity range are obtained.

These products may be used as potentially valuable lubricant components.

### EXPERIMENTAL

Copolymers of *n*-butyl methacrylate (*n*-BMA) as the polar component and the  $\alpha$ -alkyl olefins:  $\alpha$ -dodecene ( $\alpha$ -DDC),  $\alpha$ -tetradecene ( $\alpha$ -TDC) and  $\alpha$ -hexadecene ( $\alpha$ -HDC) as the non-polar components were synthesized, using tert.-butyl perbenzoate as the initiator. The reagents made by Fluka were used without purification.

The radical copolymerizations at 160°C were carried out in a semiflow reactor for 10 hours. The initial comonomer (molar) ratio was varied from 0.5/1.0 to 2.0/1.0. The initiator concentration was 3.0 mass % and in some experiments 3.9 mass % of the comonomers. The synthesis was carried out as follows: the  $\alpha$ -olefin was poured into the reaction vessel and heated to 160°C. *n*-BMA was then added dropwise during prolonged time periods (1.5, 3.0 or 5.0 hours). The initiator was added to the reacting mixture portionwise (20 portions). After the last portion of initiator was added, the reaction mixture reacted for another hour at the same temperature and was then stopped.

The copolymers obtained were characterized by measuring the kinematic viscosity values,  $\nu$ , at 40°C and 100°C, pour point determinations and viscosity indices (VI) calculations.

The kinematic viscosities were determined according to JUS B.H8.02 using a Cannon-Fenske viscometer. The pour points were measured according to JUS B.H8.034. The viscosity indices (VI) were calculated using well-known empirical equations. The miscibility of the copolymer samples with mineral base oils SN 150,

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SN 60 and brightstock was examined by applying the Federal test method.

## RESULTS AND DISCUSSION

The copolymerizations were carried out in bulk at 160°C. The copolymers obtained were colorless oily liquids with kinematic viscosity values of 13–2185 mm<sup>2</sup>/s at 40°C and 4–142 mm<sup>2</sup>/s at 100°C, viscosity indices (VI) of 156–211 and pour points of –1°C to less than –40°C. The conversions were higher than 95%. Some of these results, which were chosen as representative, are presented.

### a) The influence of comonomer molar ratio

The properties of copolymers of  $\alpha$ -HDC (comonomer A) and *n*-BMA (comonomer B) are given in Table 1. The initiator concentration was 3 mass% and comonomer B was added to the reaction mixture for 5 hours.

Comparison of the values from Table 1 leads to the following conclusions. Increase of the *n*-BMA content in the reaction mixture, i.e. the change of the initial comonomer ratio from 1.0/0.5 to 1.0/2.0, results in a significant viscosity increase, a decrease in the viscosity indices and a decrease (improvement) of the pour point values.

Table 1. Kinematic viscosities at 40°C and 100°C, VI values and pour points for  $\alpha$ -HDC and *n*-BMA

Comonomer A	Comonomer B	mol ratio A/B	$v_{40}$ (mm <sup>2</sup> /s)	$v_{100}$ (mm <sup>2</sup> /s)	VI	$t_p$ (°C)
$\alpha$ -HDC	<i>n</i> -BMA	1.0/0.5	25.63	5.95	190	–1
		1.0/1.0	103.9	15.94	164	–6
		1.0/2.0	725.7	63.94	156	–12

### b) The influence of $\alpha$ -olefin chain length

The properties of copolymers of  $\alpha$ -DDC,  $\alpha$ -TDC and  $\alpha$ -HDC (comonomer A) and *n*-BMA (comonomer B) are given in Table 2. The initial molar ratio A/B was 1.0/1.0 and the initiator concentration was 3.0 mass %. Comonomer B was added to the reaction mixture for 5 hours.

The decrease of  $\alpha$ -olefin chain length results in a viscosity decrease, an increase (improvement) of the VI values and a decrease of the pour point values.

Table 2. Kinematic viscosities at 40°C and 100°C, VI values and pour points for  $\alpha$ -DDC,  $\alpha$ -TDC and  $\alpha$ -HDC – *n*-BMA copolymers

Comonomer A	Comonomer B	mol ratio A/B	$v_{40}$ (mm <sup>2</sup> /s)	$v_{100}$ (mm <sup>2</sup> /s)	VI	$t_p$ (°C)
$\alpha$ -DDC	<i>n</i> -BMA	1.0/1.0	63.90	11.40	174	<–40
$\alpha$ -TDC		1.0/1.0	89.04	14.43	169	–26
$\alpha$ -HDC		1.0/1.0	103.9	15.94	164	–6

### c) The influence of *n*-BMA addition to the reaction mixture

The time interval of *n*-BMA addition to the reaction mixture is a very important process parameter (Table 3).

The increase of the rate or the decrease of the time interval of *n*-BMA addition to the reaction mixture causes a significant viscosity increase and the VI indices and pour points do not change appreciably.

Table 3. Kinematic viscosities at 40°C and 100°C, VI values and pour points for  $\alpha$ -DDC – *n*-BMA copolymers

Comonomer A	Comonomer B	$\tau$ (h)	$v_{40}$ (mm <sup>2</sup> /s)	$v_{100}$ (mm <sup>2</sup> /s)	VI	$t_p$ (°C)
$\alpha$ -DDC mol. ratio	<i>n</i> -BMA A/B = 1/1	5.0	63.90	11.40	174	<–40
		3.0	75.62	13.09	176	<–40
		1.5	198.3	27.66	177	<–40

### d) The influence of initiator concentration

The initiator concentration was 3.0 and 3.9 mass %. Comonomer B ( $\alpha$ -DDC) was added to the reaction mixture for 3 hours. The molar comonomer ratio A/B was 1.0/0.5. The results for  $\alpha$ -DDC – *n*-BMA copolymers are given in Table 4.

The increase of initiator concentration results, as expected, in a decrease of viscosity, while the VI and  $t_p$  values remain practically unchanged.

Table 4. Kinematic viscosities at 40°C and 100°C, VI values and pour points for  $\alpha$ -DDC – *n*-BMA copolymers

Comonomer A	Comonomer B	IN (mass %)	$v_{40}$ (mm <sup>2</sup> /s)	$v_{100}$ (mm <sup>2</sup> /s)	VI	$t_p$ (°C)
$\alpha$ -DDC mol. ratio	<i>n</i> -BMA A/B=1.0/0.5	3.0	17.61	45.49	181	<–40
		3.9	3.60	12.57	186	<–40

### e) Miscibility with industrial base oils

The miscibility of some copolymer samples with industrial base oils SN 150, SN 60 and brightstock was examined and it was found that the copolymers and industrial base oils were completely miscible.

The viscosity indices of these mixtures were somewhat higher (by 5–10%) compared to the values calculated applying the single additivity rule.

## CONCLUSION

The copolymer samples are very clear, colorless, oily liquids, which are completely miscible with mineral base oils. The pour points of the copolymers range from –1°C to < –40°C, and the viscosity indices from 156 to 190. These properties qualify the copolymers as very good components of lubricating oils.

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## IZVOD

### SINTHETIČKA MAZIVA NA BAZI KOPOLIMERA *n*-BUTILMETAKRILATA I $\alpha$ -OLEFINA

(Naučni rad)

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Sintetička ulja na bazi poli( $\alpha$ -olefina) (PAO) ili estara karbonskih kiselina (diestri–DE i neopoliolestri–NPE) primenjuju se najčešće kada konvencionalna mineralna ulja ne mogu da zadovolje zahteve kvaliteta. Obe navedene grupe sintetičkih fluida imaju niz prednosti u poređenju sa mineralnim uljima (visoka vrednost indeksa viskoznosti, izražena termička i oksidaciona stabilnost, mala isparljivost), ali imaju i izvesne nedostatke, kao što je mala rastvorljivost aditiva (PAO) i nedovoljna hidrolitička stabilnost i interakcija sa zaptivnim materijalima (DE i NPE). Ove mane se u značajnoj meri ublažavaju korišćenjem smeša PAO i estara. Tako se javila ideja da se sintetizuju fluidi u čijim bi se molekulima kombinovala svojstva nepolarnih PAO i polarnih estara. To su kopolimeri  $\alpha$ -olefina i alkilestara karbonskih kiselina sa kontrolisanim sadržajem polarnih grupa, dobijeni radikalnom polimerizacijom uz peroksidne inicijatore. U zavisnosti od molske mase i odnosa komonomera, temperature, sadržaja inicijatora i načina njegovog unošenja u sistem i trajanja kopolimerizacije dobijaju se kopolimeri različitih svojstava. To su bezbojne, uljaste tečnosti širokog opsega viskoznosti i visoke vrednosti indeksa viskoznosti.

Sintetizovani su kopolimeri *n*-butilmetakrilata i tri  $\alpha$ -olefina ( $\alpha$ -dodecena,  $\alpha$ -tetradecena i  $\alpha$ -heksadecena) uz inicijator tercijarni butilperbenzoat. Proizvodima su određene temperature stinjanja, viskoznost na 40°C i 100°C i izračunati indeksi viskoznosti. Vrednosti navedenih parametara ukazuju na mogućnost korišćenja ovih kopolimera kao kvalitetnih komponenata mazivih ulja.

Ključne reči: Kopolimeri • Alfaolefini • Alkilestri nezasićenih kiselina •  
Key words: Copolymers • alpha-olefins • Unsaturated acid alkylesters •

