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Some styrene alkyl-methacrylate copolymers as viscosity index improvers

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Abstract

Styrene alkyl-methacrylate copolymers were synthesized at different monomer per cent ratios and under varied reaction conditions. Evaluation of obtained copolymers as viscosity index improvers in multigrade motor oils had been carried out in relation to different reaction variables and a comparative evaluation with commercially available viscosity index improvers in their performance properties (*e.g.* thermal oxidation and shear stabilities) was investigated.

Key words: Viscosity index improvers, multigrade motor oils, lubricating oils.

1. Introduction

Polymers have been used with lubricating oils to improve their pour points, dispersant efficiency, viscosity and viscosity index[1]. Many types of polymers have been used to improve viscosity and viscosity index in multigrade oil formulations. Most of them belong to the types[1-3]: Isobutylene copolymers, olefin copolymers, polyalkylmethacrylates and styrene hydrocarbon copolymers. Each of these additives has some performance merit but, on the other hand, also has some disadvantages[3-10], either with regard to thermo-oxidation stability or shear stability. While polyalkyl-methacrylates have high thermal and oxidation stabilities and moderate mechanical shear stability[3-5], styrene hydrocarbon copolymers show nearly the opposite features[2,6,8,9]

The work in this paper deals with the synthesis and evaluation of styrene alkyl-methacrylate copolymers as viscosity index improvers.

2. Experimental

The acrylate monomers used in the synthesis are: methyl-acrylate, methyl-methacrylate, n-butyl-methacrylate, dodecyl-methacrylate. Styrene monomer was used for copolymerization.

Monomers were activated by percolating them into a column packed with active silica-gel, which was previously heated at 120°C for 12 hours and then used for copolymerization reactions.

Table I
Reaction conditions applied to synthesis of styrene-alkyl-methacrylate copolymers

Reaction no.	Styrene mol.	Methyl acrylate mol	Alkyl-methacrylate mol.			Benzoyl peroxide % wt.	Reaction variables			Time, h
			methyl	n-butyl	dodecyl		Solvent	Polymer/ solvent ratio (vol)	Temp°C	
1.	0.76	0.24				1	Hexane	55/45	35	3
2.	0.29			0.71		1	Hexane	55/45	35	3
3.	0.5	0.5				3.25	Neutral light base oil	63/37	68	11
4.	0.5		0.5			3.5		63/35	75	6
5.	0.5				0.5	5		50/50	90	3
6.	0.34				0.66	5		60/40	90	11
7.	0.4			0.283	0.316	9		60/40	90	11
8.	0.453			0.36	0.187	8		60/40	90	11
9.	0.02			0.47	0.51	3.9		60/40	90	11
10.	0.176			0.765	0.059	8		60/40	90	11
11.	0.34			0.25	0.41	8		60/40	90	11

Eleven copolymerization reactions were carried out (Table I) by the addition of one of the activated monomers to the solvent medium in a three-necked flask equipped with a refluxing condenser, additional funnel, temperature control device and proper stirring system. Benzoyl peroxide was then added as a catalyst. After adjusting reaction temperature, other monomers were added dropwise (Table I, reactions 7-11) over a period of 2 hours and the reaction was continued up to the required duration. Pure nitrogen gas was passed into the flask through the reaction.

The structure of the synthesized copolymers was evaluated by using infrared spectrophotometry and microelemental analysis.

To evaluate the performance of synthesized copolymers as viscosity index improvers with respect to shear stability and thermal stability of various multigrade oil blends, the following routine analytical tests were carried out: Kinematic viscosity at 40 and 100°C (IP method 71), viscosity index (IP method 226), neutralization numbers (IP method 177), oxidation stability (IP method 280) and shear stability by diesel injector rig (IP method 294). Thermal stability of the blends was carried out by heating tested samples in an evacuated sealed ampoule at temperatures 175°C for 24, 48, 72 and 96 hr.

For comparative evaluation, two commercial viscosity index improvers, one based on polyalkyl-methacrylate structure, additive (A), while the other based on styrene-isoprene copolymer structure, additive (B), were employed. Same multi-function additive package was used in all formulations at the average of 6% wt.

3. Discussion

Reactions 1,2,3,4 and 5 carried out under Table I conditions gave undissolvable solid

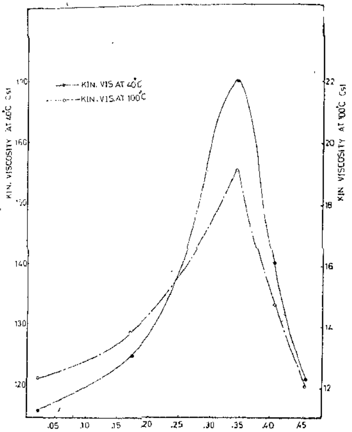

FIG. 1. Styrene content (% mol.) *vs* kinematic viscosity.

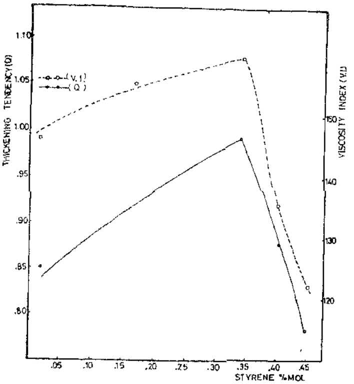

FIG. 2. Styrene content (% mol.) vs thickening tendency (Q) and viscosity index (V.I.).

copolymers. Trials to dissolve them in almost all solvents did not succeed. On the other hand, in reaction 6 (Table I) the use of alkyl-methacrylate with high carbon number (dodecyl-methacrylate) and proper neutral base oil as a solvent improved the solubility considerably. With good solubility it was therefore possible to complete the copolymerization reactions up to a period of 11 hr. In reactions 7-11 (Table I) introducing butyl group together with dodecyl group did not decrease the solubility of copolymer in base oil appreciably and consequently led to improvement in viscosity of copolymer/oil blend and good crosslinking. The resulting viscosity liquid copolymers were found soluble in most organic solvents.

3.1. Performance characteristics of synthesized copolymers

To study the effect of change in styrene content over performance properties of formulated multigrade oils, the synthesized copolymers were incorporated at concentration of 15% wt. The following is a summary of the conclusions:

Effect of styrene content

a. On viscosity properties: Maximum increase in viscosity (V), viscosity index (V.I.) and thickening tendency value (Q) are obtained at an optimum styrene content of 0.32-0.36 mol per mol copolymer (figs. 1 & 2).

b. On shear stability: Increase in styrene content beyond 0.34 mol results in remarkable decrease in shear stability (fig. 3).

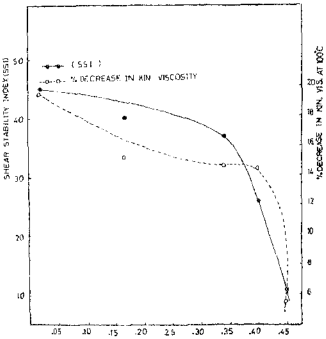

FIG. 3. Styrene content (% mol.) vs shear stability index (SSI) and % decrease in kinematic viscosity.

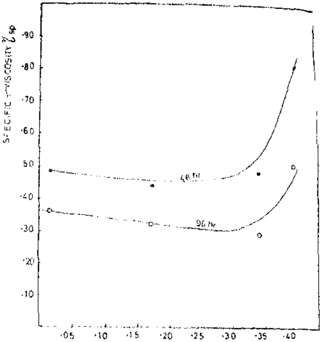

FIG. 4. Styrene content (% mol.) *vs* specific viscosity (η_{sp}) after thermal stability test at 175°C.

c. On thermal stability and specific viscosity: Specific viscosities are nearly the same up to 0.34 mol styrene but above this range increase of specific viscosity results in a decrease in the thermal stability (fig. 4).

d. Effect of change in alkyl-methacrylate content: The effect of change in alkyl-methacrylate content on performance properties was pronounced only in the n-butyl and dodecyl monomers. Increase of n-butyl-methacrylate content up to 0.35 mol range decreases viscosity and viscosity index but above this range starts to increase stepwise. Also an optimum dodecyl-methacrylate content in the range of 0.39–0.45 mol gave maximum increase in viscosity and viscosity index (fig. 5). Such effect might be due to the partial improvement of the copolymer solubility. It is more pronounced at high (100°C) than at low temperature (40°C).

3.2. Comparative evaluation of synthesized copolymers (Reaction II) with commercially available viscosity index improvers (A and B).

The three viscosity index improvers (reaction 11, additives (A) & (B)) were incorporated at different concentrations (over a range from 3 to 20% wt.) in multigrade oil formulations. All these tested formulations contained a multifunction additive package at 6% wt. concentration.

— Change in concentration: Blends containing synthesized styrene alkyl-methacrylate copolymer at 15% wt. in multigrade oil formulations have good balance in their viscosity properties (fig. 6).

— Increase in viscosity of blend *a*, containing additive (A), is stepwise, and indicates relatively low ability towards oxidation without thermal breakdown of the copolymer molecule (fig. 7).

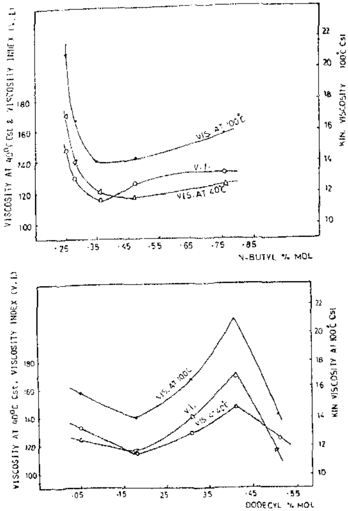

Fig. 5. Alkyl methacrylates (% mol.) *vs* kinematic viscosity at 40 and 100°C and viscosity index (V.I.).

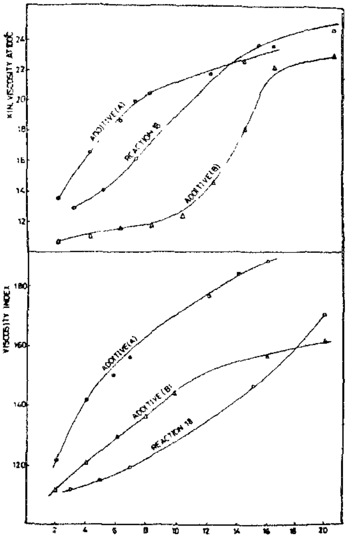

Fig. 6. Viscosity index improver (% wt.) *vs* oil blend viscosity at 100°C and viscosity index.

- Remarkable decrease in viscosity of blend *b*, containing additive (B), indicates thermal breakdown of the copolymer molecule at a magnitude relatively higher than that comes as a result of oxidation (fig. 7).
- Change in viscosity of blend *c* falls in the intermediate range of the other two blends.
- The total base no (TBN) of the three blends decrease as a result of oxidized products formed by the multifunction additive. Rate of neutralization of blend *c* is intermediate of the other two blends (fig. 7).
- Shear stability of blends containing additive (A) is inferior to those of blends containing either synthesized styrene alkly-methacrylate copolymer or additive (B), especially at high additive concentration, while the shear stability of blends containing synthesized copolymer fall in the intermediate to both the tested commercial viscosity index improvers (fig. 9).

Shear tests at temperatures of 37.8 and 150°C for blends *a,b* & *c* show the superiority in shear stability of blend *b* with styrene hydrocarbon copolymer even at a temperature of 150°C, while the shear stability of blend *c*, falls in between the other two blends (fig. 10).

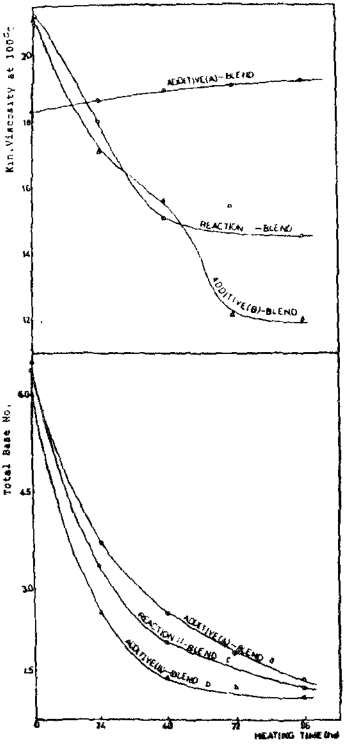

FIG. 7. Evaluation of thermal stability of tested viscosity index improvers at 175°C - viscosity and total base no. against heating time.

Additive (A) at μ% wt., Additive (B) at 20% wt., Reaction 11 at 5% wt.

4. Conclusion

Styrene alkyl-methacrylate copolymers were synthesized at different monomer per cent ratios and under varied reaction conditions of temperature, solvent, duration of copolymerization, etc. Optimum performance properties acquired by the copolymer was established as: styrene 0.34; butyl-methacrylate 0.25; dodecyl-methacrylate 0.41 mol, temperature 90°C and copolymerization duration 11 hr.

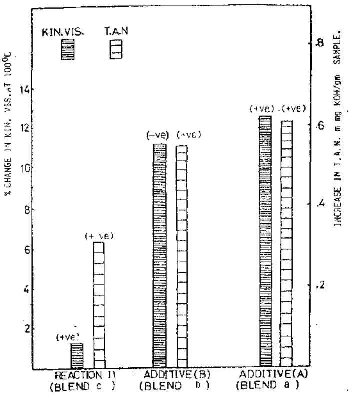

FIG. 8. Evaluation of oxidation stability, % change in kinematic viscosity at 100°C and increase in T.B.N. of tested blends.

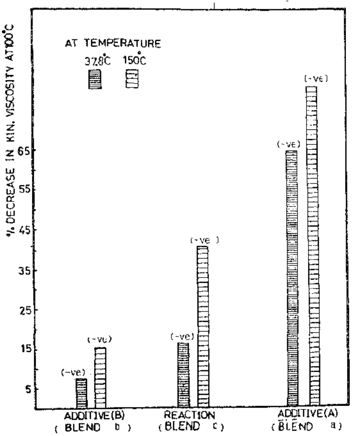

FIG. 10. Evaluation of shear stability by Bosch pump injection, percentage decrease in kinematic viscosity at 100°C.

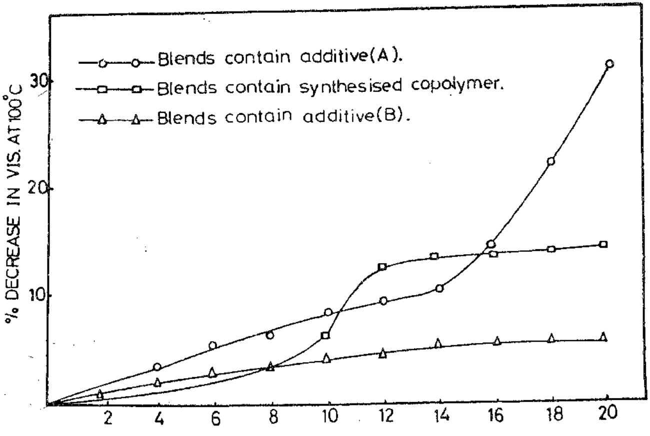

FIG. 9. Evaluation of shear stability, percentage decrease in viscosity at 100°C vs V.I. improver (% wt.) of tested blends.

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