Zvonimir Janović, Ante Jukić, Elvira Vidović, Jakov Romano, Ankica Barišić, Meri Picek

ISSN 0350-350X
GOMABN 43, 2, 87-108
Izvorni znanstveni rad / Original scientific paper
UDK665.761.2.038.62/.64 : 678.742 : 66.095.26-922 : 678.744.33 : 678.744.33 : 665.761.2

POLIMERNI ADITIVI MINERALNIH MAZIVIH ULJA NA TEMELJU TERPOLIMERA ALKIL-METAKRILATA I STIRENA

Sažetak

Ispitana su reološka primjenska svojstva otopina priređenih polimernih aditiva na temelju terpolimera stirena, dodecil-metakrilata i oktadecil-metakrilata u mineralnom baznom ulju, u području sastava do w (ST) = 25 mas. %. Aditivi su dobiveni procesom šaržne polimerizacije smjese monomera u otopini mineralnog ulja uz peroksidni inicijator i izotermne uvjete, pri 100ºC. Konverzija monomera u polimer određena je ^{1}H NMR spektroskopijom, a raspodjela i vrijednosti molekulnih masa kromatografijom isključenja po veličini. Porastom udjela stirena u monomernoj smjesi smanjuju se početna brzina reakcije i molekulne mase terpolimera. Određene su kinematičke viskoznosti otopina pri 40 ºC i 100 ºC, indeks viskoznosti, smična stabilnost i tecište i njihova ovisnost o sastavu i strukturi polimernih aditiva. Kinematička viskoznost raste s porastom molekulne mase terpolimera i ne mijenja se značajno s promjenom sastava aditiva. Vrijednosti indeksa viskoznosti smanjuju se s povećanjem udjela stirena i nalaze se u rasponu od 150 do 180, dok se smična stabilnost povećava s povećanjem udjela stirena u terpolimeru i smanjenjem molekulne mase polimera. Povećanjem udjela stirena smanuje se stinište otopina.

Istraživanja su pokazala da su polimerni aditivi za poboljšanje indeksa viskoznosti baznih mineralnih ulja na temelju stirena i alkil-metakrilata primjenjivi i u potpunosti usporedivi s komercijalnim aditivima na temelju metakrilatnih terpolimera. Dobiveni rezultati omogućuju optimiranje procesa i svojstava aditiva promjenom procesnih čimbenika, te sastava i strukture terpolimera prema zahtjevima proizvoda.

UVOD

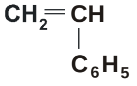
Polimerni aditivi mineralnih mazivih ulja na temelju n-alkil-metakrilata, najčešće smjese triju monomera, pripadaju skupini najznačajnijih reoloških modifikatora, posebice poboljšivača indeksa viskoznosti i depresanata stiništa[1,2]. Najčešće su to dugolančani, linearni terpolimeri sastavljeni od monomera s promjenjivim udjelom bočnih alkilnih skupina, pretežito C_1-C_{18}, a njihov omjer tako je podešen da osigurava optimalna uporabna svojstva. Osim o sastavu, primjenska svojstva polimernih aditiva ovise o većem broju strukturnih čimbenika, posebice topljivosti, viskoznosti otopina, molekulnim masama i njihovoj raspodjeli, temperaturnim konformacijskim promjenama molekula, veličini, udjelu i rasporedu sekvencija ponavljanih jedinica, vrsti i veličini bočnih alkilnih skupina kao i vrsti i svojstvima otapala, baznog mineralnog ulja[3-5]. U zadnje vrijeme, razvitak metakrilnih aditiva usmjeren je prema dobivanju i primjeni polimera na temelju dugolančanih n-alkilnih metakrilata i vinilnih monomera bez pokrajnjih skupina, kao što je stiren i njegovi derivati[6,7]. Polimeri na temelju stirena posjeduju veću toplinsku postojanost[8,9], a porastom udjela stirena u kopolimeru povećava se i veličina statističkih konformacija makromolekula, što izravno povećava i viskoznost otopina prema metakrilatnim aditivima za jednake koncentracije i jednake molekulne mase. Prisutne metakrilatne bočne alkilne skupine srednje veličine (C_{12}) pretežito utječu na konformacijske promjene makromolekula s temperaturom, dok dugolančane bočne skupine (C_{18}) doprinose smanjenju stiništa otopine[10]. Pri tome, veći udjel stirena u tim kopolimerima je ograničen međutim njihovom topljivošću.

U ovom radu opisan je postupak dobivanja i svojstva polimernih reoloških modifikatora mineralnih mazivih ulja na temelju terpolimera stirena, dodecil- i oktadecil-metakrilata. Polimerni aditivi priređeni su procesom polimerizacije u otopini uz peroksidne inicijatore, u izotermnim uvjetima. Prikazani su i opisani rezultati utjecaja sastava i strukture aditiva na važnija primjenska svojstva otopina u baznom mineralnom ulju, posebice viskoznost, indeks viskoznosti, smična stabilnost i stinište.

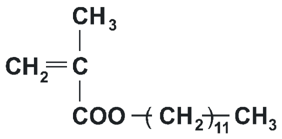
EKSPERIMENTALNI DIO

Materijali

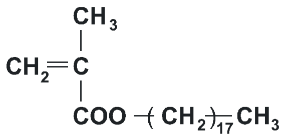
Monomeri, stiren (ST), DIOKI, Zagreb; dodecil-metakrilat (DDMA) i oktadecil-metakrilat (ODMA), RohMax Chem Co., Njemačka. Inicijator, tert-butil-peroksi-2-etilheksanoat (Trigonox 21), Akzo Chemie, Nizozemska. Bazno ulje, INA Rafinerija Rijeka: a) oznake SN-150, kinematička viskoznost 25,7 $mm^2\ s^{-1}$ pri 40 ℃ i 4,7 $mm^2\ s^{-1}$ pri 100 ℃, indeks viskoznosti 97 i tecište -12 ℃ ; b) oznake SN-200, kinematička viskoznost 40,6 $mm^2\ s^{-1}$pri 40 ℃ i 6,3 $mm^2\ s^{-1}$ pri 100 ℃, indeks viskoznosti 104 i tecište -9 ℃.


$CH_2{=}CH(C_6H_5)$

ST


$CH_2{=}C(CH_3)COO(CH_2)_{11}CH_3$

DDMA


$CH_2{=}C(CH_3)COO(CH_2)_{17}CH_3$

ODMA

Metode

Raspodjela i prosječne molekulne mase polimera, $\bar{M}_n$ i $\bar{M}_w$, određene su metodom kromatografije isključenja po veličini (SEC, Polymer Laboratories GPC 20) u otapalu tetrahidrofuranu i uz polistiren kao standard. Ostatni, nereagirani monomer određen je gravimetrijski i ^1H NMR spektroskopijom. Reološka svojstva polimernog aditiva u baznom mineralnom ulju (SN-200) utvrđena su normiranim metodama: kinematička viskoznost, ASTM D-445; indeks viskoznosti, ASTM D-2270; smična stabilnost, DIN-51382 i tecište, ISO 3016.

Proces polimerizacije

Smjesa stirena i metakrilatnih monomera u baznom mineralnom ulju SN-150, koncentracije 2 M, polimerizirana je u reaktoru volumena 1 L s plaštem za grijanje i hlađenje, spojenim na protočni uljni termostat; pod atmosferom dušika i u izotermnim temperaturnim uvjetima pri 100 ºC. Reakcija polimerizacije inicirana je tert-butil-peroksi-2-etilheksanoatom (vrijeme poluraspada, $t_{1/2}$ = 1 h pri 91 ºC). Kinetička istraživanja do niskih konverzija provedena su dilatometrijskom metodom. U procesima polimerizacije vođenim do visokih konverzija (reaktor), inicijator je dodavan u obrocima, s ciljem postizanja što manjeg ostatnog, nereagiranog monomera i veće učinkovitosti inicijatora.

REZULTATI I RASPRAVA

Kinetički model reakcije terpolimerizacije

U najjednostavnijem pristupu modeliranju reakcije terpolimerizacije radikalnim mehanizmom (terminalni model, inicijacija monofunkcionalnim inicijatorom), tri temeljna rastuća makroradikala mogu reagirati s trima prisutnim monomerima, pa se zbog razlika u reaktivnostima sastav nastalog terpolimera u pravilu razlikuje od sastava smjese monomera[4,7,11]. U šaržnim procesima to dovodi do nastajanja kopolimera različitog sastava koji se mijenja s konverzijom monomera u polimer, tzv. *konverzijske heterogenosti*. Samo u slučaju *azeotropne kopolimerizacije*, sastav kopolimera jednak je sastavu početne smjese monomera tijekom čitave konverzije. Ovisnost trenutačnog sastava kopolimera o sastavu smjese monomera opisuje se jednadžbom terpolimerizacije, kako je to prikazano u našim prijašnjim radovima[12].

Za praktične svrhe, potrebno je dobiti ujednačeni sastav polimera, jer se tako osiguravaju njegova odgovarajuća fizikalna i mehanička svojstva. Zbog toga je važno odrediti azeotropne sastave, u kojima je za sustav od tri monomera, sastav nastalog terpolimera jednak sastavu smjese monomera ($F_i = f_i$ za i = 1, 2, 3) i ne mijenja se s konverzijom. Razlikuju se i pojedinačni te binarni azeotropni sastavi. Kod pojedinačnih azeotropnih sastava molni udjel jednog od monomera u reakcijskoj smjesi jednak je molnom udjelu u terpolimeru ($f_i = F_i$). Kod binarnih azeotropnih sastava molni omjer dvaju monomera u reakcijskoj smjesi jednak je njihovom molnom omjeru u nastalom terpolimeru (f_i / f_j = F_i / F_j). Pravi azeotropni sastavi mogu se grafički prikazati kao točke u trokomponentnom, trokutnom dijagramu sastava. Pojedinačni, odnosno binarni azeotropni sastavi u takvom dijagramu tvore *krivulje azeotropnih sastava*. Krivulje pojedinačnih i binarnih azeotropa, te azeotropna točka mogu se izračunati, uz poznate vrijednosti omjera kopolimerizacijskih reaktivnosti[13], numeričkom integracijom diferencijalnog oblika Alfrey-Goldfingerove jednadžbe terpolimerizacije:

$$
\begin{aligned}
& \mathrm{d}c_{\mathrm{M}_1} : \mathrm{d}c_{\mathrm{M}_2} : \mathrm{d}c_{\mathrm{M}_3} = \\
& c_{\mathrm{M}_1}\left\{\frac{c_{\mathrm{M}_1}}{r_{31}r_{21}}+\frac{c_{\mathrm{M}_2}}{r_{21}r_{32}}+\frac{c_{\mathrm{M}_3}}{r_{31}r_{23}}\right\}\left\{c_{\mathrm{M}_1}+\frac{c_{\mathrm{M}_2}}{r_{12}}+\frac{c_{\mathrm{M}_3}}{r_{13}}\right\}: \\
& c_{\mathrm{M}_2}\left\{\frac{c_{\mathrm{M}_1}}{r_{12}r_{31}}+\frac{c_{\mathrm{M}_2}}{r_{12}r_{32}}+\frac{c_{\mathrm{M}_3}}{r_{32}r_{13}}\right\}\left\{c_{\mathrm{M}_2}+\frac{c_{\mathrm{M}_1}}{r_{21}}+\frac{c_{\mathrm{M}_3}}{r_{23}}\right\}: \\
& c_{\mathrm{M}_3}\left\{\frac{c_{\mathrm{M}_1}}{r_{13}r_{21}}+\frac{c_{\mathrm{M}_2}}{r_{23}r_{12}}+\frac{c_{\mathrm{M}_3}}{r_{13}r_{23}}\right\}\left\{c_{\mathrm{M}_3}+\frac{c_{\mathrm{M}_1}}{r_{31}}+\frac{c_{\mathrm{M}_2}}{r_{32}}\right\}
\end{aligned}
$$

Na slici 1 prikazane su krivulje binarnih azeotropnih sastava za reakciju terpolimerizacije stirena (ST, M_1), dodecil-metakrilata (DDMA, M_2) i oktadecil-metakrilata (ODMA, M_3). Simbolima su naznačeni eksperimentalni sastavi smjese monomera (w_{ST} = 5, 10, 15, 20 i 25 mas. %; $w_{DDMA} : w_{ODMA}$ = 3:1).

Utjecaj sastava smjese monomera na brzinu reakcije terpolimerizacije određen je uz promjenjiv udjel stirena i uz stalni maseni omjer DDMA/ODMA = 3/1. Početne brzine, R_p, u kvazistacionarnim uvjetima odvijanja reakcije terpolimerizacije (k_t = konst.), izračunate su iz rezultata dilatometrijskih mjerenja. Iz dobivenih je rezultata vidljivo da se porastom udjela stirena u smjesi monomera brzina polimerizacije (slika 2.) i prosječne molekulne mase terpolimera (slika 3) smanjuju, vjerojatno zbog manje brzine reakcije propagacije uzrokovane većom (rezonantnom) stabilnošću stirenskih jedinica[8]. Slijedi, da se trajanje procesa polimerizacije, odnosno vrijeme potrebno za postizanje određene jednake konverzije monomera u polimer značajno povećava s povećanjem udjela stirena u početnoj smjesi monomera, odnosno oko dva puta duže vrijeme za svako povećanje udjela stirena od ~1,5 mas. %, od početnih 3 mas. % do ukupno 12 mas. % stirena u smjesi monomera.

Konverzija monomera, X, za reakcije terpolimerizacije provedene do visokih konverzija, u ovisnosti o vremenu polimerizacije, t_p, za smjese monomera s najmanjim (w_{ST} = 5 mas. %) i najvećim (w_{ST} = 25 mas. %) sadržajem stirena prikazane su na slici 4. Vidljivo je da se povećanjem udjela stirena u smjesi monomera za proces polimerizacije s obročnim dodavanjem inicijatora, krivulja ovisnosti konverzije o vremenu približava idealnoj, linearnoj ovisnosti. Također je postignuta potpuna konverzija monomera u polimer, za smjese svih sastava, i u razmjerno kratkom vremenu za polimerizacije s velikim udjelom stirena i temperaturu reakcije od 100 ºC. Na slici 5. prikazane su prosječne molekulne mase i indeks polidisperznosti (M_w / M_n), u ovisnosti o konverziji, odnosno vremenu polimerizacije, za smjesu s udjelom stirena od 25 mas. %. Vidljivo je da masena prosječna molekulna masa i indeks polidisperznosti rastu s porastom konverzije; međutim, u zadnjem stupnju reakcije, pri konverzijama većim od 90 %, dolazi do naglog povećanja masene prosječne molekulne mase, i sukladno tomu velikog, nepoželjnog porasta polidisperznosti, koji se može negativno odraziti na uporabna svojstva polimera, posebice smičnu stabilnost[14].

Primjenska reološka svojstva polimernog aditiva

Važnija primjenska svojstva otopina polimernih aditiva u mineralnom mazivom ulju jesu: kinematička viskoznost otopina na temperaturama 40 i 100 ºC, stabilnost polimernih makromolekula prema smičnim naprezanjima, indeks viskoznosti (temperaturna ovisnost viskoznosti) prije i poslije testa smične stabilnosti, toplinska postojanost i temperatura tecišta, odnosno stinište[5]. Vrijednosti primjenskih reoloških svojstava za 5 mas. % otopine ST/DDMA/ODMA polimernog aditiva u mineralnom baznom ulju SN-200, u ovisnosti o sadržaju stirena, prikazane su grafički slikama 6-11. Za usporedbu, na slikama su naznačene i istovrsne vrijednosti ili područja za komercijalni uzorak terpolimera s metil-metakrilatom umjesto stirena (Viskokril 100, INA - Maziva Zagreb). Najvažnije svojstvo mineralnih mazivih ulja je viskoznost. Na slici 6. prikazana je ovisnost kinematičke viskoznosti otopina aditiva o sadržaju stirena u kopolimeru pri 40 i 100 ºC. Stoga je važno istaknuti da čak i polimerni aditiv s najvišim sadržajem stirena u terpolimeru, 25 mas. %, daje visoku vrijednost viskoznosti, ≥ 14 $mm^2\ s^{-1}$ pri 100 ºC. Smanjenje viskoznosti s povećanjem sadržaja stirena, osim sastava posljedica je i strukture polimera s obzirom da se povećanjem udjela stirena u terpolimeru smanjuju i prosječne molekulne mase (slika 7), a time i viskoznost[4,8,12]. Slijedi da je s povećanjem udjela stirena u monomernoj smjesi potrebno izabrati takve procesne uvjete, kao što su koncentracija monomera, temperatura, postupno dodavanje inicijatora i odabrana koncentracija regulatora molekulnih masa, da se postigne zahtijevana viskoznost otopine.

Izmjerene vrijednosti prikazane na slici 8 ukazuju da se smična stabilnost aditiva povećava porastom udjela stirenskih jedinica u kopolimeru, i smanjenjem njegove prosječne molekulne mase (slika 7). Za otopine polimera s udjelom stirena većim od

10 mas. % dobivaju se niske vrijednosti indeksa smične stabilnosti, < 15 (aditiv na osnovi metil-, dodecil- i oktadecil-metakrilata najčešće ima vrijednosti između 16 i 19). Takvo ponašanje posljedica je promjena u veličini hidrodinamičkog volumena makromolekula u otopini, koji je funkcija kemijskog sastava i strukture polimera, M_w, M_n, IP, koncentracije i temperature, kao i međudjelovanja polimera i otapala[3-5], a može se prema W.M. Kulickeu opisati sljedećom jednadžbom[15]:

$$\gamma_{\mathrm{deg}} = [1 + K_{\mathrm{H}} c[\eta] + B_{\mathrm{n}} (c[\eta])^{\frac{3.4}{\mathrm{a}} - 1}]^{-1/\mathrm{n}} \lambda_{\mathrm{o}}^{-1}$$

gdje je γ_{deg} kritična brzina smicanja kod koje dolazi do mehaničke degradacije makromolekula (u motorima s unutarnjim izgaranjem $10^5 – 10^7$ s^{-1}), λ_o relaksacijsko vrijeme, *c* koncentracija, [η] unutarnji viskozni broj, a K_H, B_n, *a* i *n* odgovarajuće konstante. Međutim, najčešće se smična stabilnost polimernih otopina opisuje smanjenjem viskoznosti i indeksom smične stabilnosti koji je jednak:

$$\mathrm{SSI} = (\nu_1 - \nu_2) \times 100 / \nu_1$$

gdje su ν_1 i ν_2 vrijednosti kinematičke viskoznosti otopine prije, odnosno nakon provedbe testa smične stabilnosti. Sastav i strukturna svojstva polimernog aditiva također značajno utječu i na promjenu viskoznosti otopina s promjenom temperature, odnosno indeksa viskoznosti i stiništa. Utjecaj temperature na promjenu viskoznosti za otopine gdje se priroda otapala ne mijenja značajno s temperaturom (vrijedi za bazna mineralna ulja) opisuje se jednadžbom[16]:

$$\frac{d \ln \eta_{\mathrm{sp}}}{dT} = \frac{K_1 d(\ln(½ - \chi_1))}{dT} + \frac{K_1 d(\ln(V_2^2 / V_1))}{dT} + \frac{K_2 d(\ln < r >_{\mathrm{o}}^2)}{dT} + \frac{K_3 d(\ln c)}{dT}$$

gdje je χ Florijev čimbenik međudjelovanja, K_i funkcije čimbenika viskozimetrijskog širenja, a V_2 i V_1 specifični volumeni polimera i otapala. Za istraživane sastave terpolimera ST/DDMA/ODMA može se zaključiti da imaju visoke vrijednosti indeksa viskoznosti s tim da je to smanjenje veće nakon provedbe testa smične stabilnosti za polimere s manjim udjelom stirena (slika 9). S obzirom na istovjetnu ovisnost smične stabilnosti o sastavu, indeks viskoznosti funkcija je i veličine molekulske mase. Povećanjem udjela stirena raste stinište (slika 10), a to povećanje može se podijeliti u dva, linearno ovisna područja. U prvom području, stinište postupno raste od -33 °C za udjel od 5 mas. % stirena na -27 °C za udjel stirena od 15 mas. %. U drugom dijelu s većim nagibom linearne ovisnosti, stinište raste do -9 °C za sadržaj stirena od 25 mas. %. Ta je vrijednost jednaka onoj čistog baznog ulja, bez dodataka, što je posljedica smanjene topljivosti terpolimera s velikim udjelom stirena, posebice pri niskim temperaturama. Stoga bi pri primjeni takvih polimernih aditiva, s visokim udjelom stirena, bilo nužno poboljšati njegova niskotemperaturna svojstva dodatkom posebnih metakrilatnih aditiva. Na snižavanje temperature stiništa moguće je također utjecati i promjenom sastava polimera, odnosno povećanjem udjela oktadecil-metakrilata u polimeru, što će biti predmet daljnjih istraživanja, budući da takvi polimeri pokazuju vrlo dobra svojstva viskoznosti, indeksa viskoznosti i smične stabilnosti[17].

Važna veličina kojom se može opisati mazivost ulja osim navedenih svojstava, omjer je specifičnih viskoznosti pri 100 i 40 ºC, koji se naziva *Q* čimbenik i izračunava prema jednadžbi[18]:

$$Q = \frac{\eta_{\mathrm{sp}}(100\ ^{\mathrm{o}}\mathrm{C})}{\eta_{\mathrm{sp}}(40\ ^{\mathrm{o}}\mathrm{C})} = \frac{(v_{100,\mathrm{UA}} - v_{100,\mathrm{U}})/v_{100,\mathrm{U}}}{(v_{40,\mathrm{UA}} - v_{40,\mathrm{U}})/v_{40,\mathrm{U}}}$$

gdje *U* i *UA* označavaju otopine čistog baznog ulja i baznog ulja s polimernom aditivom. Izračunate vrijednosti za sve ispitane sustave prikazane su na slici 11. Dobivene vrijednosti mjera su utjecaja ugušćivanja (engl.: thickening effect), odnosno učinkovitosti podmazivanja. Vrijednosti *Q* > 1, ukazuju da polimerni aditiv poboljšava indeks viskoznosti budući da je ugušćivanje izraženije pri 100 ºC nego na 40 ºC. U idealnom slučaju *Q* = 1, što znači da ugušćavanje ne ovisi o temperaturi. Premda obje veličine, i indeks viskoznosti i *Q* čimbenik, proizlaze iz vrijednosti viskoznosti, među njima nema izravne povezanosti. Prema dobivenim rezultatima prikazanim na slici 11, može se zaključiti da se ugušćivanje s povećanjem sadržaja stirena u kopolimeru smanjuje pri visokim temperaturama, a pri nižim temperaturama povećava. Važno je zamijetiti da se te vrijednosti ne razlikuju značajnije od idealne vrijednosti, što ukazuje na ravnomjernu učinkovitost podmazivanja s promjenom temperature, za polimerne aditive s širokim područjem udjela stirena.

ZAKLJUČCI

Reakcijom terpolimerizacije smjese monomera, stirena, dodecil-metakrilata i oktadecil-metakrilata, mehanizmom slobodnih radikala u otopini dobivaju se terpolimeri sa svojstvima aditiva mineralnih mazivih ulja.

U izotermnim reakcijskim uvjetima postižu se potpune konverzije monomera u polimer uz smanjenje početnih brzina reakcije i molekulnih masa s porastom udjela stirena do, *w* (ST) = 25 mas. %.

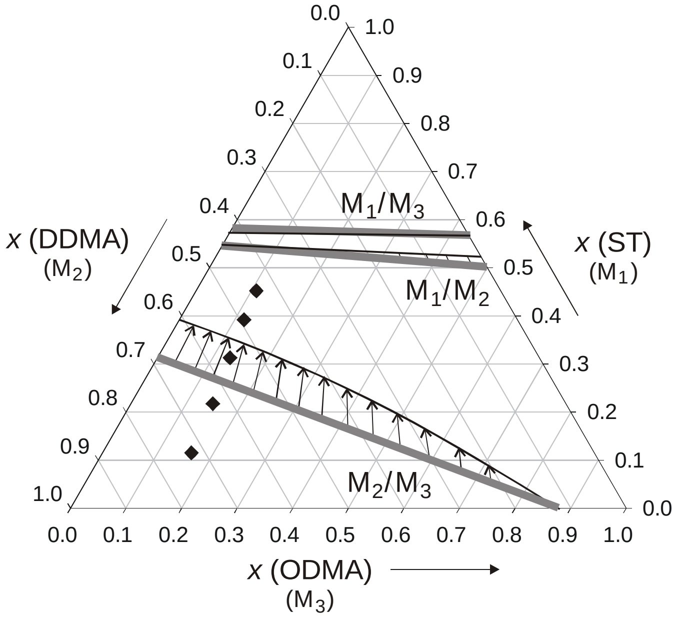
Kinematička viskoznost otopina pri 40 ºC i 100 ºC raste s porastom molekulne mase terpolimera i ne mijenja se značajno s promjenom sastava aditiva; dobivene vrijednosti veće su od onih dobivenih za otopine metakrilatnih aditiva.

Vrijednosti indeksa viskoznosti smanjuju se od početnih vrijednosti, 180, do 150 s povećanjem udjela stirena u terpolimeru i smanjenjem molekulne mase polimera.

Povećanjem udjela stirena u terpolimeru linearno se smanuje stinište otopina od -33 ºC za udjel od 5 mas. % stirena na -27 ºC za udjel stirena od 15 mas. %, s većim nagibom linearne ovisnosti, do -9 ºC za sadržaj stirena od 25 mas. %.

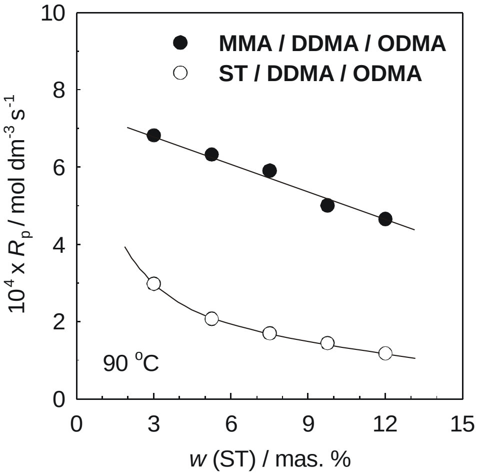
Smična stabilnost povećava s povećanjem udjela stirena u terpolimeru i smanjenjem molekulne mase polimera.

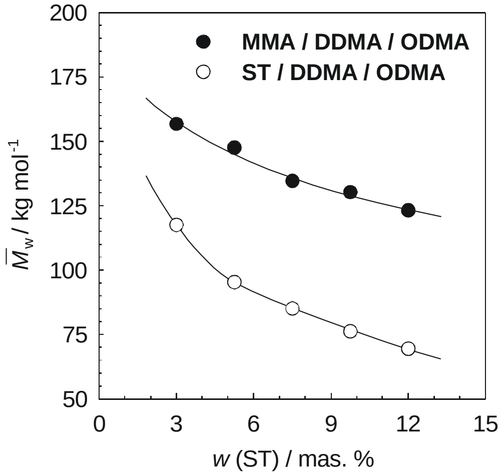
Slika 1: Krivulje binarnih azeotropnih sastava za terpolimerizacijski sustav stirena, dodecil- i oktadecil-metakrilata; ♦ – eksperimentalni sastavi smjese monomera.



Slika 2: Početna brzina reakcije terpolimerizacije u ovisnosti o sadržaju stirena u smjesi monomera stirena, dodecil- i oktadecil-metakrilata.

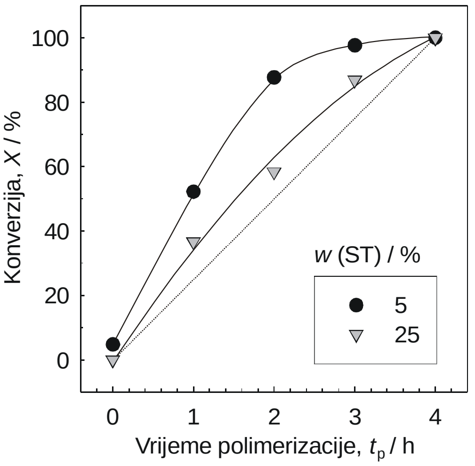
Slika 3: Prosječne molekulne mase polimera u ovisnosti o sadržaju stirena u smjesi monomera stirena, dodecil- i oktadecil-metakrilata.

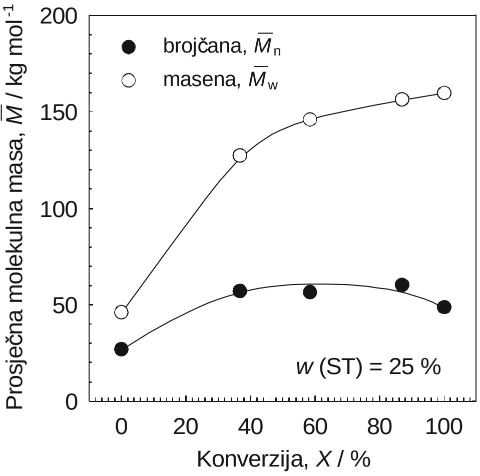




Slika 4: Konverzija monomera u ovisnosti o vremenu polimerizacije stirena, dodecil- i oktadecil-metakrilata u baznom mineralnom ulju pri 100 ºC.

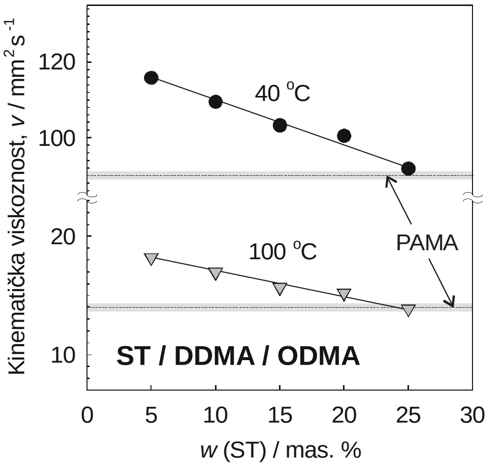
Slika 5: Prosječna molekulna masa u ovisnosti o konverziji procesa polimerizacije stirena, dodecil- i oktadecil-metakrilata u baznom mineralnom ulju pri 100 ºC.

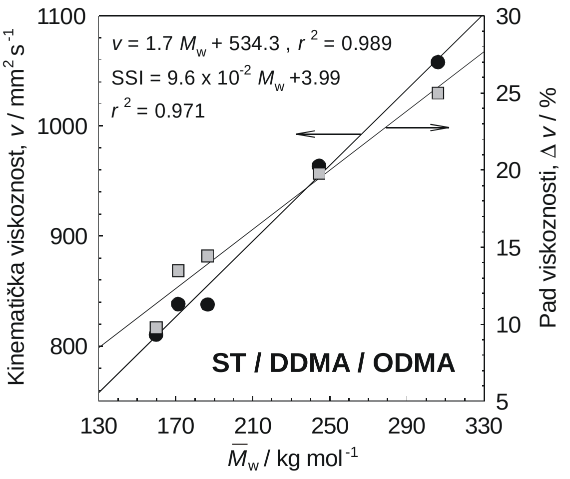




Slika 6: Kinematička viskoznost 5 mas. % otopina ST/DDMA/ODMA polimernog aditiva u baznom mineralnom ulju u ovisnosti o sastavu, na 40 i 100 ºC.

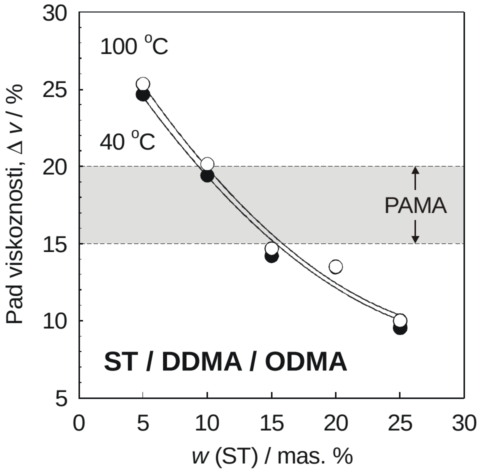
Slika 7: Kinematička viskoznost i indeks smične stabilnosti otopina ST/DDMA/ODMA polimernog aditiva (50 mas. % za viskoznost i 5 mas. % za Δv) u baznom mineralnom ulju u ovisnosti o prosječnoj molekulnoj masi polimera.

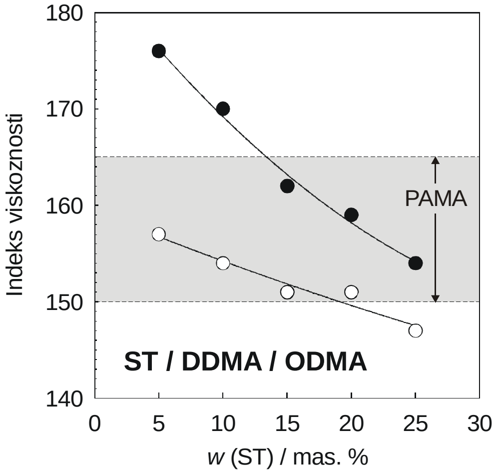




Slika 8: Smična stabilnost (pad viskoznosti) 5 mas. % otopina ST/DDMA/ODMA polimernog aditiva u baznom mineralnom ulju u ovisnosti o sastavu, na 40 i 100 ºC.

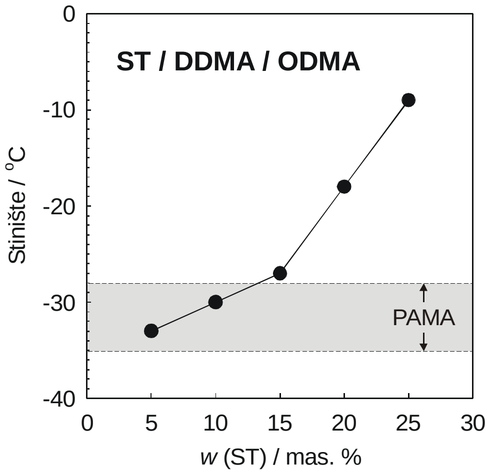
Slika 9: Indeks viskoznosti 5 mas. % otopina ST/DDMA/ODMA polimernog aditiva u baznom mineralnom ulju u ovisnosti o sastavu, prije (●) i poslije (○) provedbe testa smične stabilnosti.

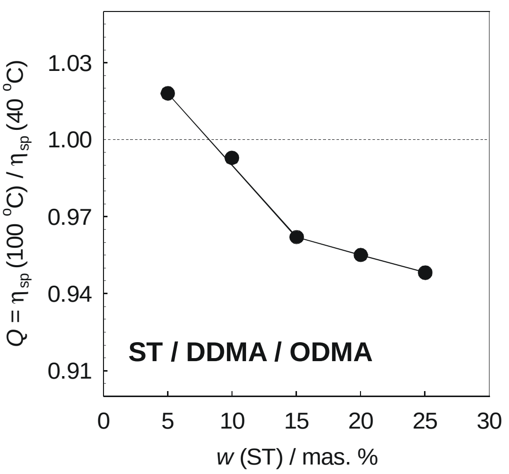




Slika 10: Stinište 0,5 mas. % otopina ST/DDMA/ODMA polimernog aditiva u baznom mineralnom ulju u ovisnosti o sastavu.

Slika 11: Omjer specifičnih viskoznosti na 100 i 40ºC, *Q*, 5 mas.% otopina ST/DDMA/ODMA polimernog aditiva u baznom mineralnom ulju u ovisnosti o sastavu.





LUBRICATING MINERAL OIL POLYMERIC ADDITIVES BASED ON STYRENE AND ALKYL METHACRYLATE TERPOLYMERS

Abstract

The applicative rheological properties of prepared polymeric additives on the basis of styrene, dodecyl methacrylate and octadecyl methacrylate in the composition range of up to 25 wt. % of styrene in base mineral oil solutions have been examined. In addition, terpolymerization reaction was thoroughly investigated. The monomer conversions were estimated by ^{1}*H NMR spectroscopy and the average molecular weights by size exclusion chromatography. The low conversion terpolymers showed a good agreement between experimental and theoretical composition data, calculated from the Alfrey-Goldfinger's terpolymerization equation. The conversional heterogeneity and lines of unique and binary azeotropic compositions were also established. The high conversion polymerizations as 50 wt. % solution of the monomer mixture in base mineral oil were carried out under isothermal reaction conditions, at 100 ºC, with peroxide initiation. By increasing styrene content in the monomer mixture, both the initial reaction rate and the molecular weight of obtained terpolymers were decreased.*

The rheological properties of polymeric additive solutions in base mineral oil were established by kinematic viscosity, viscosity index, shear stability and pour point temperature determinations. It was found that the kinematic viscosity does not change significantly in dependence of terpolymer composition and shows a linear dependence on molecular weight. Increase of styrene content in the additive resulted in a decrease of viscosity index from 176 (w_{ST} *= 5 wt. %) to 150 (*w_{ST} *= 25 wt. %), while the shear stability index also decreased. The pour point temperature increased first slightly, from -33 ºC to -27 ºC (*w_{ST} *= 15 wt. %), and then sharply. Based on the ratio of specific viscosities at 40 and 100 ºC (Q factor), for investigated additives, the value of 0.95 was obtained, which is very close to that of PAMA (Q = 1.05), showing the similar thickening effect.*

The obtained results have demonstrated that the efficiency of additives on the basis of styrene/methacrylate terpolymers is fully comparable with that of purely methacrylic additives and gives prospects for their properties' optimization through composition and structural changes.

INTRODUCTION

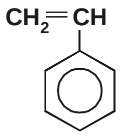
Polymeric additives of mineral lubricating oils based on n-alkyl methacrylates, most often the compound of three monomers, pertain to the group of most significant rheological modifiers, particularly viscosity index improvers and pour point depressants[1,2]. Most frequently, they are long-chained, linear terpolymers consisting of monomers with a changeable share of lateral alkyl groups, mostly C_1-C_{18}, while their ratio is set so as to ensure optimal application properties. Apart from the composition, the application properties of polymeric additives are also dependent on a number of structural factors, particularly solubility, viscosity of solutions, molecular weights and their distribution, temperature conformation changes of molecules; size, share and distribution of the repeated units sequences; kind and size of lateral alkyl groups, as well as type and properties of the solvent, the base mineral oil[3-5]. Recently, the development of methacrylic additives has been directed towards obtaining and application of copolymers based on long-chained n-alkyl methacrylates and vinyl monomers without side groups, such as maleic anhydride, N-methyl pyrolidone, styrene and its derivatives[6,7]. Polymers based on styrene have a higher thermal persistence[8,9], while with a higher share of styrene in the copolymer increases also the size of statistical conformations of macromolecules, directly increasing also the viscosity of solutions towards methacrylate additives for equal concentrations and equal molecular weights. The present methacrylate lateral alkyl groups of medium size (C_{12}) cause mostly conformation changes of macromolecules with the temperature, while the long-chained lateral groups (C_{18}) contribute to the lowering of the solution's pour point[10]. Therefore, a higher share of styrenes in these copolymers is, however, limited by their solubility.

The present paper describes the procedure of obtaining, as well as the properties of polymeric rheological modifiers of mineral lubricating oils based on terpolymers of styrene, dodecyl- and octadecyl methacrylate. Polymeric additives were prepared through polymerization process in a solution with peroxide initiators, under isothermal conditions. Presented and described are the results of the additive composition structure and on significant application properties of solutions in base mineral oil, especially viscosity, viscosity index, shear stability and pour point.

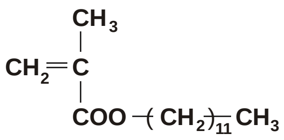
THE EXPERIMENTAL PART

Materials

Monomers, styrene (ST), DIOKI, Zagreb; dodecyl methacrylate (DDMA) and octadecyl methacrylate (ODMA), RohMax Chem Co., Germany. Initiator, tert-butyl-peroxi-2-ethylhexanoate (Trigonox 21), Akzo Chemie, Netherlands. Base oil, INA Refinery Rijeka: a) mark SN-150, kinematic viscosity 25.7 $mm^2\ s^{-1}$ at 40 °C and 4.7 $mm^2\ s^{-1}$ at 100 °C, viscosity index 97 and pour point -12 ° C; b) mark SN-200, kinematic viscosity 40.6 mm^2 s^{-1}at 40 ℃ and 6.3 mm^2 s^{-1} at 100 ℃, viscosity index 104 and pour point -9 ℃.

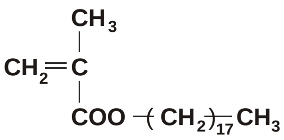


ST



$$CH_2{=}C(CH_3){-}COO{-}(CH_2)_{11}{-}CH_3$$

DDMA



$$CH_2{=}C(CH_3){-}COO{-}(CH_2)_{17}{-}CH_3$$

ODMA

Methods

The distribution and average molecular weights of polymers, $\bar{M}_n$ and $\bar{M}_w$, were determined by size exclusion chromatography method (SEC, Polymer Laboratories GPC 20) in tetrahydrofurane as solvent and polystyrene as standard. The residual, non-reacted monomer was determined gravimetrically and by ^{1}H NMR spectroscopy. The rheological properties of the polymeric additive in base mineral oil (SN-200) were determined using the following standardized methods: kinematic viscosity, ASTM D-445; viscosity index, ASTM D-2270; shear stability, DIN-51382 and pour point, ISO 3016.

The Polymerization Process

The mixture of styrene and methacrylic monomers in base mineral oil SN-150, of concentration 2 M, was polymerized in the double jacked reactor with volume of 1 L connected to the rapid oil thermostate; under nytrogen atmosphere and isothermic temperature conditions at 100 ºC. The polymerization reaction was initiated using tert-butyl-peroxy-2-ethylhexanoate (half-life time, $t_{1/2}$ = 1 h at 91 ºC). Kinetic measurements down to low conversions were performed using dilatometric method. In polymerization processes conducted up to high conversions (reactor), the initiator was added per portions, with the purpose of achieving as low as possible a quantity of residual, non-reacted monomer and higher initiator efficiency.

RESULTS AND DISCUSSION

Kinetic Model of Terpolymerization Reaction

In the simplest approach to the modelling of terpolymerization reaction using radical mechanism (terminal model, initiation through a monofunctional initiator), three basic growing macroradicals may react with the three present monomers, and so due to the differences in reactivities, the composition of generated terpolymer as a rule differs from the monomer mixture composition[4,7,11]. In batch processes, this leads to the generation of copolymers of different composition changed through monomer conversion into polymer, the so called *conversion heterogeneity*. Only in the case of *azeotropic copolymerization*, the composition of copolymers equals that of the initial monomer mixture throughout the conversion. The dependence of the actual copolymer composition on the composition of monomer mixture is described by terpolymerization equation, as shown in our previous papers[12]. For practical purposes, one must obtain an even polymer composition, for this is how its proper physical and mechanical properties are being ensured. That is why it is important to determine the azeotropic compositions, in which - for the system of three monomers - the composition of the generated terpolymer equals that of the monomer mixture ($F_i = f_i$ for i = 1, 2, 3) and does not change through conversion. The unitary, as well as binary azeotropic compositions, also differ. In the case of unitary azeotropic compositions, the molar share of one among the monomers in the reaction mixture equals the molar share in the terpolymer ($f_i = F_i$). In the case of binary azeotropic systems, the molar share of two monomers in the reaction mixture equals their molar ratio in the generated terpolymer (f_i / f_j = F_i / F_j). The real azeotropic compositions may be shown graphically as points in the threecomponential, triangular diagram of the system. Unitary i.e. binary azeotropic compositions in such a diagram create the *curves of azeotropic systems*. The curves of individual and binary azeotropes, as well as the azeotropic point, may be calculated - with the known values of the copolymerization reactivities ratios[13] - through numerical integration of the differential form of Alfrey-Goldfinger's terpolimerization equation:

$$\mathrm{d}c_{\mathrm{M_1}} : \mathrm{d}c_{\mathrm{M_2}} : \mathrm{d}c_{\mathrm{M_3}} =$$

$$c_{\mathrm{M_1}}\left\{\frac{c_{\mathrm{M_1}}}{r_{31}r_{21}} + \frac{c_{\mathrm{M_2}}}{r_{21}r_{32}} + \frac{c_{\mathrm{M_3}}}{r_{31}r_{23}}\right\}\left\{c_{\mathrm{M_1}} + \frac{c_{\mathrm{M_2}}}{r_{12}} + \frac{c_{\mathrm{M_3}}}{r_{13}}\right\}:$$

$$c_{\mathrm{M_2}}\left\{\frac{c_{\mathrm{M_1}}}{r_{12}r_{31}} + \frac{c_{\mathrm{M_2}}}{r_{12}r_{32}} + \frac{c_{\mathrm{M_3}}}{r_{32}r_{13}}\right\}\left\{c_{\mathrm{M_2}} + \frac{c_{\mathrm{M_1}}}{r_{21}} + \frac{c_{\mathrm{M_3}}}{r_{23}}\right\}:$$

$$c_{\mathrm{M_3}}\left\{\frac{c_{\mathrm{M_1}}}{r_{13}r_{21}} + \frac{c_{\mathrm{M_2}}}{r_{23}r_{12}} + \frac{c_{\mathrm{M_3}}}{r_{13}r_{23}}\right\}\left\{c_{\mathrm{M_3}} + \frac{c_{\mathrm{M_1}}}{r_{31}} + \frac{c_{\mathrm{M_2}}}{r_{32}}\right\}$$

Figure 1 shows the curves of binary azeotropic compositions for the terpolymerization reaction of styrene (ST, M_1), dodecyl-methacrylate (DDMA, M_2) and octadecyl-methacrylate (ODMA, M_3). Simbols mark the experimental compositions of monomer mixture (w_{ST} = 5, 10, 15, 20 and 25 wt. %; $w_{\mathrm{DDMA}} : w_{\mathrm{ODMA}}$ = 3:1).

The impact of the monomer mixture composition on the rate of terpolymerization reaction is determined by changeable styrene share and constant mass ratio DDMA/ODMA = 3/1. Initial rates, R_p, under quasi-stationary conditions of terpolymerization reaction development (k_t = const.), were calculated from the results of dilatometric measurements. The obtained results show that, with increased styrene share in the monomer mixture, the polymerization rate (Figure 2) and the average molecular weights of terpolymers (Figure 3) decrease, probably due to the lower rate of the propagation reaction caused by higher (resonant) stability of styrene units[8]. It follows that the polymerization process duration, i.e. the time necessary for achieving a certain equal conversion of monomer into the polymer increases significantly with the increase of styrene share in the initial monomer mixture, i.e. that the time is around two times longer for each styrene share increase of ~1.5 wt. %, from the initial 3 wt. % to the total of 12 wt. % of styrene in the monomer mixture.

Conversion of monomers, X, for terpolymerization reactions conducted up to high conversions, in dependence of polymerization time, t_p, for monomer mixtures with the lowest (w_{ST} = 5 wt. %) and the highest (w_{ST} = 25 wt. %) styrene content are shown in Figure 4. It may be seen that, with the increase of styrene share in monomer mixture for the polymerization process with the initiator being added per portions, the curve of conversion dependence on time approaches that ideal, linear. A complete conversion of monomer into polymer has also been achieved, for the mixtures of all compositions, and within a rather short polymerization time for a high share of styrene and reaction temperature of 100 ºC. Figure 5 shows structural properties of synthesized terpolymer, average molecular weight and index polydispersion index (M_w / M_n), in dependence of conversion i.e. polymerization time, for the mixture with styrene share of 25 wt. %. It may be observed that the mass average molecular weight and polydispersion index increase with conversion growth; however, in the last reaction phase, at conversions higher than 90 %, there occurs an abrupt increase of the mass average molecular weight, and hence also a considerable, undesirable polydispersion increase, which may bear a negative impact on the application properties of polymers, especially shear stability[14].

The Applicative Rheological Properties of the Polymeric Additive

More significant application properties of polymeric additive solutions in mineral lubricating oil are as follows: kinematic viscosity of solutions at temperatures of 40 and 100 ºC, stability of polymeric macromolecules towards shear stress, viscosity index (temperature dependence of viscosity) before and after shear stability test, thermal persistence and the pour point temperature[5]. Values of applicative rheological properties for 5 wt. % solutions of ST/DDMA/ODMA polymeric additive in mineral base oil SN-200, in dependence of styrene content, are shown in Figures 6-11. For comparison's sake, the Figures also indicate the same values or areas for the commercial terpolymer sample with methyl methacrylate instead of styrene (Viskokril 100, Maziva Zagreb). The most important property of mineral lubricating oils is viscosity. Figure 6 shows the dependence of kinematic viscosity of additive solutions on the styrene content in copolymer at 40 and 100 ºC. That is why it is important to point out that even the polymeric additive with the highest content of styrene in terpolymer, 25 wt. %, provides a high viscosity value, ≥ 14 $mm^2\ s^{-1}$ at 100 ºC. Viscosity lowering with styrene content increase is not only the result of composition, but also of the polymer structure, since the increase of styrene share in terpolymer reduces average molecular weights (Figure 7), and hence also viscosity[4,8,12]. It follows that, with the increase of styrene share in the monomeric mixture, one must choose such process conditions, such as monomer concentration, temperature, gradual addition of initiator and selected concentration of the molecular weight regulator, in order to achieve the demanding solution viscosity.

The measured values presented in Figure 8 show that the shear stability of additives increases with the increase of the share of styrene units in the copolymer, and the lowering of its average molecular weight (Figure 7). For polymer solutions with styrene content higher than 10 wt. %, low values of shear stability index are obtained, < 15 (additive based on methyl-, dodecyl- and octadecyl-methacrylate most frequently has values between 16 and 19). Such behaviour is the result of changes in the size of hydrodinamic volume of macromolecules in the solution, which is the function of the chemical composition and structure of polymers, M_w, M_n, IP, concentration and temperature, as well as the interactivity of the polymer and the solvent[3-5], while – according to W.M. Kulicke – it may be described with the following equation[15]:

$$\gamma_{\mathrm{deg}} = [1 + K_\mathrm{H} c[\eta] + B_\mathrm{n} (c[\eta])^{\frac{3.4}{\mathrm{a}} - 1}]^{-1/\mathrm{n}} \lambda_\mathrm{o}^{-1}$$

where γ_{deg} is the critical shear velocity where a mechanical degradation of macromolecules occurs (in internal combustion engines 10^5 – 10^7 s^{-1}), λ_o relaxation time, c concentration, $[\eta]$ inner viscosity number, and K_H, B_n, a and n respective constants. However, the shear stability of polymeric solutions is most frequently described by viscosity lowering and shear stability index equalling:

$$\mathrm{SSI} = (\nu_1 - \nu_2) \times 100 / \nu_1$$

where ν_1 and ν_2 are the solution's kinematic viscosity values before and after the shear stability test, respectively. The composition and structural properties of polymeric additive also have a considerable impact on the solutions' viscosity change with the change of temperature, i.e. viscosity index and pour point. The impact of temperature on viscosity change for solutions where the nature of the solvent does not change considerably with temperature (which is true of base mineral oils) is described with the following equation[16]:

$$\frac{d \ln \eta_{\mathrm{sp}}}{dT} = \frac{K_1\, d(\ln(½ - \chi_1))}{dT} + \frac{K_1\, d(\ln(V_2^2 / V_1))}{dT} + \frac{K_2\, d(\ln \langle r \rangle_\mathrm{o}^2)}{dT} + \frac{K_3\, d(\ln c)}{dT}$$

where χ is the Flory's interactivity factor, K_i functions of viscometric spread factors, and V_2 and V_1 specific volumes of polymer and solvent. For the investigated compositions of terpolymers ST/DDMA/ODMA we may conclude that they have high viscosity index values, the lowering being more pronounced after the shear stability test for polymers with a lower share of styrene (Figure 9). Given the same dependence of shear stability on the composition, the viscosity index is a function also of the molecular weight size. Increased styrene share causes pour point to raise, while this increase may be divided in two lineary dependent areas. In the first area, the pour point gradually increases from -33 ºC for a 5 wt. % styrene share to -27 ºC for a styrene share of 15 wt. % (Figure 10). In the second part, with the greater linear dependence inclination, the pour point increases up to -9 ºC for styrene content of 25 wt. %. This value is equal to that of pure base oil, with no additions, which is probably due to lowered solubility of terpolymers with a high share of styrene, especially at low temperatures. That is why in the application of such polymer additives with a high styrene content it would be necessary to improve its low temperature properties by adding special metacrylic additives. The pour point temperature reduction may also be achieved by changing polymer composition i.e. by increasing its octadecyl-metacrylate share, which will be the object of further research, since such polymers show very good properties of viscosity, viscosity index and shear stability[17].

An important value which may describe oil lubricity apart from the above properties is the ratio of specific viscosities at 100 and 40 ºC, called Q factor and calculated according to the following equation[18]:

$$Q = \frac{\eta_{\mathrm{sp}}(100\ ^{\mathrm{o}}\mathrm{C})}{\eta_{\mathrm{sp}}(40\ ^{\mathrm{o}}\mathrm{C})} = \frac{(v_{100,\mathrm{UA}} - v_{100,\mathrm{U}})/v_{100,\mathrm{U}}}{(v_{40,\mathrm{UA}} - v_{40,\mathrm{U}})/v_{40,\mathrm{U}}}$$

where *U* and *UA* are solutions of pure base oil and base oil with polymer additive. Values calculated for all tested systems are shown in Figure 11. The obtained values are the measure of the thickening effect impact i.e. of lubrication efficiency. The values $Q > 1$, show that the polymeric additive improves the viscosity index since thickening is more pronounced at 100 ºC than at 40 ºC. Ideally, $Q = 1$, which means that the thickening is not dependent on temperature. Although both these values, viscosity index and Q factor, result from viscosity value, they are not directly connected. According to the obtained results shown in Figure 11, we may conclude that the thickening with increased styrene content in the copolymer is reduced at high temperatures, while it increases at lower temperatures. It is important to notice that these values do not differ significantly from that ideal, which points to an even lubrication efficiency with temperature change for the polymeric additives with a wide area of styrene content.

CONCLUSIONS

By terpolymerization reaction of a styrene, dodecyl methacrylate and octadecyl methacrylate monomer mixture, through the free radical initiation in the solution, terpolymers are obtained having the properties of mineral lubricant oil additives.

Under isothermal reaction conditions, complete conversions of monomer into polymer are achieved, with the reduction of initial reaction velocities and molecular weight as content of styrene was increased up to, w (ST) = 25 wt. %.

Kinematic viscosity of solutions at 40 ºC and 100 ºC grows with the increase of terpolymer molecular weight and does not change considerably with the additive composition changes; the values obtained are higher than those obtained for methacrylate additives solutions.

Viscosity index values are reduced with regard to initial values: 180, down to 150, with increased styrene terpolymer content and reduced polymer molecular weight.

Increased styrene terpolymer share causes a linear solutions' pour point depression from -33 ºC for a 5 wt. % styrene content to -27 ºC for a styrene share of 15 wt. %, with a higher linear dependence inclination, and to -9 ºC for a 25 wt. % styrene content.

Shear stability lineraly increases with increased styrene terpolymer content and by lowewring the polymer molecular weight.

Fig. 1. Azeotropic lines of binary composition for the terpolymerization system styrene / dodecyl methacrylate / octadecyl methacrylate; ♦ – experimental monomer feed compositions.

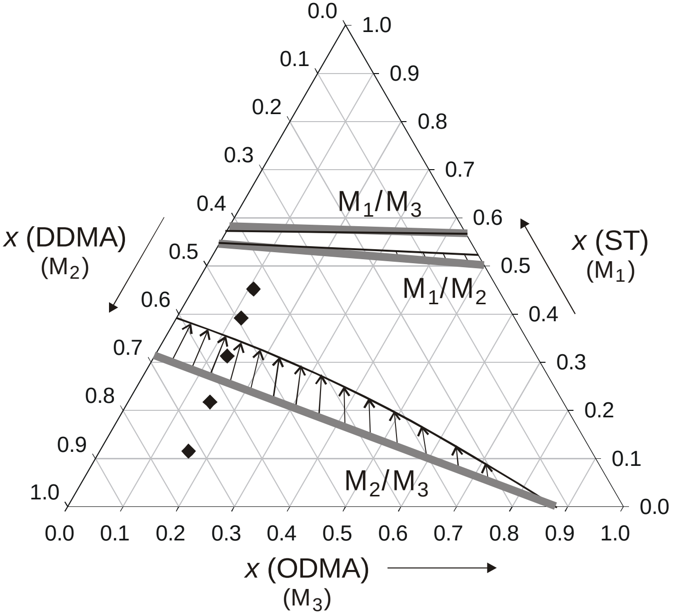
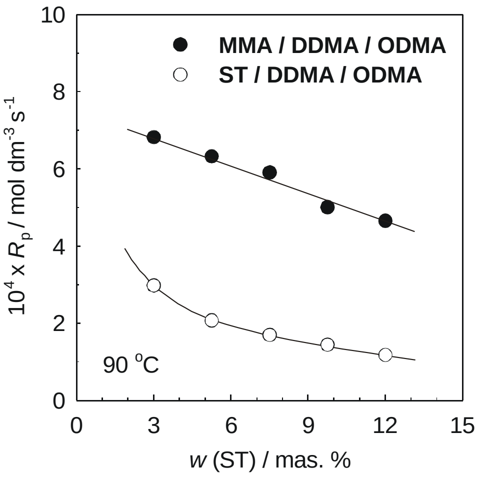


Fig. 2. Initial terpolymerization rate dependence on styrene content in monomer mixture of styrene, dodecyl- and octadecyl methacrylate.

Fig. 3. Average polymer molecular weights dependence on styrene content in monomer mixture of styrene, dodecyl- and octadecyl methacrylate.



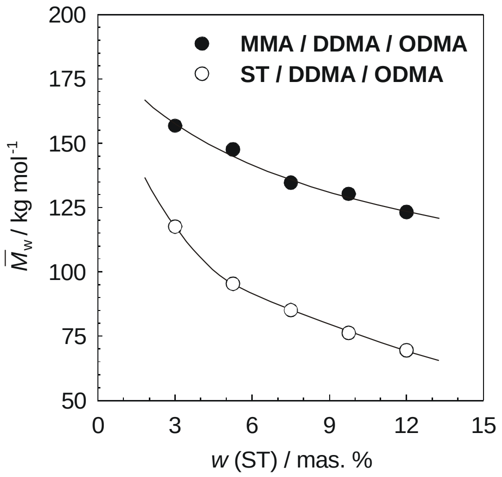
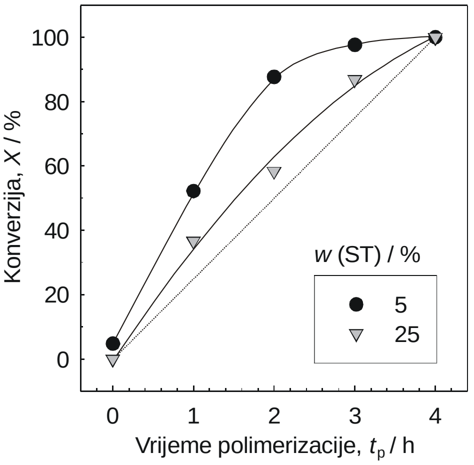


Fig. 4. Monomer conversion dependence on terpolymerization reaction time of styrene, dodecyl- and octadecyl methacrylate.

Fig. 5. Average molecular polymer weights dependence on monomer conversion of terpolymerization reaction of styrene, dodecyl- and octadecyl methacrylate in base mineral oil at 100 °C.



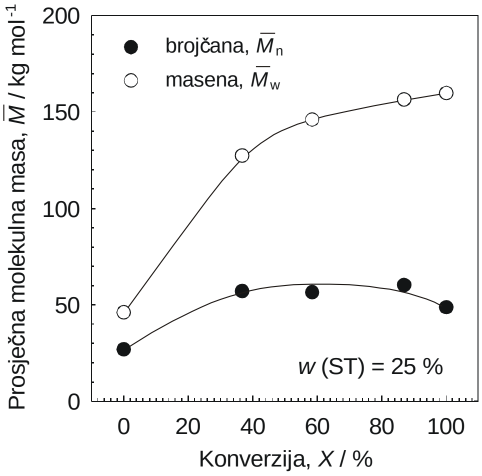
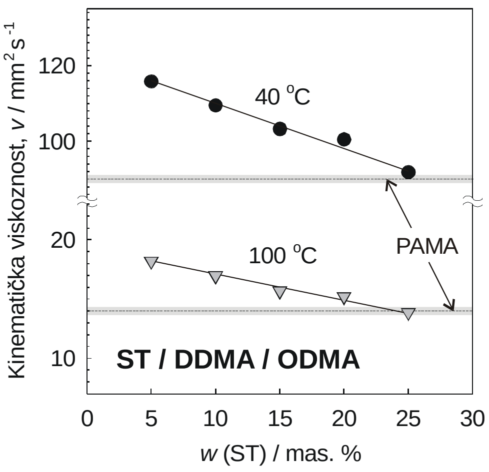


Fig. 6. Kinematic viscosity of 5 wt. % ST/DDMA/ODMA polymeric additive solutions in base mineral oil in dependence of composition at 40 and 100 °C.

Fig. 7. Kinematic viscosity and shear stability of ST/DDMA/ODMA polymeric additive solutions in base mineral oil (50 wt. % for v and 5 wt. % for Δv) in dependence of average polymer molecular weights.



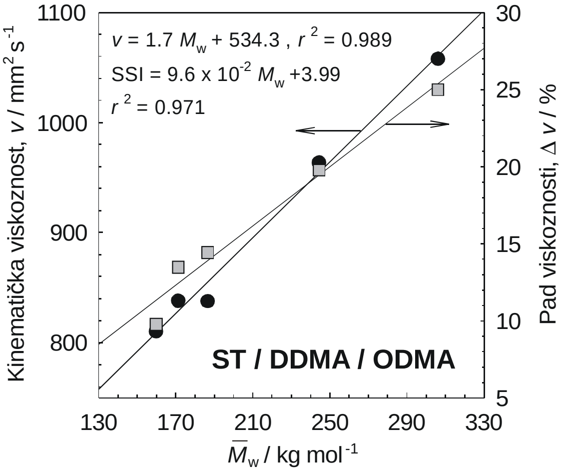
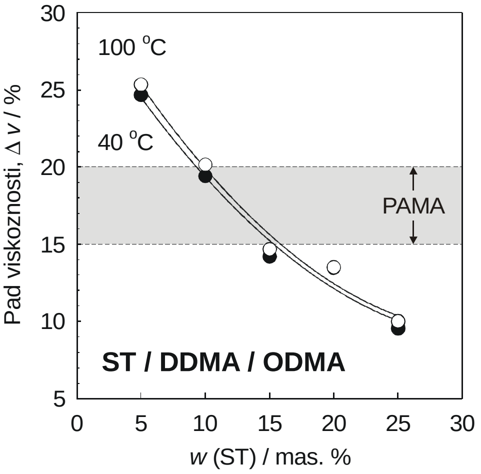


Fig. 8. Shear stability of 5 wt. % ST/DDMA/ODMA polymeric additive solutions in base mineral oil in dependence of composition at 40 and 100 ºC.
Fig. 9. Viscosity index of 5 wt. % ST/DDMA/ODMA polymeric additive solutions in base mineral oil in dependence of composition, before (●) and after (○) shear stability test.



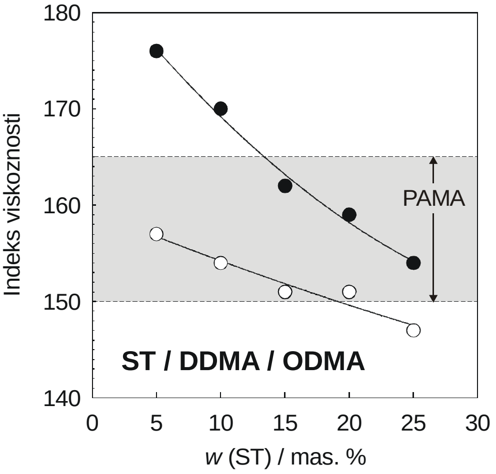
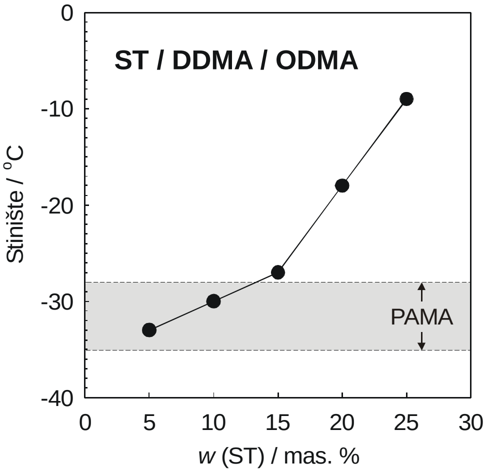
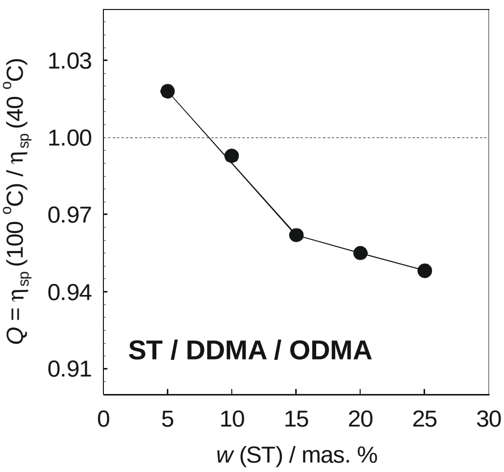


Fig. 10. Pour point temperature of 0.5 wt. % ST/DDMA/ODMA polymeric additive solutions in base mineral oil in dependence of composition.
Fig. 11. Q factor of 5 wt. % ST/DDMA/ODMA polymeric additive solutions in base mineral oil in dependence of composition.





Literatura / References

1. SHULZ D., GLASS J., *Polymers as Rheology Modifiers*, American Chemical Society, Washington, 1991.
2. MORTIER R.M., ORSZULIK S.T., *Chemistry and Technology of Lubricants*, Balckie Academic and Professional, London, 1997.
3. MUNK P., *Introduction to Macromolecular Science*, John Wiley & Sons, New York, 1989.
4. ELIAS H.G., *Macromolecules*, John Wiley, New York, 1977.
5. BRIANT J., DENIS J., PARC G., *Rheological Properties of Lubricants*, Technip, Paris, 1985.
6. BIELMEIER E., CAMERA F., NEVEU C.D., *Zbornik sažetaka*, Legiša I. (ur.), XXXVI. stručno-znanstveni skup MAZIVA, Rovinj; Hrvatski inženjerski savez - Hrvatsko društvo za goriva i maziva, Zagreb, C1, 2003.
7. JANOVIĆ, Z., JUKIĆ A., TOMAŠEK LJ., ROMANO J., BARIŠIĆ A., PICEK M., *Zbornik sažetaka*, Legiša I. (ur.), XXXVI. stručno-znanstveni skup MAZIVA, Rovinj; Hrvatski inženjerski savez - Hrvatsko društvo za goriva i maziva, Zagreb, C3, 2003.
8. JANOVIĆ Z., *Polimerizacije i polimeri*, HDKI – Kemija u industriji, Zagreb, 1997.
9. TURI E.A. (ur.), *Thermal Charact. of Polymeric Materials*, Academic Press, London, 1997.
10. DENIS J., *Lubr. Sci.* 1, 103, 1989.
11. KUCHANOV S., *Adv. Polym. Sci.* 103, 1, 1992.
12. JUKIĆ A., ROGOŠIĆ M., SARIĆ K., JANOVIĆ Z., *Kem. Ind.* 52, 478, 2003.
13. VIDOVIĆ E., SARIĆ K., JANOVIĆ Z., *Croatica Chem. Acta* 75, 769, 2002.
14. PALACIOS J.M., BAJÓN M.L., *Trybology Int.* 16, 27, 1983.
15. GRIGORESCU G., KULICKE W.M., *Adv. Polym. Sci.* 152, 1, 2000.
16. BOHDANECKÝ M., KOVÁŘ J., *Viscosity of Polymer Solutions*, Elsevier, Amsterdam, 1982.
17. VIDOVIĆ E., *Magistarski rad*, Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Zagreb, 2001.
18. BATAILLE P., SHARIFI-SANJANI N., *Lubr. Eng*. 51, 996, 1995.

ključne riječi:	key words:
665.761.2.038.62/.64 aditiv za reološka svojstva mineralnih baznih ulja	aditive for rheological properties of mineral base oils
678.742 stiren/DDMA/ODMA terpolimer	styrene/DDMA/ODMA terpolymer
66.095.26-922 azeotropna terpolimerizacija	azeoztropic terpolymerization conditions
678.744.33 dodecil metakrilat (DDMA)	dodecyl methacrylate
678.744.33 oktadecil metakrilat (ODMA)	octadecyl methacrylate
665.761.2 mineralno bazno ulje	mineral base oil

Autori / Authors:
dr. sc. Zvonimir Janović[1], mr. sc. Ante Jukić[1], mr. sc. Elvira Vidović[1]
[1]Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu, Savska 16, Zagreb
Jakov Romano[2], dipl.ing.
[2]INA Sektor strateškog razvoja, istraživanja i investicija, Lovinčićeva bb, Zagreb
Ankica Barišić[3], dipl.ing., Meri Picek[3], dipl.ing.
[3]Maziva Zagreb d.o.o., član INA grupe, Radnička 175, Zagreb

Primljeno / Received:
31.3.2004.