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SNIŽAVALA STINIŠTA MAZIVIH ULJA NA TEMELJU KOPOLIMERA ALKIL-METAKRILATA I STIRENA

Sažetak

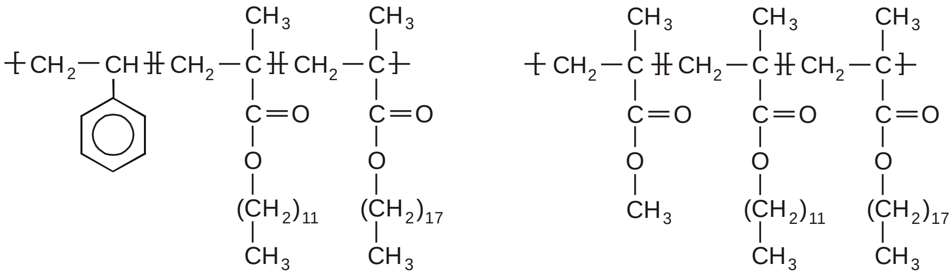
U radu su opisana niskotemperaturna svojstva mineralnih mazivih ulja uz polimerne aditive na osnovi terpolimera stirena s dodecil-metakrilatom i oktadecil-metakrilatom (PAMA-S). Dobiveni rezultati uspoređeni su s djelovanjem konvencionalnih aditiva na temelju dugolančanih metakrilata. Sastav i strukturne značajke terpolimera određeni su metodama magnetske rezonancije (NMR) i kromatografije isključenja po veličini (SEC). Povećanjem udjela stirena u terpolimeru postupno se povećavaju vrijednosti stiništa mazivoga ulja, od -33 ºC za udjel stirena od 5 mas. % do -27 ºC za udjel stirena od 15 mas. %, a zatim, za veće udjele stirena i do vrijednosti stiništa baznog ulja pri -9 ºC. Mehanizam djelovanja aditiva utvrđen je na osnovi vrijednosti stiništa otopina terpolimera u ulju, kao i svojstvenih toplinskih veličina terpolimera: stakläšta, tališta, entalpije taljenja i udjela kristalne faze, dobivenih metodom diferencijalne pretražne kalorimetrije. Potvrđen je mehanizam sniženja stiništa kokristalizacijom dugolančanih n-alkilnih skupina metakrilatnih polimera i n-parafinskih ugljikovodika baznog ulja. Optimalna niskotemperaturna svojstva PAMA-S postižu se odgovarajućim sastavom i omjerom dugolančanih alkilnih skupina, sukladno sastavu parafinskih ugljikovodika baznoga ulja.

Uvod

Polimerni aditivi mineralnih mazivih ulja uspješno se upotrebljavaju već dugo vremena, posebice za dobivanje multigradnih ulja, a imaju višestruku namjenu: poboljšavala su indeksa viskoznosti, snižavala stiništa i disperzanti, odnosno detergenti karboniziranih taloga. Nalaze se u koncentracijama od 0,5⋯5,0 mas. % i zato se ponašaju kao razrijeđene, odnosno polurazrijeđene polimerne otopine. Od velikog broja tih aditiva najviše se upotrebljavaju poliolefinski kopolimeri na temelju etilena i propilena (OCP, EPC) i kopolimeri dugolančanih alkilnih metakrilata (PAMA), a zatim hidrogenirani kopolimeri butadiena, odnosno izoprena sa stirenom, kao i poli(izobuten)[1,2]. Također se upotrebljavaju i kopolimeri s funkcionalnim skupinama, koje doprinose detergentnim svojstvima. Poliolefinski aditivi posjeduju izvrsna svojstva viskoznosti i smične stabilnosti, a loša su im niskotemperaturna svojstva. Suprotno, PAMA posjeduje visoke vrijednosti indeksa viskoznosti i izvrsnih je niskotemperaturnih svojstava. 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. Pri tome, udjel stirena u kopolimerima ograničen je, međutim, njihovom topljivošću. Snižavala stiništa djeluju mehanizmom usmjeravanja procesa kristalizacije parafinskih ugljikovodika prisutnih u baznom mineralnom ulju prema nastajanju manjih kristala i sprječavanju nastajanja kristalnih nakupina i gelova[10,11]. Temeljni im je učin sniženje stiništa mazivih ulja za 15···20 ºC, a u nekim slučajevima i za više od 30 ºC. Među prvim djelotvornim aditivima za sniženje stiništa bili su kopolimeri etilena i vinil-acetata. Mehanizam njihova djelovanja osniva se na adsorbciji acetatnih funkcionalnih skupina na plohama rastućih parafinskih kristala, usporavajući time njihov rast, uz nastajanje kristala malih izmjera.

Aditivi za sniženje stiništa mogu se razvrstati u tri velike skupine: poli(ugljikovodike), polimere s polarnim kisikovim skupinama i kopolimere koji sadrže i ugljikovodike i polarne skupine[10-14]. Prvoj skupini pripadaju poli(alfa-olefini), kopolimeri alfa-olefina i vinilnih aromatskih monomera kao što su stiren, vinil-naftalen i njihovi alkilni derivati. Drugu skupinu sačinjavaju dugolančani stearamidi, kopolimeri vinilnih estera, akrilata, metakrilata i fumarata. Trećoj skupini pripadaju kopolimeri alfa-olefina ili stirena s anhidridom maleinske kiseline i njezinim esterima, kopolimeri etilena i vinilnih estera, alkilirani vinil-naftaleni i dr. Mehanizam djelovanja dugolančanih estera metakrilne kiseline pretpostavlja kokristalizaciju parafinskih ugljikovodika baznoga ulja s bočnim alkilnim skupinama estera, dok polarne kiselinske skupine ostaju na kristalnim površinama i sprječavaju nastavak procesa kristalizacije.

U ovom radu, u nastavku istraživanja polimernih aditiva na temelju stirena i dugolančanih metakrilata, ispitan je utjecaj i mehanizam djelovanja terpolimera stiren / dodecil-metakrilat / oktadecil-metakrilat (PAMA-S) (shema I.a) na niskotemperaturna svojstva baznog mineralnog ulja. Osim stiništa, diferencijalnom pretražnom kalorimetrijom određene su svojstvene toplinske veličine priređenih terpolimera, prvenstveno temperature staklastog prijelaza, tališta i entalpije taljenja kristala. Dobiveni rezultati uspoređeni su s djelovanjem konvencionalnih aditiva na temelju dugolačanih metakrilata (shema I.b).



(a) (b)

Shema I. Kemijska struktura polimernih poboljšavala niskotemperaturnih svojstava mineralnih mazivih ulja: terpolimer stiren / dodecil-metakrilat / oktadecil-metakrilat (a); terpolimer metil-metakrilat / dodecil-metakrilat / oktadecil-metakrilat (b).

Eksperimentalni dio

Polimerni aditivi na temelju stirena (ST), kao i metil-metakrilata (MMA), i dugolančanih n-alkil-metakrilata (AMA), n-dodecil-metakrilata (DDMA) i n-oktadecil-metakrilata (ODMA) dobiveni su procesom polimerizacije smjese monomera u otopini baznog mineralnog ulja ili ksilena, uz peroksidni inicijator i pri izotermnim temperaturnim uvjetima, kako je to prije opisano[7,15]. Prosječne molne mase polimera, $\bar{M}_n$ i $\bar{M}_w$, određene su metodom kromatografije isključenja po veličini (SEC, GPC) u tetrahidrofuranu, uz polistirenske standarde; instrument Polymer Laboratories GPC-20. Sastav kopolimera određen je ^{1}H NMR spektroskopijom; instrument Bruker NMR 250. Stiništa su određena normiranom metodom ISO 3016. Toplinska svojstva polimera određena su metodom diferencijalne pretražne kalorimetrije (DSC) u temperaturnom području od -150 do +50 ºC, brzinom od 10 K min^{-1} u atmosferi dušika; instrument Mettler DSC. Da bi se otklonio utjecaj toplinske povijesti uzorka na izgled termograma, kalorimetrijska pretraga ponovljena je tri puta, a svojstvene toplinske veličine, staklište (T_g), entalpija taljenja kristala (ΔH_t) i talište (T_t), određene su iz termograma dobivenih drugom i trećom pretragom.

Rezultati i rasprava

Polimerni aditivi mineralnih mazivih ulja na temelju kopolimera n-alkil-metakrilata pripadaju skupini najvažnijih poboljšavala reoloških svojstava, posebice indeksa viskoznosti i stiništa[2,16,17]. Najčešće su linearni terpolimeri s alkilnim skupinama do dvadeset atoma ugljika, a sastav im se mijenja prema zahtijevanim primjenskim svojstvima. Djelotvornost PAMA aditiva kao snižavala stiništa mazivog ulja prikazana je kao ovisnost stiništa o koncentraciji aditiva slikom 1. Iz dobivenih je rezultata vidljivo da već i vrlo niske koncentracije PAMA aditiva snizuju stinište na vrijednosti manje od -30 ºC.

Tecljivost mineralnih ulja pri niskim temperaturama prvenstveno ovisi o svojstvima baznog mineralnog ulja, zatim brzini hlađenja, te vrsti i koncentraciji prisutnih aditiva. Većina baznih ulja ima stinište između -4 i -15 ºC, ovisno o strukturi i zastupljenosti pojedinih parafinskih ugljikovodika. Proces njihove kristalizacije (slika 2.), prema mnogobrojnim istraživanjima, najjednostavnije se istražuje metodom diferencijalne pretražne kalorimetrije[9,18-20]. Bazna ulja s većim udjelom dugolančanih parafinskih ugljikovodika veće su viskoznosti i imaju više vrijednosti stiništa. Relativni udjeli parafinskih ugljikovodika u ovisnosti o broju ugljikovih atoma i strukturi molekule, normalnoj ili izo- (2-metil i 3-metil), na temperaturi stiništa za odabrano bazno ulje SN-140[18], prikazani su na slici 3. Najzastupljeniji su ravnolančani, normalni parafini s brojem C atoma u rasponu od 17 do 27, s najvećim udjelom C22; najzastupljenije molekule izoparafina sadrže 24 (2-metil) i 25 (3-metil) C atoma. Mehanizam djelovanja polimernog aditiva na sniženje stiništa mineralnog ulja ispitan je DSC metodom na modelnim spojevima, smjesi poli(dodecil-metakrilata) i n-dodekana[19]. Iz endotermnih vrhova kalorimetrijskih krivulja (slika 4.) dobivenih za sastavnice i njihove smjese, vidljivo je da se s porastom udjela polimera postupno smanjuje parafinski endotermni vrh, a nakon udjela polimera od 50 mol. % nazočan je samo odziv povezan s kristalizacijom polimera. Također se može zaključiti da ne dolazi do izdvojene kristalizacije n-dodekana. Prema literaturnim podacima[19] rendgenskom je difrakcijom utvrđen smanjen udjel kristalne faze n-dodekana od očekivanog prema sastavu, kao i promjene u morfologiji kristala polimera nastale ugradnjom parafinskih molekula. Slijedi da učinkovitost snižavala stiništa na temelju dugolančanih poli(alkil-metakrilata) znatno ovisi o sastavu i strukturi kopolimera, posebice udjelima i duljini pojedinih bočnih alkilnih skupina, kao i njihove strukturne podudarnosti s parafinskim molekulama baznoga ulja.

Utjecaj sastava PAMA-S aditiva, iskazan udjelom stirena u terpolimeru, pri čemu je stalan omjer dodecil-metakrilata prema oktadecil-metakrilatu i iznosi 3 / 1 masenih udjela, na stinište baznog ulja SN-150 prikazan je slikom 5. Povećanjem udjela stirena postupno se povećavaju vrijednosti stiništa, a to povećanje može se podijeliti u dva, linearno ovisna područja. U prvom području, stinište postupno raste od -33 ºC za udjel stirena od 5 mas. % na -27 ºC za udjel stirena od 15 mas. %. To povećanje vjerojatno je posljedica utjecaja stirenskih ponavljanih jedinica u terpolimeru, odnosno njihovih steričkih smetnji procesu kristalizacije. U drugom dijelu, s većim nagibom linearne ovisnosti, stinište raste do -9 ºC za sadržaj stirena od 25 mas. %. Ta je vrijednost jednaka onoj baznog ulja, bez dodataka, što je vjerojatno posljedica i smanjene topljivosti terpolimera s velikim udjelom stirena, posebice pri niskim temperaturama. Utjecaj omjera dugolančanih alkil-metakrilata na stinište prikazan je na slici 6. za otopine terpolimera sa stalnim sadržajem stirena od 15 mas. %. Najniže stinište dobiveno je za omjer dodecil-metakrilata prema oktadecil-metakrilatu od 50 / 50, masenih udjela.

Izvanredna svojstva kopolimera dugolančanih n-alkil-metakrilata kao poboljšavala niskotemperaturnih svojstava, posebice stiništa mineralnih mazivih ulja moguće je objasniti mehanizmom postavljenim na temelju rezultata kalorimetrijskih pretraga. Termodinamička svojstva i fazni prijelazi terpolimera stirena ili metil-metakrilata, dodecil-metakrilata i oktadecil-metakrilata istraženi su metodom diferencijalne pretražne kalorimetrije u području temperatura od -150 do +50 ºC, brzinom od 10 K min^{-1} u atmosferi dušika. Dobiveni termogrami prikazani su u ovisnosti o sastavu i vrsti polimera na slikama 7. i 8. Na slikama je vidljivo da se oba terpolimera u istraženom području temperatura slično ponašaju. Termogrami se mogu podijeliti u tri svojstvena temperaturna područja prema fizičkim, deformacijskim stanjima terpolimera[8]. Prvo je područje temperatura od -150 do približno -80 ºC u kojemu je polimer u staklastom stanju; u području od približno -80 ºC do približno -30 ºC opažaju se staklasti prijelazi polimera; u trećem se području temperatura, od približno -30 ºC do +50 ºC, polimeri nalaze u visko-elastičnom stanju. Daljnjim zagrijavanjem, polimer prelazi u visko-fluidno stanje, nakon čega pri još višim temperaturama dolazi do kemijske razgradnje polimernih makromolekula. S obzirom na uska područja molnih masa istraživanih terpolimera, kao i njihove razmjerno visoke vrijednosti, $\bar{M}_w > 120 \times 10^3$ g mol^{-1} (stupanj polimerizacije: $350 < DP_n < 550$), pretpostavlja se da te razlike ne utječu značajno na temperature stakilšta, tališta i općenito toplinsko ponašanje terpolimera. Stoga se promjene toplinskih veličina pripisuju razlikama u njihovu sastavu. Kao što je razvidno na slikama 7. i 8., staklasti prijelaz svih istraživanih kopolimera slabo je izražen i nalazi se u širokom području temperatura, i bez uočljivog završetka prelazi u jasno izražen endotermni vrh. Područjem temperatura od -30 ºC do približno +20 ºC, tj. u visko-elastičnom području, prevladava jasno izražen endotermni vrh. Njegova površina predstavlja entalpiju taljenja, razmjernu sadržaju kristalne faze u polimernom uzorku, pri čemu oblik krivulje ovisi o raspodjeli veličina kristalita. Vrijednosti udjela kristalne faze u terpolimeru (x_c) određene su usporedbom izmjerenih entalpija taljenja s teorijskom entalpijom taljenja 100 % kristalnog polietilena[20] od 290 J g^{-1}:

$$x_c = \Delta H_t / \Delta H_{t,o}$$

Dobiveni rezultati u ovisnosti o vrsti i sastavu terpolimera prikazani su na slici 9. Udjel kristalne prema amorfnoj fazi smanjuje se smanjenjem sadržaja dugolančanih n-alkil-metakrilata, odnosno s povećanjem sadržaja stirena ili metil-metakrilata u terpolimeru. Istodobno se najniža vrijednost endotermnog vrha taljenja kristalne faze, $T_{t,min}$, s porastom udjela stirena ili metil-metakrilata u terpolimeru pomiče prema nižim temperaturama (slika 10.). Dobiveni rezultati pokazuju da nastajanje kristalne faze ne proizlazi iz temeljnog lanca, već da je povezano s bočnim skupinama, odnosno dugolančanim (C_{12} i C_{18}) n-alkilnim dijelom metakrilatnih jedinica. Iz dobivenih termograma može se zaključiti da snižavanjem temperature dolazi do smanjenja pokretljivosti dugolančanih alkilnih segmenata polimernih makromolekula, njihova usmjeravanja, a zatim i djelomične kristalizacije, shematski prikazane slikom 11. Time unutar mase polimera nastaju kristalne domene nano-veličine[21,22]. Procesu dodatno pogoduje i asocijacija makromolekula kopolimera dugolančanih alkil-metakrilata u otopinama mineralnog mazivog ulja, kako je utvrđeno prethodnim istraživanjima[23,24].

Udjel kristalne faze, odnosno sastav PAMA-S terpolimera moguće je izravno povezati s vrijednostima stiništa otopina u mineralnom ulju. Kao što je vidljivo na slici 12., povećanjem udjela kristalne faze, tj. dugolančanih alkil-metakrilata u kopolimeru, snizuje se stinište otopina u ulju, čime se potvrđuje da su bočne dugolančane skupine n-alkil-metakrilata aktivna sastavnica kopolimera koja snizuje stinište mineralnoga ulja. U sustavu ulje / polimer, snižavanjem temperature, nepolarne molekule dugolančanih parafina kokristaliziraju s nepolarnim kristalnim nano-domenama dugolančanih alkana, tj. alkilnih segmenata polimernih makromolekula i njihovih asocijata. Pri tome je važno istaknuti, da polimerna kristalna faza nastaje pri višim temperaturama u usporedbi s nastajanjem parafinskih kristala. Na taj način polimerne molekule usmjeravaju proces kristalizacije parafinskih ugljikovodika prisutnih u baznom mineralnom ulju prema nastajanju manjih kristala, ograničavaju njihov rast i sprječavaju nastajanje većih nakupina i stvaranje gelova. Time se postiže odgovarajuća tecljivost, odnosno zadržavaju poželjna maziva svojstva mineralnog ulja i pri niskim temperaturama.

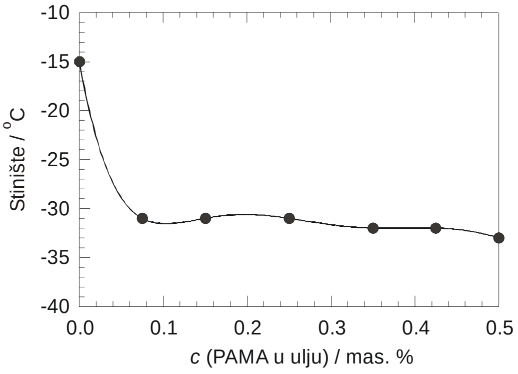
Zaključak

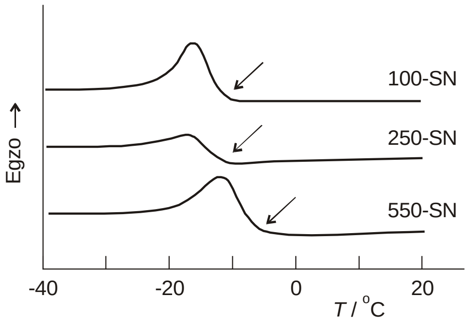
Istraživanjem niskotemperaturnih svojstava mineralnih mazivih ulja uz dodatak polimernih aditiva na temelju stirena ili metil-metakrilata s dodecil-metakrilatom i oktadecil-metakrilatom (PAMA-S i PAMA), potvrđen je mehanizam sniženja stiništa izravnim djelovanjem bočnih dugolančanih alkilnih skupina terpolimera.

Toplinska svojstva i fazni prijelazi polimernih aditiva: staklište, talište, entalpija taljenja i udjel kristalne faze određeni su diferencijalnom pretražnom kalorimetrijom, metodom prikladnom za istraživanje djelovanja polimernih snižavala stiništa mazivih ulja. Polimerni aditiv, stiren / dodecil-metakrilat / oktadecil-metakrilat terpolimer djelotvorno je poboljšavalo niskotemperaturnih svojstava mazivosti pri manjim udjelima stirena. Povećanjem udjela stirena postupno se povećavaju vrijednosti stiništa, a to povećanje može se podijeliti u dva, linearno ovisna područja. U prvom području, stinište postupno raste od -33 ºC za udjel od 5 mas. % stirena na -27 ºC za udjel stirena od 15 mas. %. To povećanje vjerojatno je posljedica utjecaja stirenskih ponavljanih jedinica u terpolimeru i njihovih steričkih smetnji procesu kristalizacije. U drugom dijelu, s većim nagibom linearne ovisnosti, stinište raste do -9 ºC za udjel stirena od 25 mas. %. Ta je vrijednost jednaka onoj baznog ulja, bez dodataka, što je vjerojatno posljedica i smanjene topljivosti terpolimera s velikim udjelom stirena, posebice pri niskim temperaturama. Optimalna niskotemperaturna svojstva PAMA-S postižu se odgovarajućim sastavom i omjerom dugolančanih alkilnih skupina, sukladno sastavu parafinskih ugljikovodika baznoga ulja.

Slika 1: Stinište mineralnog mazivog ulja u ovisnosti o koncentraciji poli(alkil-metakrilatnog) (PAMA) aditiva.

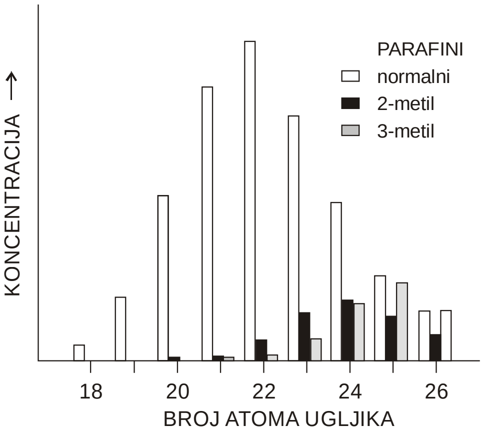
Slika 2: DSC krivulje procesa kristalizacije parafina baznoga mineralnog ulja.

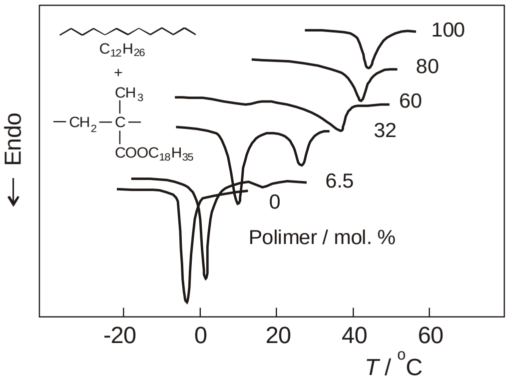




Slika 3: Koncentracija normalnih i izo-parafinskih ugljikovodika pri stiništu baznoga mineralnog ulja SN-140.

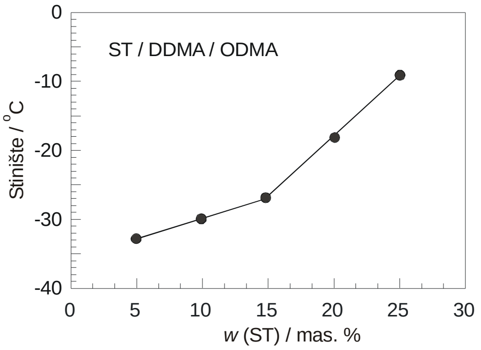
Slika 4: DSC krivulje procesa kristalizacije poli(n-oktadecil-metakrilata), n-dodekana i njihovih smjesa.

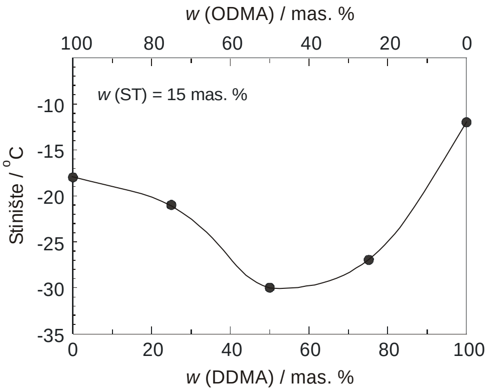




Slika 5: Stinište otopina stiren / dodecil-metakrilat / oktadecil-metakrilat (ST/DDMA/ODMA) polimernog aditiva u mineralnom ulju u ovisnosti o udjelu stirena u terpolimeru.

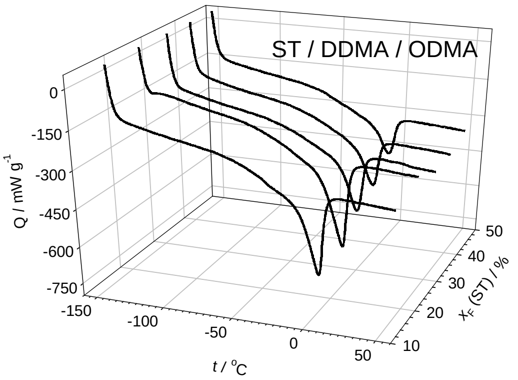
Slika 6: Stinište otopina stiren / dodecil-metakrilat / oktadecil-metakrilat (ST/DDMA/ODMA) polimernog aditiva u mineralnom ulju u ovisnosti o omjeru dugolančanih alkil-metakrilata u terpolimeru.

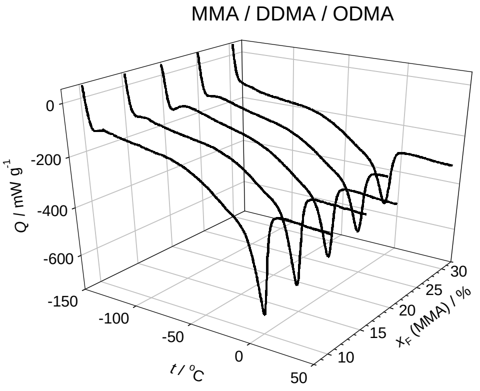




Slika 7: DSC krivulje stiren / dodecil- metakrilat / oktadecil-metakrilat (ST/DDMA/ODMA) terpolimera snimljene u području temperatura od -150 do +50 ºC brzinom promjene temperature od 10 K min^{-1} u atmosferi dušika.

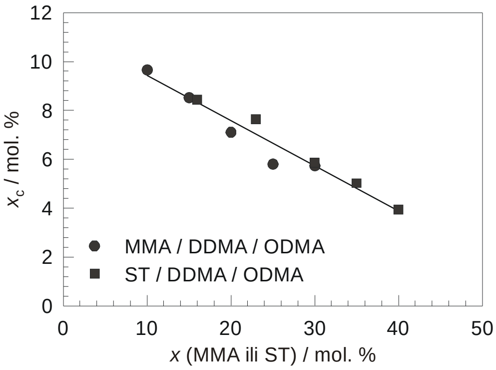
Slika 8: DSC krivulje metil-metakrilat / dodecil- metakrilat / oktadecil-metakrilat (MMA/DDMA/ODMA) terpolimera snimljene u području temperatura od -150 do +50 ºC brzinom promjene temperature od 10 K min^{-1} u atmosferi dušika.

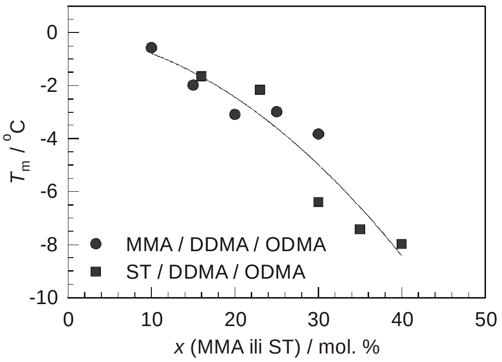




Slika 9: Udjel kristalne faze u ovisnosti o sastavu stiren / dodecil- metakrilat / oktadecil-metakrilat (ST/DDMA/ODMA) i metil-metakrilat / dodecil-metakrilat / oktadecil-metakrilat (MMA/DDMA/ODMA) terpolimera.

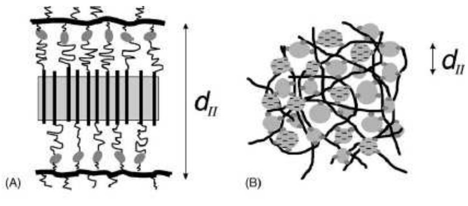
Slika 10: Talište kristalne faze u ovisnosti o sastavu stiren / dodecil- metakrilat / oktadecil-metakrilat (ST/DDMA/ODMA) i metil-metakrilat / dodecil-metakrilat / oktadecil-metakrilat (MMA/DDMA/ODMA) terpolimera.

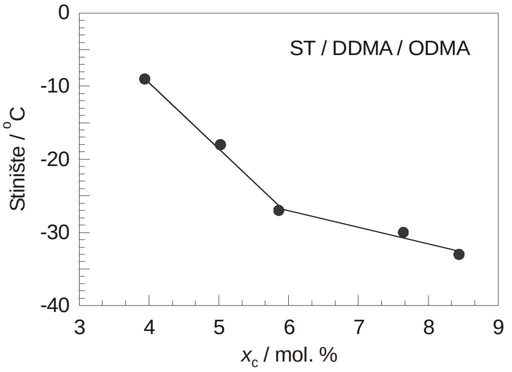




Slika 11: Shematski prikaz kvazi-jednodimenzijskog modela (A) i trodimenzijskog prikaza (B) morfologije nanofazno-razdijeljenih polimera s dugim bočnim lancima. (A) Debela crna linija predstavlja osnovni lanac, kristalno područje označeno je sivim, a tanke linije amorfne ili krute dijelove alkilnog lanca. (B) Siva područja predstavljaju alkilne nakupine, pri čemu su kristalne iscrtkane. Kristalne domene su iscrtkane. Dipolne karboksilne skupine prikazane su malim elipsama.

Slika 12: Stinište otopina stiren / dodecil-metakrilat / oktadecil-metakrilat (ST/DDMA/ODMA) polimernog aditiva u mineralnom ulju u ovisnosti o udjelu kristalne faze u terpolimeru.





LUBRICATING OILS POUR POINT DEPRESSANTS BASED ON ALKYL METHACRYLATE AND STYRENE COPOLYMERS

Abstract

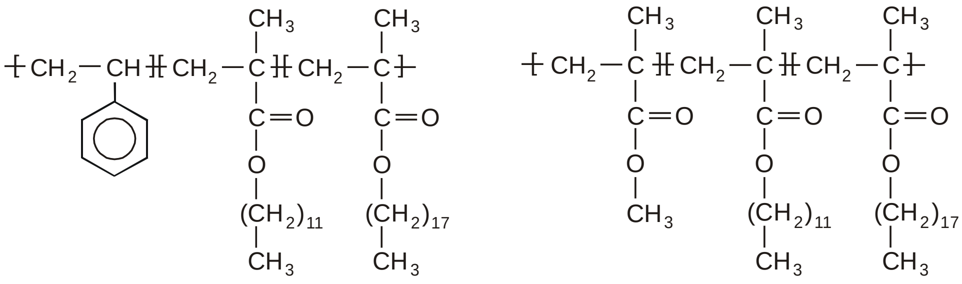
The paper describes low-temperature properties of mineral lubricating oils with polymeric additives based on terpolymers of styrene with dodecyl methacrylate and octadecyl-methacrylate (PAMA-S). The obtained results were compared with the efficiency of conventional additives based on long-chained methacrylates. The composition and structural properties of terpolymers were determined using the methods of NMR and size exclusion chromatography (SEC). By increasing styrene content in terpolymer, there occurs a gradual increase of the lubricating oil pour point values, from -33 °C for a 5 wt. % styrene content to -27 °C for a 15 wt. % styrene content, and then, for higher styrene values, up to the lubricating oil pour point value of -9 °C. The additive activity mechanism was established based on the pour point values of terpolymer oil solutions, as well as the specific thermal terpolymer values: glass transition temperature, melting point, melting enthalpy and crystal phase content – obtained by the method of differential scanning calorimetry. Confirmed was the mechanism of pour point reduction through the co-crystalization of long-chained n-alkyl groups of methacrylate polymers and n-paraffinic base oil hydrocarbons. Optimal low-temperature properties of PAMA-S are obtained by a proper composition and ratio of the long-chained alkylate groups, in compliance with the composition of base oil paraffinic hydrocarbons.

Introduction

Polymeric additives of mineral lubricating oils have been successfully used for long time, especially for obtaining multigrade oils, while they are multifunctional: they improve viscosity index; act as pour point depressants and dispersants i.e. detergents of carbonized sludge. They are found in concentrations from 0.5···5.0 wt. %, which is why they act as diluted i.e. semi-diluted polymeric solutions. Out of a large number of these additives, mostly used are polyolephinic copolymers based on ethylene and propylene (OCP, EPC), and copolymers of long-chained alkyl methacrylates (PAMA), as well as hydrogenated copolymers of butadiene or isoprene with styrene, and poly(isobutene)[1,2]. Also used are copolymers with functional groups, contributing to detergent properties. Polyolephinic additives own excellent viscosity and shear stability properties, while they have poor low temperature properties. Contrary to that, PAMA has high viscosity index properties end excellent low temperature properties. Most frequently, they are straight, long-chained, linear terpolymers consisting of monomers with a changeable content of lateral alkyl groups, mostly C_1-C_{18}, while their ratio is set in such a way so as to ensure optimal performances. Apart from the composition, applicative properties of polymeric additives are dependent mostly on a large number of structural factors, especially solubility, solution viscosity, molecular mass and their distribution, temperature conformation changes of molecules; size, content and distribution of the repeated units' sequences, kind and size of lateral alkyl groups, as well as the type and properties of solvent, the mineral base oil[3-5]. Recently, the development of methacrylic additives has been directed towards obtaining and applying polymers based on long-chained n-alkyl methacrylates and vinyl monomers without side groups, such as styrene and its derivatives[6,7]. Styrene-based polymers have a higher thermal stability[8,9], while the increased styrene content in the copolymer increases also the size of statistical conformations of macromolecules, directly increasing also the solution viscosity towards methacrylate additives for equal concentrations and equal molecular masses. Styrene content in copolymers is, however, limited by their solubility. Pour point depressants act through the mechanism of directing the crystalization process of paraffinic hydrocarbons present in mineral base oil towards the generation of smaller crystals, and preventing the generation of crystal clusters and gels[10,11]. Its basic effect is to reduce the lubricating oils' pour point by 15⋯20 ºC, and, in some cases, for over 30 ºC. Among the first efficient additives for the reduction of pour point were the copolymers of ethylene and vinyl acetate. The mechanism of their activity is based on the adsorbtion of acetate functional groups on the surfaces of growing paraffinic crystals, thus slowing down their growth, and generating crystals of small dimensions.

Additives for reducing pour point may be classified in three large groups: poly(hydrocarbons), polymers with polar oxygen groups and copolymers containing hydrocarbons and polar groups[10-14]. The first group includes poly(alpha-olefins), copolymers of alpha-olefins and vinyl aromatic monomers, such as styrene, vinyl-naphthalene, and their alkyl derivatives. The second group consists of long-chained stearamides, copolymers of vinyl ester, acrylate, methacrylate, and fumarate. The third group includes copolymers of alpha-olefin or styrene with anhydride of maleinic acid and its esters; copolymers of ethylene and vinyl esters, alkylated vinyl naphthalenes, etc. The activity mechanism of metacrylic acid long-chained esters presuposes the co-crystallization of paraffinic base oil hydrocarbons with side alkyl ester groups, while polar acid groups remain on crystal surfaces and prevent the continuation of the crystallization process.

In the present paper, as a continuation of researching polymeric additives based on styrene and long-chained methacrylates, we have investigated the impact and the activity mechanism of terpolymers styrene / dodecyl methacrylate / octadecyl methacrylate (PAMA-S) (scheme I.a) in terms of low temperature properties of base mineral oil. Apart from the pour point, differential scanning calorimetry has determined specific thermal values of the prepared terpolymers, primarily the glass transition temperature, melting point, and crystal melting enthalpy. The obtained results were compared with the activity of conventional additives on the basis of long-chained methacrylates (scheme I.b).



(a) (b)

Scheme I. Chemical structure of mineral lubricating oils low temperature properties polymeric improvers: terpolymer styrene / dodecyl methacrylate / octadecyl methacrylate (a); terpolimer methyl methacrylate / dodecyl methacrylate / octadecyl methacrylate (b).

Experimental part

Styrene (ST) based polymeric additives, as well as those based on methyl methacrylate (MMA), and long-chained n-alkyl methacrylates (AMA), n-dodecyl methacrylate (DDMA) and n-octadecyl methacrylate (ODMA) were obtained by polymerization process of monomer in mineral base oil or xylene solution, with peroxide initiator and at isothermal temperature conditions, as described before[7,15]. Average molar masses of polymers, $\overline{M}_n$ and $\overline{M}_w$, were determined by the method of size exclusion chromatography (SEC, GPC) in tetrahydrofurane, with polystyrene standards; instrument: Polymer Laboratories GPC-20. Copolymer composition was determined using ^{1}H NMR spectroscopy; instrument: Bruker NMR 250. Pour points were determined by standardized method ISO 3016. Thermal polymer properties were determined using the method of differential scanning calorimetry (DSC) in the temperature range from -150 to +50 ºC, with the velocity of 10 K min^{-1} in nitrogen atmosphere; instrument: Mettler DSC. In order to remove the impact of the sample's thermal history on the appearance of thermogram, the calorymetric search was repeated three times, while the specific thermal values, glass transition temperature (T_g), crystal melting enthalpy (ΔH_t) and melting point (T_t), were determined based on the termograms obtained in the second and third searches.

Results and discussion

Polymeric additives of mineral lubricating oils based on copolymers of n-alkyl methacrylates pertain to the group of the most significant improvers of rheological properties, especially viscosity index and pour point[2,16,17]. Most frequent are the linear terpolymers with alkyl groups of up to twenty carbon atoms, while their composition changes according to the required performances. The efficiency of PAMA lube oil pour point depressants is presented as pour point dependence on additive concentration in Figure 1. The obtained results show that already very low concentrations of PAMA additives reduce the pour point to the values below -30 ºC.

Fluidity of mineral oils at low temperatures depends primarily on the properties of the mineral base oil, cooling velocity, and concentration of the present additives. Most base oils have a pour point between -4 and -15 ºC, depending on the structure and content of individual paraffinic hydrocarbons. The process of their crystalization (Figure 2.), according to extensive research, is most easily investigated through the method of differential scanning calorimetry[9,18-20]. Base oils with a higher content of long-chained paraffinic hydrocarbons have higher viscosities and higher pour point values. Relative contents of paraffinic hydrocarbons in dependence of the number of carbon atoms and molecule structure, normal or iso- (2-methyl and 3-methyl), at pour point temperature for the selected base oil SN-140[18], are shown in Figure 3. Most numerous are the straight-chained, normal paraffins with the number of C atoms ranging from 17 to 27, with the highest content of C22; the most numerous molecules of isoparaffin contain 24 (2-methyl) and 25 (3-methyl) C atoms. Activitiy mechanism of polymeric additive on the mineral oil pour point reduction was tested using the DSC method on model compounds; compound of poly(dodecyl methacrylate) and n-dodecane[19]. From the endothermal peaks of calorymetric curves (Figure 4.) obtained for the components and their mixtures, it may be seen that the increased content of polymers gradually reduces the paraffinic endothermal peak, while after a 50 mol. % polymer content, there is only the response associated with polymer crystalization. It may also be concluded that there is no isolated crystalization of n-dodecane. According to the data from the references,[19] X-ray diffraction has revealed a lowered content of crystal phase of n-dodecane than the expected one according to the composition, as well as changes in the morphology of crystal of polymers created by the building in of paraffinic molecules. It follows that the efficiency of pour point depressants based on long-chained poly(alkyl methacrylates) is very much dependent on the composition and structure of copolymers, and especially the contents and the length of individual side alkyl groups, as well as their structural matching with the base oil paraffiic molecules.

The impact of the composition of PAMA-S additives, expressed in terms of styrene content in terpolymer, with a constant ratio of dodecyl methacrylate and octadecyl methacrylate, amounting to 3/1 mass content, to the pour point of base oil SN-150, is shown in Figure 5. By increasing styrene content, there occurs a gradual increase of the pour point values, which may be broken down into two, linearly dependent areas. In the first area, the pour point gradually increases from -33 ºC for a styrene content of 5 wt. % to -27 ºC for a styrene content of 15 wt. %. The increase in question probably results from the impact of styrene repeated units in terpolymer i.e. their steric disturbances caused to the crystallization process. In the second part, with a greater inclination of linear dependence, the pour point increases to -9 ºC for a styrene content of 25 wt. %. This value is equal to that of base oil, with no additions, probably resulting also from reduced solubility of the terpolymer with a high styrene content, especially at low temperatures. The impact of the ratio of long-chained alkyl methacrylates to the pour point is shown in Figure 6 for terpolymer solutions with a constant styrene content of 15 wt. %. The lowest pour point was obtained for the ratio of dodecyl methacrylate and octadecyl methacrylate of 50 / 50, by mass.

Exceptional properties of copolymers of long-chained n-alkyl methacrylates as improvers of low temperature properties, especially the pour point of mineral lube oils, may be explained through the mechanism based on the results of calorymetric search. Thermodynamical properties and phase transitions of terpolymers of styrene or methyl methacrylate, dodecyl methacrylate and octadecyl methacrylate, were investigated using the method of differential scanning calorimetry within the temperature range from -150 to +50 ºC, with the velocity of 10 K min^{-1} in nitrogen atmosphere. The obtained thermograms are shown in dependence of the composition and type of polymers in Figures 7 and 8. It may be seen that both terpolymers within the investigated temperature range behave similarly. The thermograms may be broken down into three proper temperature ranges, according to physical, deformational conditions of terpolymers[8]. The first temperature range is from -150 to ca. -80 ºC in which the terpolymer is in glass condition; in the area from ca. -80 ºC to ca. -30 ºC one may observe glass polymer transitions; in the third area, with the temperature from ca. -30 ºC to +50 ºC, the terpolymers are in the visco-elastic state. Through further heating, the polymer passes to a highly fluid state, after which, at even higher temperatures, there occurs a chemical decomposition of polymeric macromolecules. Given the narrow areas of molar masses of the investigated terpolymers, as well as their rather high values, $\overline{M}_\text{w} > 120 \times 10^3$ g mol^{-1} (polymerization degree: $350 < DP_\text{n} < 550$), it is assumed that these differences do not have a considerable impact on the temperatures of glass transition temperature or melting point, and generally on the thermal behaviour of terpolymers. That is why the changes of thermal values are ascribed to the differences in their composition. As may be seen from Figures 7 and 8, the glass transition of all researched copolymers is poorly pronounced and may be found within a wide temperature range, without any visible ending transforming to a clearly expressed endothermal peak. The temperature range from -30 ºC to ca. +20 ºC, is dominated by a clearly pronounced endothermal peak. Its surface presents melting enthalpy corresponding to the crystal phase content in the polymeric sample, with the curve form depending on the distribution of crystallite size. The values of the crystal phase content in terpolymer (x_c) are determined by the comparison of measured melting enthalpies with the theoretical melting enthalpy of a 100 % crystal polyetihyene[20] of 290 J g^{-1}:

$x_c = \Delta H_t / \Delta H_{t,o}$

The obtained results in dependence of the type and composition of terpolymers are shown in Figure 9. The content of crystal to the amorphous phase is reduced with the reduction of the content of long-chained n-alkyl methacrylates i.e. with the increase in the content of styrene or methyl methacrylate in terpolymer. At the same time, the lowest value of the endothermal peak of crystal phase melting, $T_{t,min}$, with increased content of styrene or methyl methacrylate in terpolymer is moved towards lower temperatures (Figure 10.). The obtained results indicate that the generation of crystal phase does not result from the basic chain, but that it is rather associated with the side chains, i.e. long-chained (C_{12} i C_{18}) n-alkyl part of methacrylate units. It may be concluded from the obtained thermograms that temperature lowering causes reduction in the mobility of long-chained alkyl segments of polymeric macromolecules, their direction, and then also partial crystalization, outlined in Figure 11. In this manner, within the polymer mass, generated are the crystal domains of nano-size[21,22]. The process in question is additionally stimulated by the association of copolymer macromolecules of long-chained alkyl methacrylates in the solutions of mineral lube oil, as established by previous research[23,24].

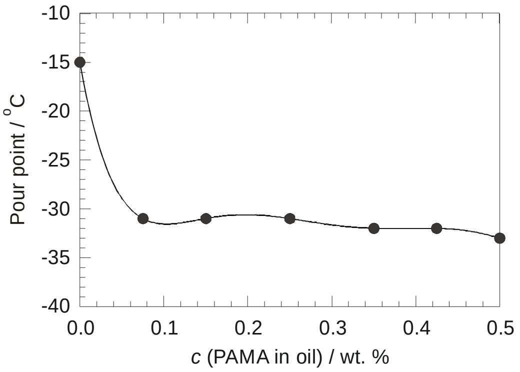
The content of crystal phase i.e. the composition of PAMA-S terpolymers may be directly associated with pour point values of mineral oil solutions. As may be seen in Figure 12, by increasing the content of crystalline phase i.e. long-chained alkyl methacrylates in copolymer, lowered is the pour point of oil solutions, thus confirming that the side long-chained groups of n-alkyl methacrylate are an active component of the copolymer that reduces the mineral oil pour point. In the oil / polymer system, by lowering the temperature, non-polar molecules of long-chained paraffins co-crystalize with non-polar crystal nano-domains of long-chained alkanes i.e. alkyl segments of polymeric macromolecules and their associates. It is important to point out that the polymeric crystal phase is generated at higher temperatures compared to the creation of paraffinic crystals. In this way, polymeric molecules are directing the crystalization process of paraffinic hydrocarbons present in mineral base oil towards the generation of smaller crystals; limit their growth and prevent the generation of larger clusters and creation of gels. This results in adequate fluidity i.e. the keeping of desirable lubricating properties of the mineral oil even at low temperatures.

Conclusion

By investigating low temperature properties of mineral lube oils with an addition of polymeric additives on the basis of styrene or methyl methacrylate with dodecyl methacrylate and octadecyl methacrylate (PAMA-S and PAMA), the mechanism of pour point reduction through a direct activity of side long-chained alkyl terpolymer groups was confirmed. Thermal properties and phase transitions of polymeric additives: glass transition temperature, melting point, melting enthalpy and crystal phase content, are determined by a differential scanning calorimetry – a method suitable for investigating the activity of polymeric lube oil pour point depressants. Polymeric additive, styrene / dodecyl methacrylate / octadecyl methacrylate terpolymer is an efficient improver of the low temperature lubrication properties at low styrene contents. By increasing the content of styrene, there is a gradual increase of the pour point values, while this increase may be broken down into two, linearly dependent areas. In the first area, the pour point gradually increases from -33 ºC for a content of 5 wt. % of styrene to -27 ºC for a styrene content of 15 wt. %. The increase probably results from the impact of styrene repeated units in the terpolymer and their steric disturbances of the crystalization process. In the second part, with a greater linear dependence inclination, the pour point increases up to -9 ºC for a styrene content of 25 wt. %. The value is the same as that of the base oil, without additions, which probably results also from reduced terpolymer solubility with a large styrene content, especially at low temperatures. Optimal low temperature properties of PAMA-S are achieved through an adequate composition and ratio of long-chained alkyl groups, in consistence with the composition of the base oil paraffinic hydrocarbons.

Fig. 1: Pour point of lubricating mineral oil in dependence on poly(alkyl methacrylate) (PAMA) additive concentration.

Fig. 2: Base mineral oil DCS curves of paraffin-wax crystallization process.



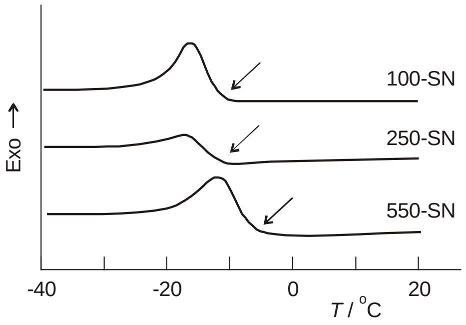
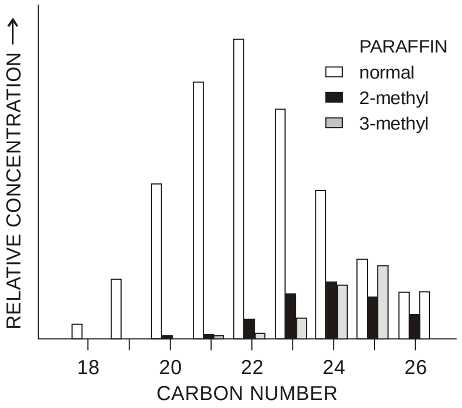


Fig. 3: The normal and iso-paraffines present at the pour point of SN-140 mineral oil.

Fig. 4: DSC curves of poly(n-octadecyl methacrylate), n-dodecane and their blends.



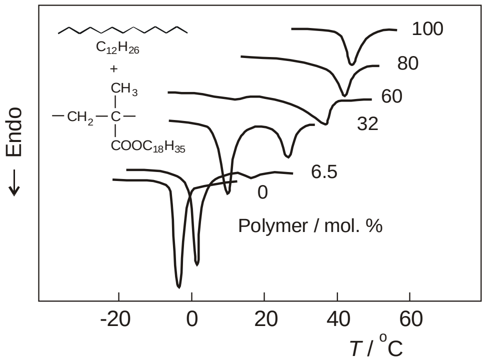
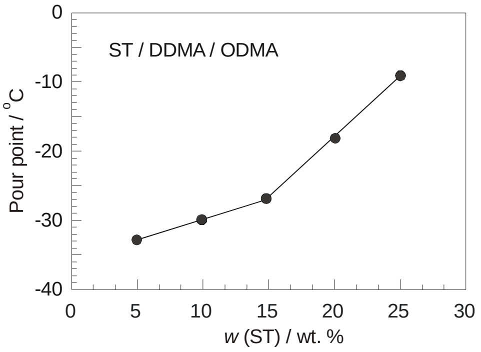


Fig. 5: Pour point of styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) terpolymer solutions in mineral oil in dependence on styrene content in terpolymer.

Fig. 6: Pour point of styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) terpolymer solutions in mineral oil in dependence on methacrylate units content in terpolymers.



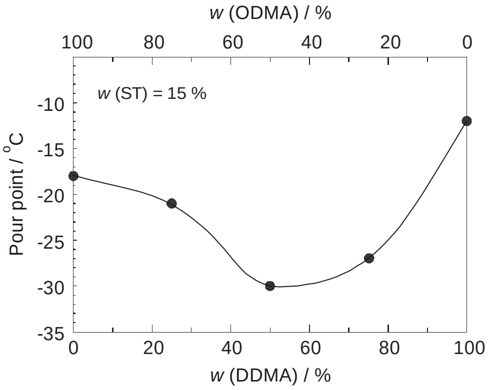
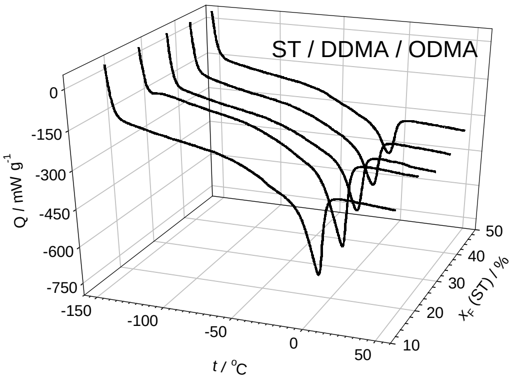


Fig. 7: DSC curves of styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) terpolymers in temperature range from -150 to +50 ºC.

Fig. 8: DSC curves of methyl methacrylate / dodecyl methacrylate / octadecyl methacrylate (MMA/DDMA/ODMA) terpolymers in temperature range from -150 to +50 ºC.



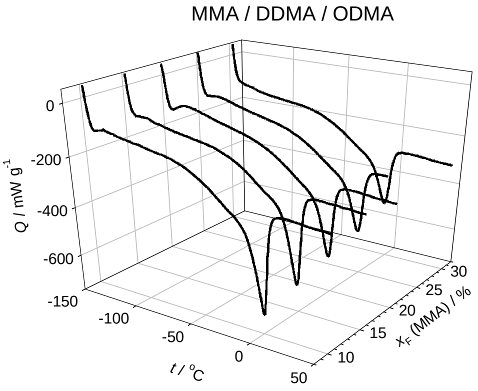
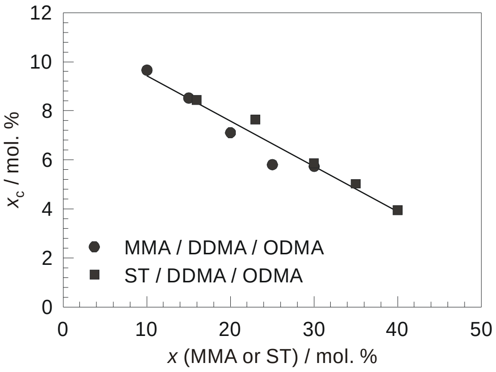


Fig. 9: Crystalline phase content in dependence on styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) or methyl methacrylate / dodecyl methacrylate / octadecyl methacrylate (MMA/DDMA/ODMA) terpolymer composition.

Fig. 10: Melting temperatures of crystalline phase in dependence on styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) or methyl methacrylate / dodecyl methacrylate / octadecyl methacrylate (MMA/DDMA/ODMA) terpolymer composition.



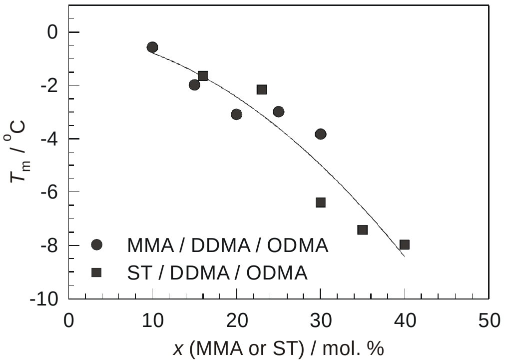
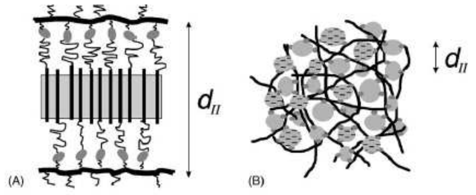
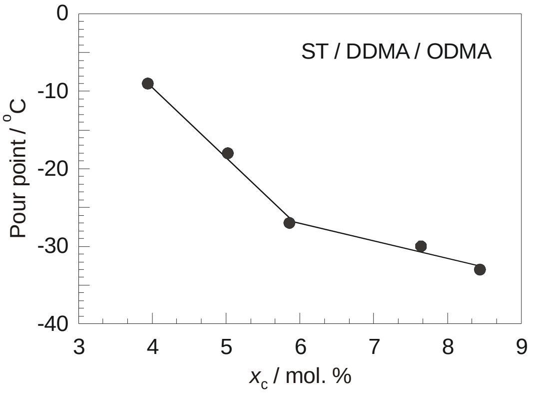


Fig. 11: Schematic representation of a quasi one-dimensional model (A) and a more global three-dimensional picture (B) for the morphology of nanophase-separated side chain polymers. The bold lines represent the backbones, the crystalline region is shown in gray, the thin lines are amorphous or rigid amorphous parts of the alkyl rest. (B) The backbones are the bold lines and the gray regions are aggregated alkyl rests. The hatching indicates crystalline regions. In both parts, the small ellipses represent the dipoles in the carboxyl groups.

Fig. 12: Pour point of styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) terpolymer solutions in the mineral oil in dependence on terpolymer crystalline phase content.





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UDK	Ključne riječi:	Key words:
665.753.4.038.64	interakcija parafina s depresantom stiništa	paraffine interaction with pour point depressant
678.744.33	polialkilmetakrilatni poboljšivač indeksa viskoznosti	polyalkylmetacryilate VI improver (PAMA)
678.744.33	oktadecil metakrilat	octadecilmetacrylate (ODMA)
543.544.153	kromatografija isključenjem po veličini	size exclusion chromatography (SEC)
544.228	odnosi kristalne strukture i svojstava	relation of crystal structure and properties
544.234.2	odnosi amorfnog i kristalnog stanja	relation of amorfphous and crystalline state

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