

Preparation and oil-absorptivity of crosslinked polymers containing stearylmethacrylate, 4-*t*-butylstyrene, and divinylbenzene

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Summary

The crosslinked polymers, poly(stearylmethacrylate-*co*-divinylbenzene) [CP(SMA-*co*-DVB)] and poly(*t*-butylstyrene-*co*-divinylbenzene) [CP(tBS-*co*-DVB)], and CP(SMA-*co*-DVB)/PtBS IPNs, were prepared by the polymerization of corresponding monomer pairs in the presence of BPO. The structures and thermal properties of CP(SMA-*co*-DVB), CP(tBS-*co*-DVB), and the IPN were determined by FT-IR, DSC, and TGA.

The oil-absorptivities of CP(SMA-*co*-DVB) and CP(SMA-*co*-DVB)/PtBS IPN decreased with increasing concentrations of DVB and tBS, respectively. The highest oil-absorptivities of CP(SMA-*co*-DVB) and the IPN(PtBS : 25%) were 615 % and 330 %, respectively. The toluene absorptivity of the synthesized polymers decreased in following order : CP(tBS-*co*-DVB) > CP(SMA-*co*-DVB) > IPN(PtBS : 25 %) > IPN(PtBS : 50 %) > IPN(PtBS : 75 %) at immersion above 60 min.

Introduction

Recently, the functional polymers for the environment are of great importance in the theoretical and practical standpoints.¹⁻⁸ Among them, some polymers have been reported on the removal of the aromatic compounds in water.⁸⁻¹⁰ Shono T *et al*¹⁰ prepared the gel type polyurethane resins containing cyclodextrin units as specific sorption sites by a cross-linking of β -cyclodextrin with diisocyanates ; the sorption capacities of these gel-type absorbents are comparable to or higher than those of Amberlite XAD-2 and XAD-7¹¹ which are used as commercial sorbents to absorb aromatic compounds from aqueous solutions. M. Morcellet *et al*¹² reported that porous polymer sorbents containing amino groups and crosslinked with divinylbenzene or ethyleneglycol dimethacrylate are suitable for the sorption of organic pollutants in water.

As can be seen from the above polymers, the oil-absorptive polymers have crosslinked three-dimensional hydrophobic networks that do not dissolve, but swell in oil. It has been known that one of the useful methods for the preparation of a crosslinked polymer is the interpenetrating polymer network (IPN) technique.^{13,14}

The aim of this work was to prepare new crosslinked polymers and polymeric composites with good physical strength which can be used in the removal of spilt oil. In this study, the crosslinked poly(stearylmethacrylate-*co*-divinylbenzene)[CP(SMA-*co*-DVB)] and the crosslinked poly(*t*-butylstyrene-*co*-divinylbenzene) [CP(tBS-*co*-DVB)]

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were synthesized from a small amount of divinylbenzene (DVB) with stearymethacrylate(SMA) and t-butylstyrene(tBS), respectively, and the CP(SMA-*co*-DVB)/PtBS IPNs were prepared by the radical polymerization of CP(SMA-*co*-DVB) preswelled with tBS and DVB in order to compare oil-absorptivity between the crosslinked polymers and the IPNs. The structures of the synthesized polymers were identified by FT-IR spectra. The thermal properties of the synthesized polymers were measured by TGA and DSC to estimate the processing temperatures and thermal properties. The oil-absorptivities of the synthesized polymers were evaluated by the ASTM method (F726-81).

Experimental

Materials

Stearylmethacrylate(SMA) and 4-*t*-butylstyrene (tBS) monomers were purchased from Aldrich Chemicals Co.(USA) and washed twice with aqueous 10% sodium hydroxide solution in order to remove inhibitors, and then they were dried over calcium chloride for 24h and distilled under reduced pressure. DVB (WAKO Chem. Japan) was used as a 55% mixture of ethylvinylbenzene. BPO was recrystallized from methanol. Toluene and methanol were distilled prior to use. Crude oil was obtained from Yugong Coporation in Korea.

Synthesis of CP(SMA-*co*-DVB)

The CP(SMA-*co*-DVB) was synthesized by the free-radical bulk polymerization of SMA (5g; 0.015mol), DVB (1.0 - 10.0 mol % to SMA mol), and BPO(0.04 g, 1.5×10^{-4} mol) under the nitrogen atmosphere at $70 \pm 0.05^\circ\text{C}$ for 20h. The products were poured into excess methanol with stirring. The obtained precipitate was filtered and dried *in vacuo* at 30°C until kept at a constant weight. The noncrosslinked poly(stearyl-methacrylate) [PSMA] was removed by extraction with THF using Soxhlet apparatus. The insoluble product was dried *in vacuo* to a constant weight.

Preparation of CP(tBS-*co*-DVB)

The CP(tBS-*co*-DVB) was prepared by the solution polymerization of tBS (4.8 g; 0.03 mol), DVB (0.39 g; 0.003 mol), and BPO (0.07 g; 3×10^{-4} mol) in the round bottom flask at $70 \pm 0.05^\circ\text{C}$ for 24 h. The products were poured into excess THF. The poly(DVB), poly(tBS-*co*-DVB), and noncrosslinked PtBS were removed by extraction with THF. The insoluble product, CP(tBS-*co*-DVB), was filtered and dried *in vacuo* at 30°C until kept at a constant weight.

Preparation of CP(SMA-*co*-DVB)/PtBS IPNs

The crosslinked poly(stearylmethacrylate-*co*-divinylbenzene-intercross-poly(*t*-butylstyrene) [CP(SMA-*co*-DVB)/PtBS] IPNs were prepared from CP(SMA-*co*-DVB) swelled in the bulk solution of DVB(1.0 g, 7.7×10^{-4} mol), BPO(0.04 g, 1.5×10^{-4} mol), and various tBS concentrations as shown in Table 3. After charging N_2 at $70 \pm 0.05^\circ\text{C}$ for 20h. The products were poured into excess methanol with stirring. The obtained precipitate was filtered. The noncrosslinked PtBS was extracted with THF using

Soxhlet apparatus. The insoluble CP(SMA-*co*-DVB)/PtBS IPNs were dried *in vacuo* until kept at a constant weight. The isolation procedure of CP(SMA-*co*-DVB)/PtBS IPN and conversion are shown in Figure 1 and Table 3.

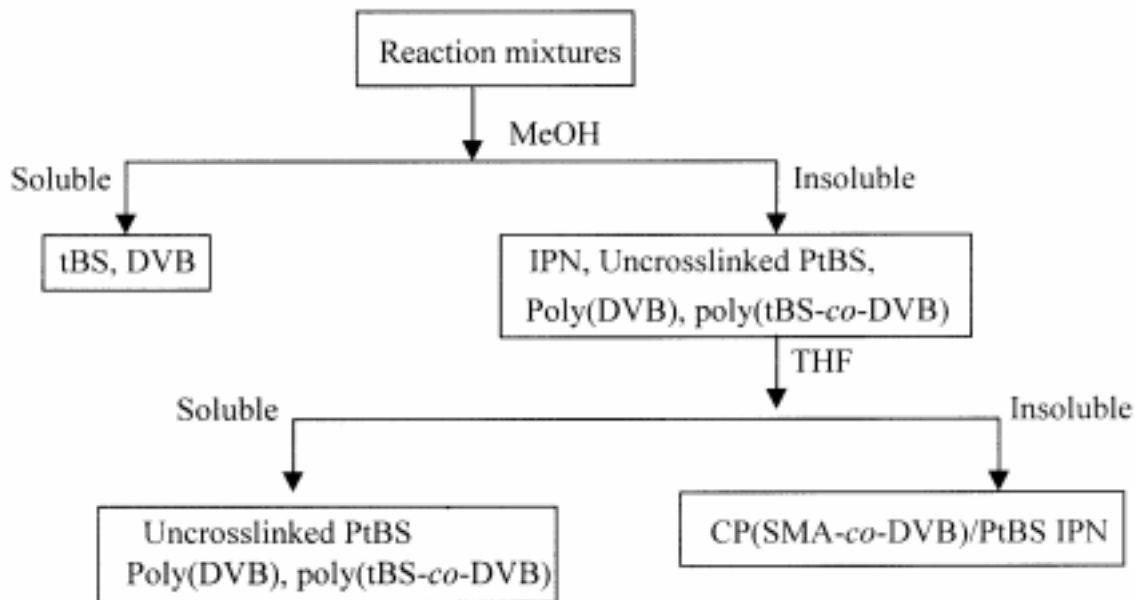


Figure 1. Block diagram of isolation procedure for CP(SMA-*co*-DVB)/PtBS IPNs.

Measurements

Infrared (IR) Spectroscopy

The spectra of the [CP(SMA-*co*-DVB)] and CP(SMA-*co*-DVB)/PtBS IPNs were recorded on a FT-IR spectrophotometer (Perkin-Elmer 1330).

Differential Scanning Calorimetry (DSC)

The crystalline melting temperatures (T_m s) were measured by using a differential scanning calorimetry (DSC; DuPont 2100). The thermograms of crosslinked CP(SMA-*co*-DVB) and CP(SMA-*co*-DVB)/PtBS IPNs were obtained at a heating rate of 10 °C/min.

Thermogravimetric Analysis (TGA)

The thermal decompositions of the synthesized [CP(SMA-*co*-DVB)] and CP(SMA-*co*-DVB)/PtBS IPNs were examined by a Shimadzu DT 30A TGA instrument at a scanning rate 15 °C/min in nitrogen.

Oil-absorption Test

The dried polymer samples with highly porous structure were obtained by rapidly drying the polymers swelled with THF at room temperature *in vacuo*. After immersing the sample in oil (toluene or crude oil diluted with toluene) at room temperature for given time periods, the sample was taken out of the oil and tapped with filter paper to remove excess oil from the sample surface. The sample was then weighed. The oil-absorptivity was evaluated by $(W_s - W_p)/W_p$, where W_s is the weight of the dried

polymer sample and absorbed oil, and W_p is that of the dried polymer sample.

Results and discussion

Characterization and General Properties

The structure of the synthesized polymer was identified by an IR spectrophotometer (Perkin-Elmer 1330). The IR spectrum of CP(SMA-*co*-DVB) exhibits characteristic absorption bands at 3025 cm^{-1} (aromatic C-H stretching), 2926 cm^{-1} (aliphatic C-H stretching), 1730 cm^{-1} (C=O stretching), 1465 cm^{-1} (CH_2 bending), 1361 cm^{-1} (CH_3 bending), and 1149 cm^{-1} (C-O stretching) with disappearance of vinyl absorption at 1640 cm^{-1} which appeared in DVB moiety of noncrosslinked CP(SMA-*co*-DVB). The IR spectrum of CP(tBS-*co*-DVB) shows the characteristic absorption bands at 3066 cm^{-1} (aromatic C-H stretching), 2962 cm^{-1} (aliphatic C-H stretching), 1361 cm^{-1} (CH_3 bending), and 900~650 cm^{-1} (aromatic C-H out-of-plane bending). And the CP(SMA-*co*-DVB)/PtBS IPN has the characteristic absorption peaks at 3066 cm^{-1} (aromatic C-H stretching) and 1730 cm^{-1} (C=O stretching). These results mean that the remaining one vinyl group of DVB in noncrosslinked CP(SMA-*co*-DVB) participates in an inter crosslinking. The behavior of the prepared oil-absorptive polymers in solvents is shown in Table 1.

Table 1. Behavior of CP(SMA-*co*-DVB), CP(tBS-*co*-DVB), and CP(SMA-*co*-DVB)/PtBS IPNs in solvents

Solvents	Samples		
	CP(SMA- <i>co</i> -DVB)	CP(tBS- <i>co</i> -DVB)	IPN
H ₂ O	× ^a	×	×
DMF	×	×	×
Methanol	×	×	×
Acetone	×	×	×
MEK	×	○ ^b	○
THF	⊙ ^c	⊙	⊙
Ethyl acetate	×	×	×
Chloroform	⊙	⊙	⊙
Diethyl ether	⊙	×	○
Benzene	⊙	⊙	⊙
Toluene	⊙	⊙	⊙

×^a: no swelling, ○^b: slightly swelling, ⊙^c: good swelling.

The polymers were swelled in benzene and toluene but they were not swelled in water, DMF, methanol, or acetone.

CP(SMA-*co*-DVB) has a considerable tackiness and its gels formed by oil-absorption were ruptured due to their weak toughness. CP(tBS-*co*-DVB) has a high brittleness and a low oil-absorptivity at an early stage, however it has good strength after oil-absorption. The synthesized IPNs do not have a tackiness like CP(SMA-*co*-

DVB) or brittleness as CP(tBS-*co*-DVB), and they have a good toughness after oil-absorption.

Thermal property

The crystalline melting temperatures (T_m)s of CP(SMA-*co*-DVB) with various DVB contents and CP(SMA-*co*-DVB)/PtBS IPNs containing different tBS concentration are shown in Table 2 and Table 3, respectively.

Table 2. Effect of DVB mol % to SMA in feed on Conversion (%) and T_m of Prepared CP(SMA-*co*-DVB)

Mol ratio of DVB (%)	Conversion (%)	T_m (°C)
1.0	93	33
2.5	87	30
5.0	97	29
7.5	93	24
10.0	95	21

Polymerization Conditions : SMA, 1.5×10^{-4} mol; Time, 20h; Temperature, 70 °C; BPO, 1 mol %.

Table 3. Effects of tBS mol % to CP(SMA-*co*-DVB) in the CP(SMA-*co*-DVB)/PtBS IPNs on Conversion, T_m , Thermal Decomposition Temperature, and Toluene-Absorptivity

Polymer	Conversion(%)	T_m (°C)	Decomposition Temp. (°C)	Toluene-Absorptivity(%)
CP(SMA- <i>co</i> -DVB)	97	28	277	360
CP(SMA- <i>co</i> -DVB)/PtBS IPN (25) ^a	84	20	317	330
CP(SMA- <i>co</i> -DVB)/PtBS IPN (50)	77	18	356	280
CP(SMA- <i>co</i> -DVB)/PtBS IPN (75)	92	17	375	190
CP(tBS- <i>co</i> -DVB)	97	-	427	380

^aMol% of tBS in feed. Polymerization Conditions : Time, 20h; Temp., 70 °C; BPO, 1 mol %.

The T_m values decreased with an increasing concentration of DVB for CP(SMA-*co*-DVB) and tBS for the IPNs, respectively as shown in Table 2 and Table 3. These results are ascribed to the increasing disorder caused by the introduction of DVB or tBS. However the thermal decomposition temperatures increased with an increasing concentration of PtBS moiety in the CP(SMA-*co*-DVB)/PtBS IPNs. This phenomenon may be attributed to the thermal stability of PtBS moiety in the CP(SMA-*co*-DVB)/PtBS IPNs.

Morphology

The scanning electron micrographs of CP(SMA-*co*-DVB)(A), CP(tBS-*co*-DVB)(B), and the IPNs(C and D) are shown in Figure 2. The micrograph of Figure 2(A) CP(SMA-*co*-DVB) (DVB content : 1%) shows the surface with the unruptured small cavities and CP(tBS-*co*-DVB) of Figure 2(B) exhibits the surface with relatively unruptured larger and longer cavities as compared with CP(SMA-*co*-DVB). However, the IPN (PtBS contents : 50%) of Figure 2(C) shows the surface with slightly ruptured cavities and Figure 2(D) of the IPN (PtBS contents : 75%) exhibits a surface with largely ruptured cavities.

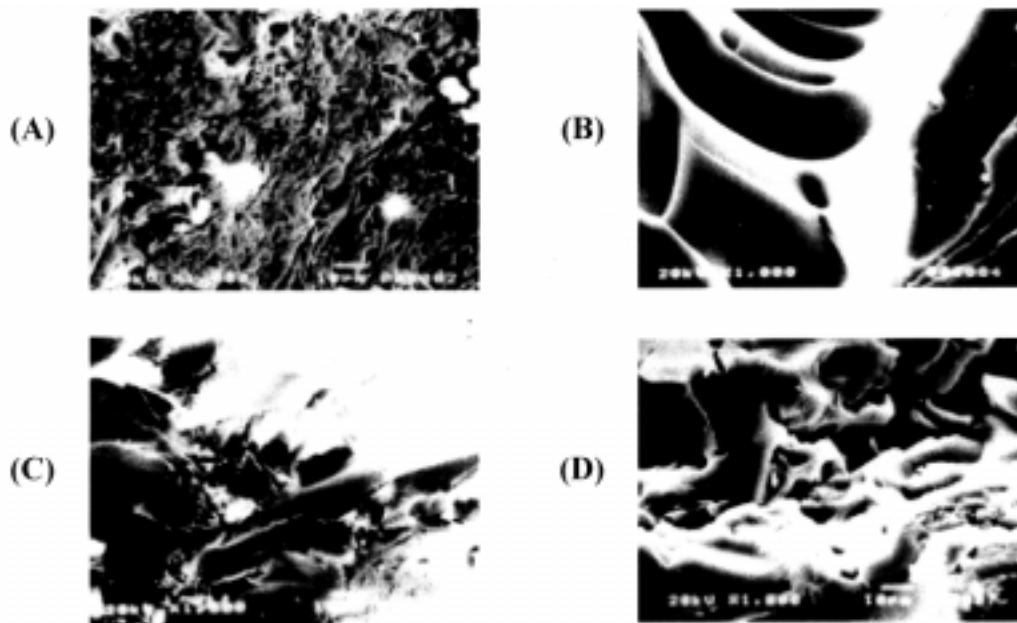


Figure 2. The scanning electron micrographs of (A)CP(SMA-*co*-DVB), (B)CP(tBS-*co*-DVB), (C)IPN (PtBS contents : 50 %), and (D)IPN (PtBS contents : 75 %).

Oil-absorptivity

Figure 3 shows the toluene-absorptivities of CP(SMA-*co*-DVB) prepared with various DVB contents. The toluene-absorptivity of CP(SMA-*co*-DVB) increased with decreasing DVB concentration and that of CP(SMA-*co*-DVB) increased up to about 30 min. and leveled off at above 60 min. The effect of a tBS concentration in the CP(SMA-*co*-DVB)/PtBS IPNs on oil-absorptivity is shown in Figure 4. The toluene-absorptivity of the synthesized polymers was found to be in following order as shown in Figure 4: CP(tBS-*co*-DVB) > CP(SMA-*co*-DVB) > IPN(PtBS : 25 %) > IPN(PtBS : 50 %) > IPN(PtBS : 75 %) at 60 min. The oil-absorptivities of CP(tBS-*co*-DVB) and CP(SMA-*co*-DVB) were higher than those of the IPNs, regardless of the tBS concentration.

These results agreed with their morphologies as explained above: CP(tBS-*co*-DVB) has relatively large unruptured cavities due to a bulky *t*-butyl group in tBS and CP(SMA-*co*-DVB) has many small unruptured cavities because of a long stearyl group in SMA. The unruptured cavities can effectively contain oil absorbed by capillary force. However, the toluene-absorptivity of the IPNs decreased with increasing tBS concentrations. This order for the IPNs may be ascribed to the slightly ruptured cavities in which they cannot effectively contain oil absorbed by the capillary force because

absorbed oil leaks out. That is, the free cavities in the IPN are much smaller and more ruptured than CP(SMA-*co*-DVB) or CP(tBS-*co*-DVB) because the cavities in the IPNs can either be filled or ruptured with PtBS molecules, used in the preparation of the IPNs. The decreasing of oil-absorptivity with the decreasing of size of the free cavities in the IPN agreed with the fact that the absorption ability of porous poly(styrene-*co*-divinylbenzene) was decreased by the shrinkage of the resin.¹²

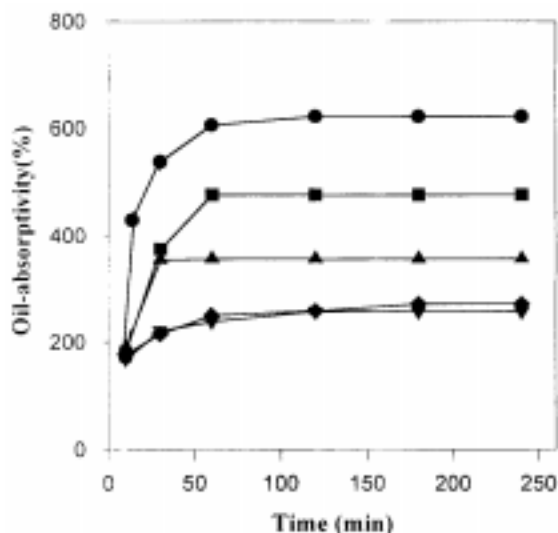


Figure 3. The toluene-absorptivity of CP(SMA-*co*-DVB)s as a function of time : DVB mol % in CP(SMA-*co*-DVB); 1.0%(●), 2.5%(■), 5.0% (▲), 7.5% (▼) and 10.0% (◆).

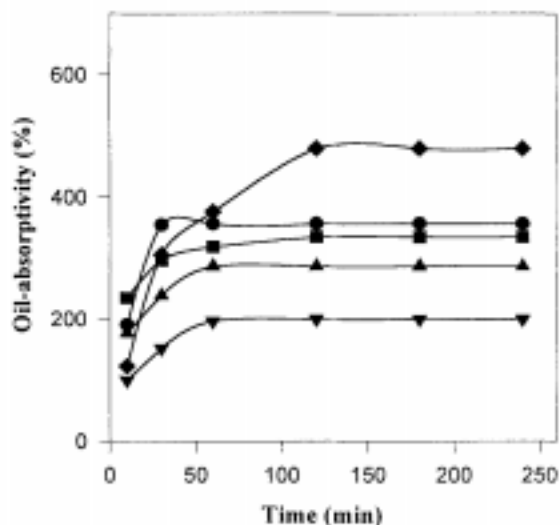


Figure 4. The toluene-absorptivity of CP(SMA-*co*-DVB)/PtBS IPNs as a function of time : PtBS mole ratio in IPNs; 0% (●), 25% (■), 50% (▲), 75% (▼), 100%(◆).

The effects of the oil-absorptivity of CP(SMA-*co*-DVB) on DVB contents and CP(SMA-*co*-DVB)/PtBS IPNs on PtBS contents are shown in Figure 5 and Figure 6. The highest oil absorptivity of CP(SMA-*co*-DVB) containing DVB of 1 % was 615 % for toluene and 750 % for 10 % crude oil diluted with toluene for 1 h immersion (Figure 5), and that of the CP(SMA-*co*-DVB)/PtBS IPN containing PtBS of 25 % was 330 % in toluene and 510 % in 10 % crude oil (Figure 6). The toluene absorptivity of CP(SMA-*co*-DVB) with 1% DVB for 10 minutes immersion was similar to that of polymeric α -gel-1000 (commercialized by ALPHA JAPAN INC, Tokyo, Japan). From the measured absorptivity values, it can be concluded that the oil-absorptivities of the synthesized polymers are more effective against 10% crude oil diluted with toluene than neat toluene.

Considering the merit points for general properties of the synthesized polymers as described in the characterization and general properties section of the results and discussion, the synthesized IPN containing PtBS of 25 % is a potential material for removing spilled oil.

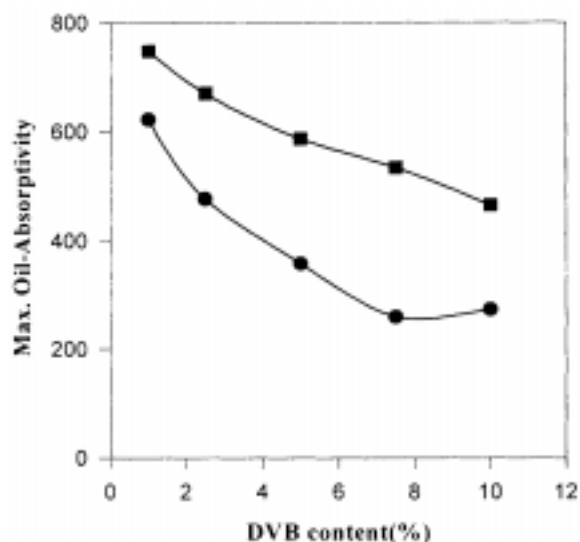


Figure 5. The oil-absorptivity of CP(SMA-co-DVB) in toluene (●) and diluted crude oil (■).

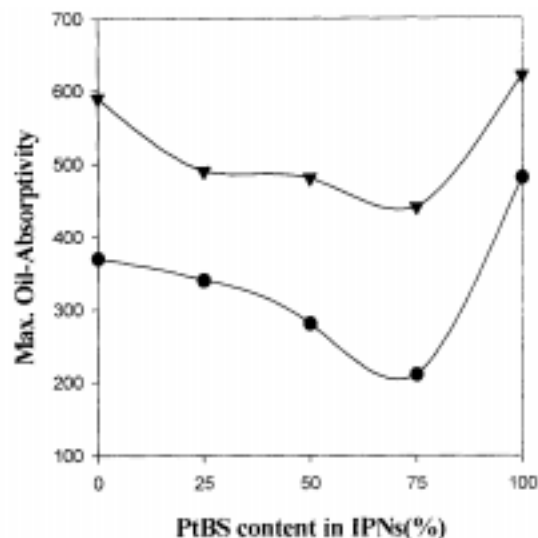


Figure 6. The oil-absorptivity of CP(SMA-co-DVB)/PtBS IPNs in toluene (●) and diluted crude oil (▼).

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