Synthesis and Characterization of Porous Crosslinked Copolymers for Oil Spill Sorption

Abdel-Azim A. Abdel-Azim,[1] A. Mahmoud Abdul-Raheim,[1] [2] Ayman Mohamady Atta,[1]* Witold Brostow [2] and A. Fawzy El-Kafrawy [3]

[1]* Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt; fax +20-2-274-7443; email: khaled_00atta@yahoo.com
[2] Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, POBox 305310, Denton, TX 76203-5310, USA; brostow@unt.edu; http://www.unt.edu/LAPOM/
[3] Chemistry Department, Faculty of Science, Ain Shams University, Abassia, Cairo, Egypt.

Abstract: Cinnamoyloxy ethyl methacrylate (CEMA) was copolymerized with different monomer feed ratios of octadecyl acrylate (ODA) and crosslinked using azobisisobutyronitrile (AIBN) as the initiator and N,N',N''-trisacryloyl melanine (AM) or N,N',N''-trismethacryloylmelanine (MM) crosslinkers. The networks are characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). For crosslinked CEMA/ODA copolymer sol fraction values are lower when MM is used rather than AM. The thermal stability of crosslinked network increases with increasing ODA concentration and also in the presence of MM crosslinker, a consequence of higher crosslinking density. SEM results show a porous structure; micropores are formed when ODA contents increases. According to DMA results, the flexibility of the network is enhanced by incorporation of MM rather than AM. Since our crosslinked networks are both flexible and porous, they are applicable as oil sorber networks to alleviate pollution from oil spills.

Introduction

Crosslinked polymers have a wide range of uses [1 - 5]. In water treatment, soil conditioning, chromatography, biomedical and biochemical applications, solid phase organic synthesis, enzyme immobilization, solvent ion separation and in several other areas crosslinked polymers are principal substrates. Crosslinking (chemical as well as physical) results in elasticity and swelling behavior [6 -11]. Porous structures can be formed as a result of a phase separation during polymer network formation process [12 -17].

Along with extensive use of petroleum, contamination of the environment by oil spills is a problem which requires immediate solution. Porous network polymers can absorb nonpolar solvents. Thus, the networks can be used as absorbents of oil or other organic solvents spilled on water. However, very few literature studies report on formation of porosity in alkyl acrylate polymers; exceptions deal mainly with loosely crosslinked networks. One of us and Arndt [17] has obtained porous alkyl acrylate networks by using e-beam irradiation. The present study deals with synthesis and formation mechanisms of elastic and also porous alkyl acrylate copolymers crosslinked with new crosslinkers. A number of porous crosslinked octadecyl acrylate (ODA) + cinnamoyloxy ethyl methacrylate (CEMA) copolymers were prepared.

Effects of various synthesis parameters such as type and content of crosslinkers and copolymer composition on total conversion and gel fraction have been determined. Thermal stabilities and morphologies of the crosslinked copolymers were determined by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively.

Results and Discussion

Characterization of the synthesized crosslinkers and crosslinked copolymers

The synthesized N,N',N",-trisacryloyl-melanine (AM), N,N',N",-trismethacryloyl-melanine (MM) crosslinkers and CEMA were characterized by ^{1}H NMR and Fourier-transform infrared (FT-IR) spectroscopy. ^{1}H NMR spectra were recorded on a 270 MHz Brukker W-P-270 SY spectrometer with $CDCl_3$ as the solvent. IR spectra were recorded in KBr pellets using a Brukker FT-IR model IF 566 spectrometer at 258 ^{o}C. Sol fraction (SF) of the crosslinked xerogels discs was determined from the weight of the dried gel before and after solvent Soxhlet extraction. Toluene is a good solvent for CEMA, ODA and their copolymers since it can extract unreacted residual polymer molecules from xerogel discs. We meant by zerogel the crosslinked copolymers before extraction of uncrosslinked monomers or copolymers and we prepare it in the disc form to measure the mechanical and dynamic properties by Dynamic mechanical analyzer. All discs were dried at room temperature after solvent extraction for 24 h, and then oven dried at 100 ^{o}C before being weighed. SF values were calculated as $SF = (W_0 − W) \cdot 100/W_0$, where W_0 and W are the weight of disc before and after extraction, respectively. TGA was performed in N_2 flow (20 cm$\cdot$min^{-1}) at the heating rate 10 K/minute with a Perkin Elmer TGA-7 apparatus. Differential scanning calorimetry (DSC) results were obtained with Perkin Elmer DSC-7 at the heating rate of 10 K/minute in N_2 atmosphere. Dynamic mechanical analysis (DMA) was carried out using a Perkin Elmer DMA-7e model from -50 ^{o}C to +100 ^{o}C at 5 K/minute at the sinusoidal frequency of 1.0 Hz. The TGA, DSC and DMA techniques are well explained by Menard [18] and also by Lucas and her colleagues [19].

Scanning electron microscopy (SEM) was used to study the morphology of the crosslinked polymers with a JEOL JSM-5800 model. Dried crosslinked polymers were cut to expose their inner structure and coated with a thin layer of Pd + Au alloy before SEM characterization.

Chemical structures of the networks

Properties of crosslinked polymers are known to be highly influenced by crosslink density and to a lesser extent by the functionality of crosslinkers. Wide varieties of acrylate crosslinkers have been used to form crosslinked networks. In bulk or solution polymerization there is a wide choice of crosslinkers. Much effort has been expended on attaining high levels of purity in the monomers, but the literature indicate otherwise with regard to the crosslinking agents. In this respect, a simple method was used to synthesize two crosslinkers based on polyfunctional acrylate and methacrylate [20]. The chemical structures of the prepared crosslinkers were elucidated by FT IR, ^{1}H NMR and ^{13}C NMR. The ability to use these new crosslinkers to synthesize a novel series of porous crosslinked polymers is important for the objective of this work.

Good agreement between experimental and theoretical values of C, H, O and N contents reveal that the syntheses of purified AM and MM monomers were performed successfully. An IR spectrum of AM is displayed in Fig. 1.
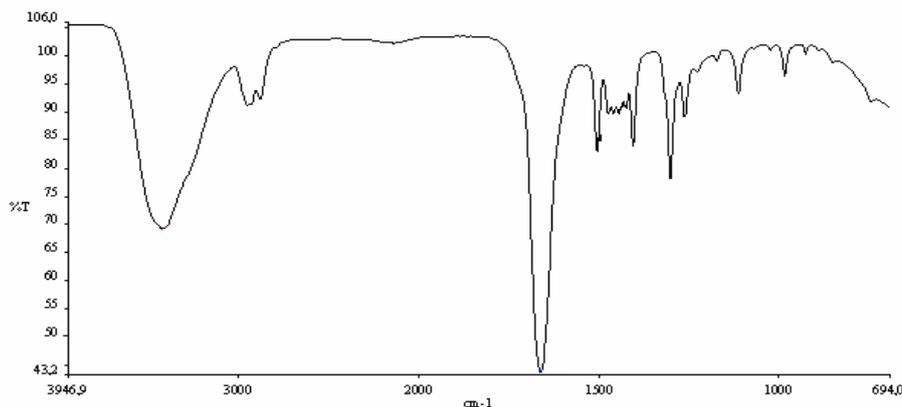
Fig. 1. IR Spectrum of AM.

Both crosslinkers, show multiple bands at 3350–3200 cm^{-1}, typical of –NH stretching bands of secondary amide due to hydrogen bonding. A strong band at 1680 cm^{-1} is observed in the spectra of both crosslinkers and assigned to O=CNH stretching. These peaks indicate the formation of amide linkage in the structure of both AM and MM crosslinkers. Strong peaks at 3075 cm^{-1} (–CH stretching) and 1614 cm^{-1} (C=C stretching) confirm the presence of acrylate and methacrylate moieties in the structure of AM and MM. Moreover, the presence of bands at 2965–2870 cm^{-1} (CH bending of CH$_3$) indicates the incorporation of MC with melamine.

Copolymerization of CEMA with ODA and crosslinking

CEMA was prepared and purified as reported in an earlier article [9]. Cinnamoyl chloride was condensed with HEMA to produce CEMA. The synthesized CEMA was characterized by FTIR and ^{1}H NMR spectroscopy [9]. The CEMA monomer was copolymerized with different alkyl acrylase macromonomers; we have added to ODA 1, 2 and 4 wt. % of trimethylolpropane triacrylate (TPT) crosslinker in the presence of AIBN as initiator [10]. Copolymerization of CEMA with ODA) was performed in the range of 10 – 90 % in the feedstock. Crosslinked CEMA/ODA copolymers were prepared by bulk polymerization in the presence of AIBN and a hexafunctional crosslinker.

To understand the distribution of crosslinks in the network, reactivity of various double bonds in the system must be determined. This includes the reactions between double bonds of CEMA and ODA, the initial double bonds in the crosslinker, and various double bonds remaining in polymeric chains after incorporation of the crosslinker. Our copolymer systems are composed essentially of CEMA with varying amounts of ODA comonomer to provide hydrophobicity so as to enhance oil affinity.

In a crosslinking system we have soluble and insoluble portions, the latter swell in good solvents providing a gel. According to the Flory swelling theory [21, 22], swelling behavior is affected by elasticity, affinity to solvent and crosslinking density. We have determined swelling behavior of gels with different amounts of the crosslinkers, 0.01 – 4 wt. %, mostly below 1 % to provide super absorbents with high swelling capacity and low soluble polymer content. Polymer chains not attached to the infinite network can be extracted from the gel fraction; their effect is difficult to treat and usually neglected in the theories. While these chains of course do not contribute to the modulus, they can be solvated and contribute to the swelling.

Clearly it is desirable to eliminate or minimize the content of these extractable molecules. The percentage of the extracted (soluble) fraction) depends on: (a) the type and concentration of the monomers, and (b) the type and concentration of crosslinking agent [21, 22].

In the present investigation the polymer rods were post cured at 380 K in an air oven for 24 hours to achieve complete polymerization. The sol fractions of these polymeric materials were determined via Soxhlet extraction technique. In this respect, the dried xerogel discs were transferred into an extraction thimble and were subjected to Soxhlet extraction with chloroform. After extraction for 24 h, the samples were dried in atmosphere for several hours and then dried to a constant weight in vacuum oven at 308 K. However, no further extraction was seen after 24 hours, hence this Soxhlet extraction time was adopted for all samples. Reactivity of AM and MM crosslinkers towards CEMA/ODA copolymer was evaluated in terms of the degree of conversion and SF results. The effect of crosslinker concentrations on SF values was determined through crosslinking of CEMA (50 mol %)/ODA (50 mol %) copolymer using 1 wt. % of either AM or MM crosslinkers and 0.02 wt. % AIBN as the initiator. SF % values obtained in chloroform are listed in Table 1.

Tab. 1. Soluble fraction values of crosslinked CEMA/ODA copolymers.

Xerogel composition of (CEMA/ODA)	Crosslinker Content (wt. %)	SF of crosslinked gel in toluene in %	
		AM	MM
90/10	1.0	29	22
70/30	1.0	25	20
	0.5	29	25
50/50	1.0	20	15
	2.0	15	10
	4.0	10	8
30/70	1.0	18	12
10/90	1.0	15	8

Table 1 tells us that SF decreases with increasing ODA concentration in the copolymer. Apparently the ODA homopolymer has higher reactivity towards either of the crosslinkers than CEMA/ODA copolymers. In other words, the alkyl acrylate polymers are used up before a significant number of CEMA would incorporate in the network structure. We also find that the *SF* values for crosslinked CEMA/ODA copolymers with MM are lower than those for crosslinking in the presence of AM. This can be attributed to the high reactivity of the CEMA/ODA copolymer towards methacrylate crosslinker - much higher than for acrylate crosslinkers.

Thermal characteristics of crosslinked CEMA-ODA copolymers

Thermal stability of crosslinked CEMA/ODA copolymers was assessed in terms of the initial decomposition temperature (IDT). TGA is a technique to determine weight continuously while heating a sample [18, 19]. Several degradation schemes are proposed for crosslinked polymers based on the principles of the cleavage of simple ethers and the products obtained from the pyrolysis study. Our samples were subjected to TGA before extraction of SF. Figure 2 shows for our copolymers two degradation steps; typically crosslinked polymers have only one degradation step.

The lower temperature loss may be due to the breaking of ester linkages present in the networks and the second step to degradation of the crosslinked polymers. Apparently the unextracted soluble fractions of linear polymers have different thermal characteristics than those crosslinked by either AM or MM crosslinkers. Accordingly, the determined weight loss values from 25 ^{o} to 350 ^{o}C can be correlated with the SF results from Soxhlet extraction. Careful inspection of the data indicates a good agreement between SF values and thermal decomposition at 350 ^{o}C. Furthermore, the thermal stability of crosslinked networks increases with increasing ODA concentration, higher crosslinker contents and the presence of MM crosslinker. This can be attributed to increase of crosslinking densities in the CEMA/ODA copolymers.
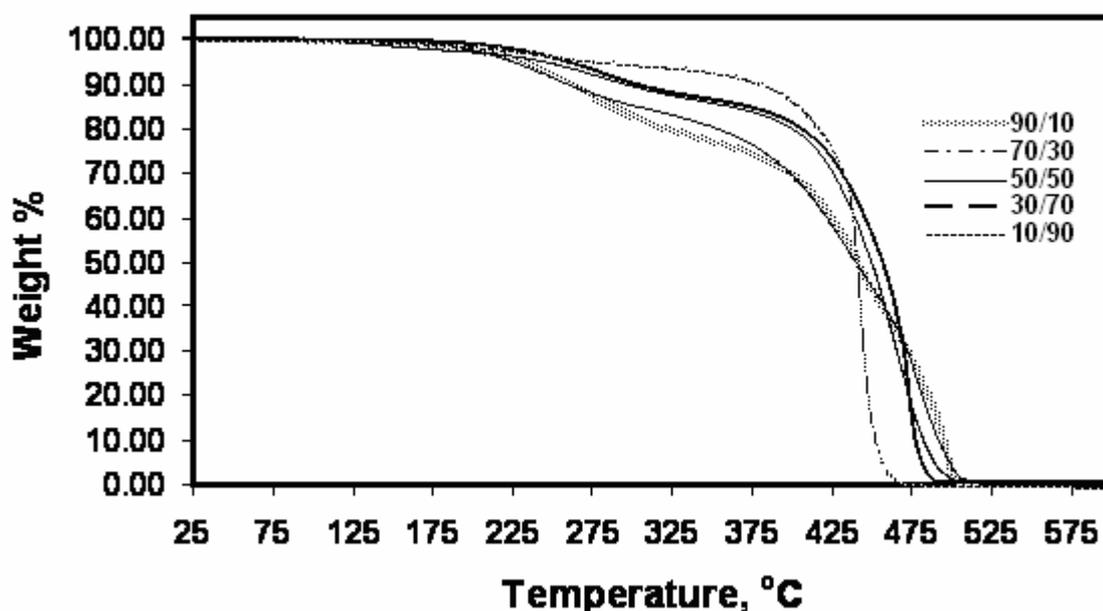
Fig. 2. TGA curves of CEMA/ODA crosslinked copolymers with different molar ratios for 1 % MM crosslinker.

Morphology of crosslinked polymers

Porous polymers including networks can be obtained by several techniques [23 - 26]. Submicrometer-sized gel particles respond to external stimuli more quickly than bulk gels [27]. Networks with dangling chains can easily expand or collapse upon an external stimulus because one side of the dangling chain is free [28]. A network with an interconnected pore structure can be formed through polymerization below lower critical solution temperature (LCST) and then elevating the temperature above LCST [29]. It is now well understood that a phase separation during the network formation process is mainly responsible for the formation of porous structures in dry state.

In order to obtain macroporous structure, a phase separation must occur during the course of the crosslinking process so that the two-phase structure is fixed by the formation of additional crosslinks. Depending on the synthesis parameters, phase separation takes place on a macroscale or on a microscale. In the first case, when the networks start to form a crosslinked structure, the network collapses at the critical point for phase separation and becomes a microsphere; the separated liquid phase remains as continuous phase in the reaction system. As the reaction proceeds, new

microspheres are continuously generated due to the successive separation of the growing polymers. Agglomeration of microspheres leads to formation of a macroporous network consisting of two continuous phases. In the second case, phase separation results in the formation of a dispersion in the reaction system. Thus, the liquid phase during the gel formation process separates in the form of the small droplets inside the gel and becomes discontinuous. Due to slowness of the volume change of the gel sample, the initiator of the sample is initially under constant volume condition; further polymerization and crosslinking reactions fix the two-phase structure in the final material. In the present system, two distinct new crosslinkers were used to prepare porous crosslinked CEMA/ODA networks. We have determined the pore sizes from SEM pictures. SEM photos for crosslinked CEMA 90 mol % and CEMA 10 mol % with MM and AM crosslinkers are shown in Figure 3.

| CEMA/ODA 90/10 1 % MM | CEMA/ODA 10/90 1 % MM |
| CEMA/ODA 90/10 1 % AM | CEMA/ODA 10/90 1 % AM |
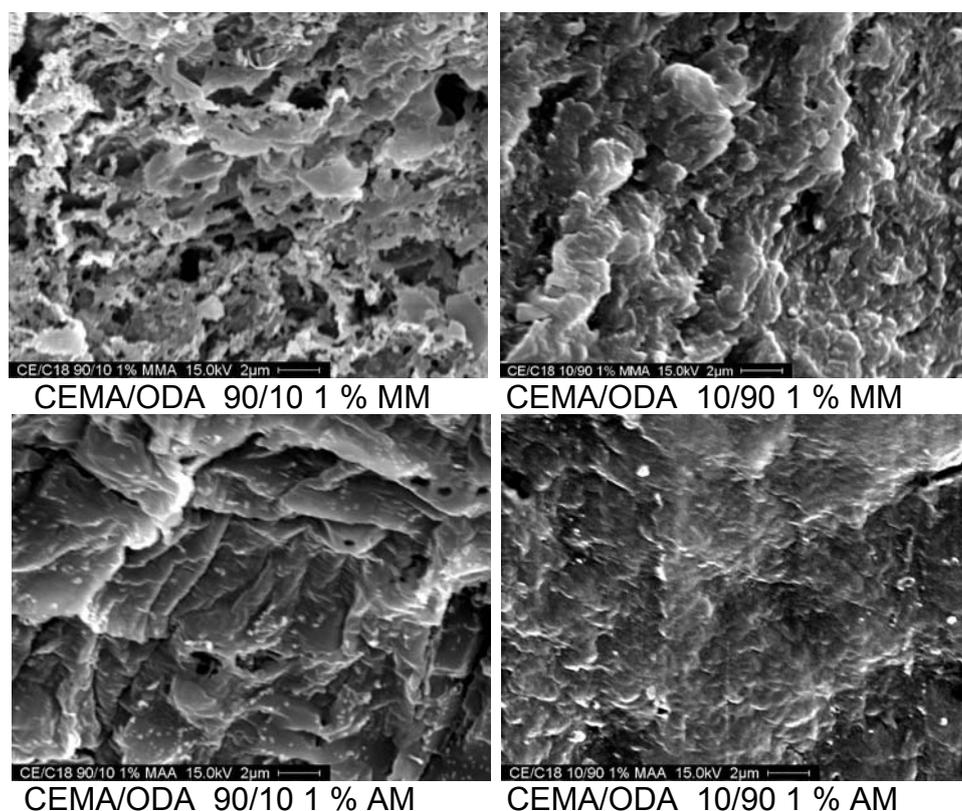
Fig. 3. SEM Images of CEMA/ODA.

Effects of crosslinker concentrations on the network porosity are represented in Figure 4 i.e. heterogeneity in the networks depending on the crosslinker type and content; at 0.5 wt. % of MM we see large polymer domains with also large discontinuities between the domains. For the crosslinker contents of 2 wt. %, the morphology changes drastically, aggregates of spherical domains appear. At 4 wt. % crosslinker we see aggregates of 1 - 2 μm of well defined microspheres. Individual microspheres have diameters ≈ 0.1 - 0.5 μm. The structure looks like cauliflowers, typical for a macroporous copolymer network.

SEM photographs of CEMA/ODA crosslinked with different weight ratios of AM are different than that those for samples crosslinked with MM. Large pores are formed at low AM contents (0.5 wt %). The pores convert to micropores when the AM content

increases up to 4 wt. %. Okay reported that low concentrations of monomer during gel formation and higher crosslinker contents favor gel heterogeneity [30].

CEMA/ODA 50/50 0.5% MM	CEMA/ODA 50/50 4% MM
CEMA/ODA 50/50 0.5% AM	CEMA/ODA 50/50 4% AM
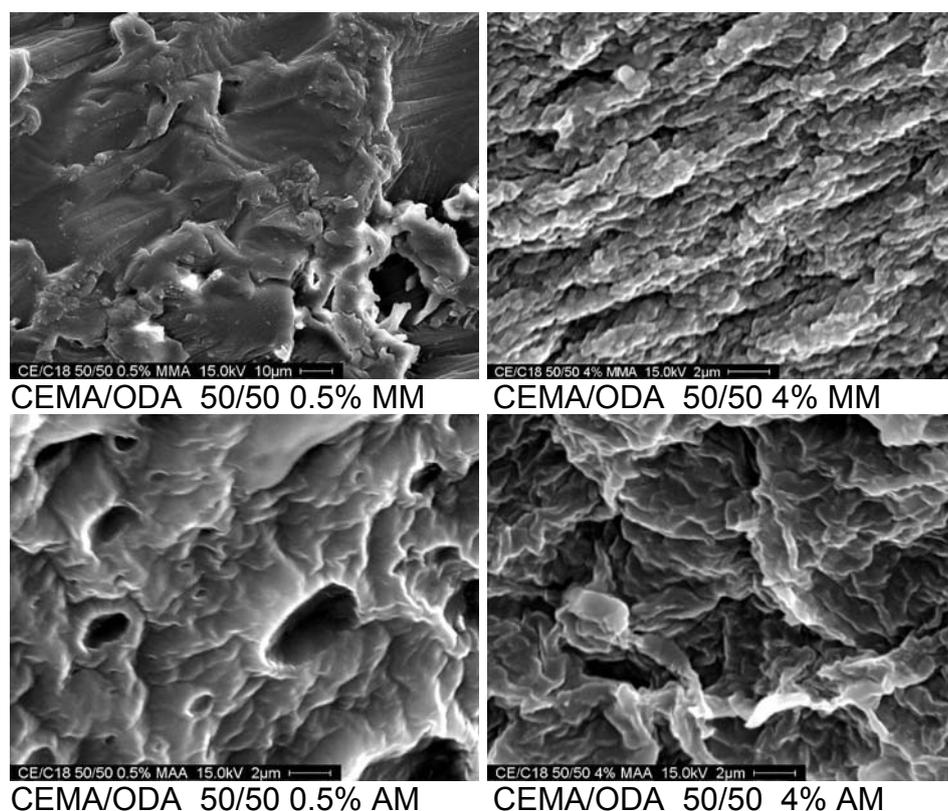
Fig. 4. SEM images of CEMA (50 mol %) /ODA crosslinked with different weight ratios of MM and AM crosslinkers.

The morphology can be correlated with SF values in Table 1. We recall higher crosslinking densities with the MM crosslinker. Large pores are formed with increasing CEMA content in the copolymers in the presence of MM. Accordingly, we formulate the following scheme for the formation of heterogeneous CEMA/ODA networks with microspheres. When the polymerization is initiated by the decomposition of AIBN molecules, the primary radicals formed start to grow by adding the monomers of CEMA and ODA and a crosslinker, either MM or AM. Initially, the primary molecules contain CEMA/ODA, CEMA and ODA units, MM or AM units with two unreacted methacrylate or acrylate (pendant vinyl groups) and MM or AM units involved in cycles. As the time goes on, more and more primary molecules are formed so that the intermolecular crosslinking reactions between the primary molecules may also occur. Funke and coworkers noted the importance of cyclization reactions in free radical crosslinking copolymerization [31]. Apparently cyclization dominates over the intermolecular crosslinking reactions. Since every cycle reduces the coil dimension of the molecule as well as the solvent content inside the coil, the structure of the formed polymers is fairly compact and clusterlike. When the cyclization density of the clusters exceeds a critical value, the clusters phase separate and form primary particles microspheres of ≈ 0.1 - 0.5 μm in diameter. The microspheres are nonporous and constitute a highly crosslinked region of the network. The agglomeration of the microspheres during crosslinking polymerization through their peripheral pendant vinyl groups and radical ends leads to formation of large shapeless discrete

agglomerates of 10 - 100 μm in diameter - which agglomerate further to form the final network. Macropores constitute the interstices between the microspheres while the voids between the agglomerates build the large pores in the network.

Elasticity of CEMA-ODA networks

Comparing the reactivities of the CEMA and ODA monomers with MM or AM crosslinkers in free radical copolymerization, we find the crosslinkers reactivity is at least twice the CEMA and ODA – a consequence of the existence of three vinyl groups on each crosslinker molecule. Thus, molecules formed earlier should contain more MM or AM units and be more crosslinked than those formed later. Due to rapid consumption of MM or AM monomers during polymerization, the density of clusters should decrease as the monomer conversion increases. At high conversion degrees, structure of the clusters will approach that of the primary molecules. Thus, the microspheres formed earlier (located in the interior of agglomerates) probably form the highly crosslinked regions of the final material, interconnected with loosely crosslinked regions. The presence of such regions causing spatial inhomogenities has been known before.

In our copolymerization processes there are three possibilities to form crosslinked CEMA/ODA copolymer or homopolymers of CEMA and ODA. Properties of copolymeric systems depend not only on their chemical composition but also on the distribution of the units along the macromolecular chains and on the relative stereochemical configuration of side chains. It is worthwhile to analyze the influence of these factors on the rigidity or flexibility of the final material. In an earlier paper [11] the reactivity ratios and microstructures of CEMA/ODA copolymers were determined. The data indicate that the copolymers have random distribution sequence. The monomer reactivity ratios for the copolymerization of CEMA with ODA are 0.265 and 0.982, respectively. The product of reactivity ratio suggests a random distribution with longer sequences of ODA units in the copolymer chain. The data of SF values (see again Table 1) indicate that the crosslinking efficiency increases with increased crosslinker and ODA contents. Accordingly, the rigidity of copolymers increases with increasing crosslinking density of the prepared networks. This hypothesis can be proven by DMA results represented in Figs. 5 - 8.
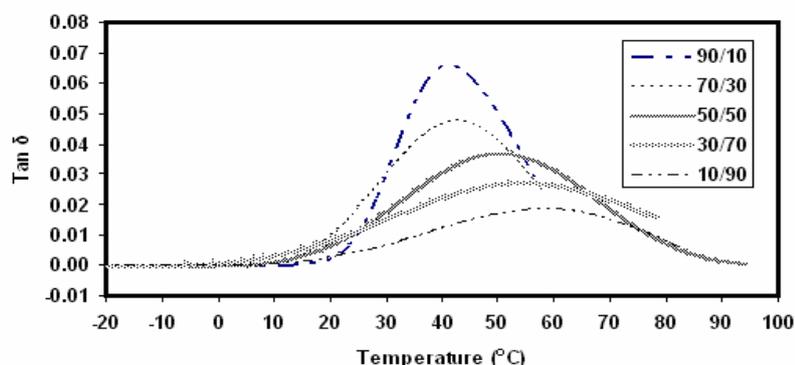
Fig. 5. Tan δ vs. temperature for different molar ratios of crosslinked CEMA/ODA with 1 wt. % of AM crosslinker.
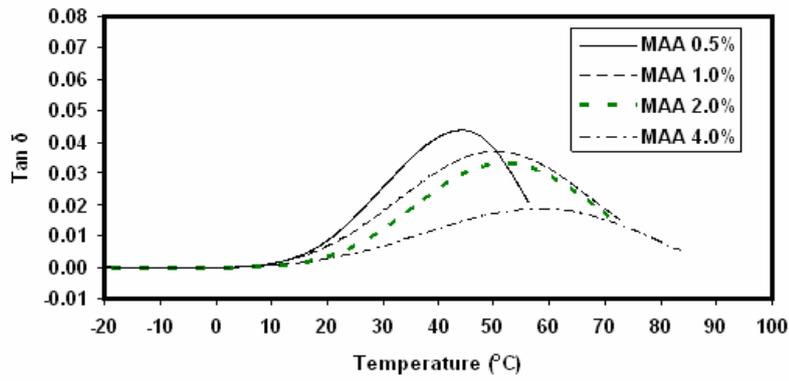
Fig. 6. Tan δ vs. temperature for 50/50 molar ratio of crosslinked CEMA/ODA at different concentrations of AM crosslinker.
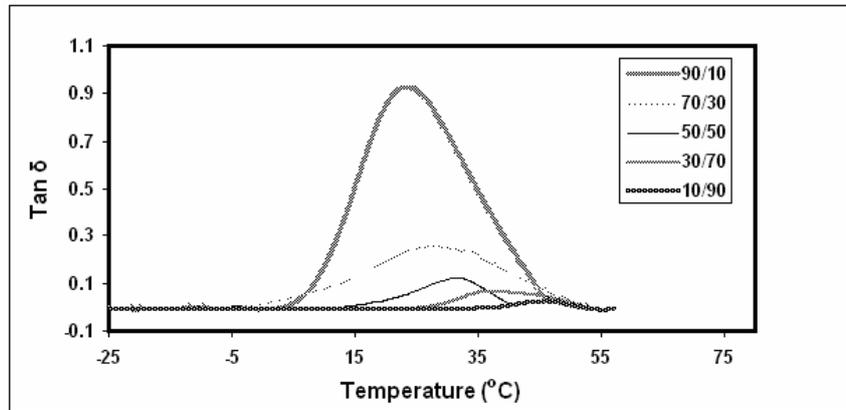
Fig. 7. Tan δ vs. temperature for different molar ratios of crosslinked CEMA/ODA with 1 wt. % of MM crosslinker.
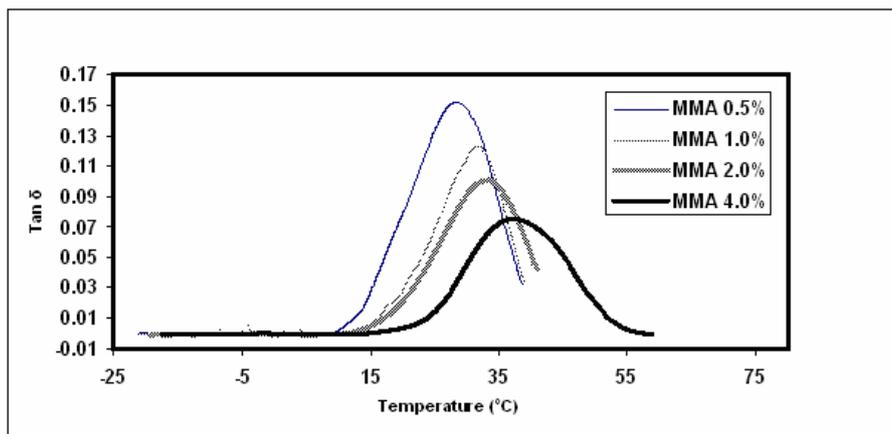
Fig. 8. Tan δ vs. temperature for 50/50 molar ratios of crosslinked CEMA/ODA at different concentrations of MM crosslinker

We see that the height of tan δ decreases with increasing both crosslinker and ODA contents. We explain this by strong dipolar interactions between polar groups related to the side substituents and crosslink density of the polymeric chains.

The presence of long flexible n-alkyl substituents has a significant effect on flexibility of macromolecules, including poly (alkylstyrenes) [32], polyacrylates [33] and polymethacrylates [34]. As the length of the n-alkyl side chain increases, flexibility increases within each of these families of polymers. Clearly introduction of a spacer group increases the flexibility of the repeating unit. In our system we expected that the introduction of ODA should increase flexibility of the polymer segments by decreasing the steric hindrance of the rigid aromatic side groups of CEMA located near the chain backbones. The results show, however, that this is not the case.

To explain our results we recall the conclusion of DiMarzio [35] that the flexibility depends on the backbones as well as on the side groups of the chains. We observe that the tan δ values decrease with incorporation of AM instead of MM in the network structure. In other words, the flexibility of the network increases with incorporation of MM rather than AM crosslinker. Polymethacrylates have a total of four flexible bonds per monomer unit, polyacrylates three while polystyrene has only two since the rotation of the benzene ring (CEMA) about the bond connecting it to the polymer backbone does not give a configurationally distinguishable position [34]. Given the chemical structures of MM and AM crossklinkers, the crosslinker based on methacryl groups leads to more flexible networks than that based on acrylate. Our DMA results support this explanation.

Experimental part

Materials

Melamine (2,4,6-triamino-1,3,5-triazine) pure grade (assay ≥ 99%) was supplied by Fluka Chemical Co. Acryloyl chloride (AC) was supplied by Aldrich Chemical Co. Methacryloyl chloride (MC) and triethylamine (TEA) were from Sigma-Aldrich Corp. 1-Methyl-2-pyrrolidone (*ReagentPlus*®, 99%), tetrahydrofuran and toluene (from Aldrich) were used as received. 2-Hydroxyethyl methacylate (HEMA) monomers were supplied by Aldrich. 2,2' Azobisisobutyronitrile (AIBN) was used as the initiator. Cinnamoyl chloride, octadecyl acrylate (ODA) and HEMA were purified by washing with 5 % aqueous sodium hydroxide, drying over anhydrous CaCl$_2$ and distilling under vacuum. TEA was refluxed with acetic anhydride and with KOH and then distilled. AIBN recrystallized from ethanol was used as a thermal polymerization initiator. Tetrahydrofuran (THF) was obtained from Fluka Chemical Co.

Synthesis and purification of N-melamine acrylamide crosslinkers

As previously described [13], melamine (0.1 mole) was dissolved in NMP (100 ml) at room temperature for 24 h. The solution was transferred into a four-necked flask fitted with a mechanical stirrer, thermometer, nitrogen inlet and dropping funnel. Triethyl amine (0.3 mole) was added to the solution. Acryloyl chloride or methacryloyl chloride (0.3 mole) was added dropwise at room temperature for 2 h. The reaction temperature had increased by no more than 10 K for 6 h, a precipitate of the triethylamine hydrochloride appeared immediately. The reaction mixture was stirred for 48 h at room temperature and the precipitate was removed by filtration. The filtrate was diluted with THF and the unreacted melamine was removed from the

aqueous layer by addition of saturated hot aq. NaCl. THF was evaporated from the filtrate under vacuum. The remaining products were added to toluene and the precipitate was removed by filtration. The final viscous products were recovered after evaporation of toluene and NMP under vacuum using a rotary evaporator. The products of reaction between AC or MC with melamine are designated here as AM and MM, respectively. The reaction is represented in scheme (1).

H_2N—triazine—NH_2 / NH_2 + $CH_2=C(R)COCl$ $\xrightarrow[\text{NMP}]{(C_2H_5)_3N}$

R= H or CH3

$HCOC(R)=CH_2N$—triazine—$NHCO\,C(R)=CH_2$ / $NHCOC(R)=CH_2$
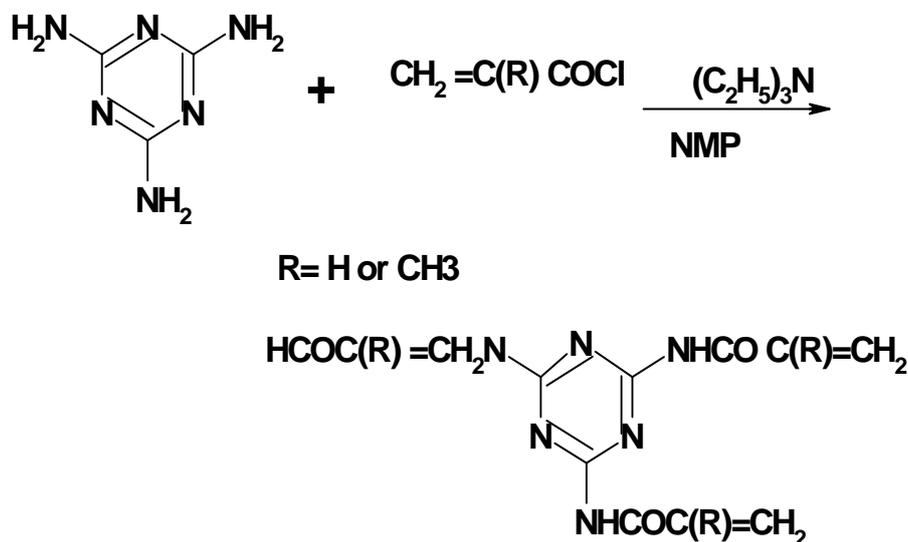
Scheme 1. Synthesis of melamine crosslinkers.

Synthesis of Cinnamoyloxy ethyl methacrylate (CEMA)

A solution of 66 mmol of HEMA and 66 mmol of TEA was refluxed in 100 ml of THF for 2 h in the absence of air or moisture, and then the clear solution was cooled to 273 K in an ice bath. Then, 79 mmol of cinnamoyl chloride was added drop-wise with vigorous stirring for 2 h at 273 K and then for 4 h at room temperature. The triethylamine hydrochloride salt formed was filtered out and the filtrate was concentrated on a rotary evaporator. The product was purified by pouring the solution in THF into 500 ml of n-hexane. The precipitate was filtered out and the solvent was distilled off using cuprous chloride to inhibit polymerization.

Synthesis of Crosslinked CEMA/octadecyl acrylate

The crosslinked CEMA/ODA copolymers were obtained through bulk polymerization. The monomers were mixed together with AIBN initiator 0.02 wt. % and different weight ratios of melamine-based crosslinker (MM, AMAm) ranging from 0 - 4 wt. %. The mixture was bubbled with nitrogen. This procedure was repeated with different monomer feed ratios (mol % CEMA/mol% acrylate) viz. 90/10, 70/30, 50/50, 30/70 and 10/90 to prepare different compositions of crosslinked copolymers. The copolymerization reactions were performed in siliconized test tubes under N_2 atmosphere at 65 °C for 24 h. The polymer rods were post-cured at 110 °C in an air oven for 24 h to ensure complete polymerization.

References

[1] Mark, H. F. *J. Mater. Ed.* **1990**, 12, 65.
[2] Brostow, W. editor, *Performance of Plastics*, Hanser, Munich – Cincinnati **2000**.
[3] Bilyeu, B.; Brostow, W.; Menard, K.P. *J. Mater. Ed.* **1999**, 21, 297.
[4] Bilyeu, B.; Brostow, W.; Menard, K.P. J. Mater. Ed. **2000**, 22, 107.
[5] Bilyeu, B.; Brostow, W.; Menard, K.P. *J. Mater. Ed.* **2001**, 23, 189.
[6] Zhou, M. H.; Ha, C. and Cho, W. *J. Appl. Polym. Sci.* **2001**, 81, 1277.
[7] Bertrand, P. H. *J. Mater. Res.* **1993**, 8, 1749.
[8] Anthony, W. S. *Appl. Eng. in Agr.* **1994**, 10, 357.
[9] Atta, A. M.; El-Ghazawy, R. A.; Farag, R. K.; El-Kafrawy, A. F. and Abdel-Azim, A. A. *Polym. Int.* **2005,** 54, 1088.
[10] Atta, A. M.; El-Ghazawy, R. A.; Farag, R. K.; and Abdel-Azim, A. A. *Reactive & Functional Polymers* **2006**, 66, 931.
[11] Atta, A. M.; El-Ghazawy, R. A.; Farag, R. K. and Abdel-Azim, A. A. *J. Polym. Res;* **2006**, 13, 257.
[12] Okay, O. and Gurun, C. *J. Appl. Polym. Sci.* **1992**, 46, 401.
[13] Kameko, Y.; Nakamura, S.; Sakai, K.; Aoyagi , T.; Kikuchi, A.; Sakurai, Y. and Okano, T. *Macromolecules* **1998**, 31, 6099.
[14] Zhou, M. H.; Cho, W. *Polym. Int.* **2001**, 50, 1193.
[15] Jang, J. and Kim, B. *J. Appl. Polym. Sci.* **2000**, 77, 914.
[16] Gotoh, T.; Nakatani, Y. and Sakohara, S. *J. Appl. Polym. Sci.* **1998**, 69, 895.
[17] Atta, A. M. and Arndt, K. F. *Polym. Int.* **2001**, 50, 1360.
[18] Menard, K.P. Ch. 8 in *Performance of Plastics*, Brostow, W., editor, Hanser, Munich - Cincinnati **2000**.
[19] Lucas, E.F.; Soares, B.G. and Monteiro, E; Caracterização de Polimeros, e-papers, Rio de Janeiro **2001**.
[20] Atta, A. M. and Arndt, K. F. *Polym. Adv. Technol.* **2005**, 16, 442.
[21] Flory P.J. *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, **1953**, Chapter 13.
[22] Mark, J.E.; Erman, B. Ch. 17 in *Performance of Plastics*, Brostow, W., editor, Hanser, Munich- Cincinnati **2000**.
[23] Sayil, C. and Okay, O. *Polymer*, **2001**, 42, 7639.
[24] Yan, F. and Texter, J. *Soft Matter* **2006**, 2, 109.
[25] Yan, F. and Texter, J. *Chem. Commun.* **2006**, 2696.
[26] Yan, F. and Texter, J. *Angew. Chem. Int. Ed.* **2007**, 46, 2440.
[27] Oh, K.S.; Oh, J.S.; Choi, H.S. and Bae, Y.C. *Macromolecules*, **1998**, 31, 7328.
[28] Yoshida, R.; Uchida, K.; Kaneko, Y.; Sasaki, K.; Kikuchi, A.; Sakurai, Y. and Okano, T. *Nature*, **1995**, 374, 240.
[29] Kabra, B. G. and Gehrke, S. H. *Polym. Commun.* **1991**, 32, 322

[30] Okay, O. *Progr. Polym. Sci.* **2000**, 25, 711.

[31] Funke, W.; Okay, O. B.; Joos-Muller. *Adv. Polym. Sci.* **1998**, 136, 139.

[32] Barb, W.G. *J. Polym. Sci.* **1959**, 37, 515.

[33] Shitter, J. A. *J. Polym. Sci. Lett*ers **1963**, 1, 209.

[34] Rogers, S. S. and Mandelkern, L. *J. Phys. Chem.* **1957**, 61, 985.

[35] DiMarzio, E. A. *Polymer*, **1990**, 31, 2294.