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Fish oil thermosetting polymers: synthesis, structure, properties and their relationships

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Abstract

The cationic copolymerization of native or conjugated fish oil (FO or CFO) with divinylbenzene (DVB), norbornadiene (NBD) or dicyclopentadiene (DCP) comonomers initiated by boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) was conducted in an effort to develop useful biodegradable polymers with rationally designed structures from natural renewable resources. Polymers ranging from rubbers to hard plastics have been obtained. ^1H NMR, ^{13}C NMR, solid state ^{13}C NMR, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) have been used to characterize the structures and physical properties of the fish oil polymers. The results indicate that the products are typical thermosetting polymers with densely crosslinked structures. These polymer materials have densities of approximately 1000 kg/m^3, which appear to be independent of their compositions. The structure of the bulk polymer is composed of 40–85 wt% of crosslinked polymer networks plasticized by 15–60 wt% of unreacted free oil. The moduli of the FO (~0.8 GPa) and CFO (~1.1 GPa) polymers at room temperature are found to be comparable to those of conventional petroleum-based plastics. The glass transition temperatures of the polymers range from 50 to 150°C with a broad transition region. Thermogravimetric analysis (TGA) indicates three distinct decomposition temperature regions, i.e. 200–400°C, 400–560°C, and 560–800°C, which correspond to evaporation of the unreacted free oil, carbonization of the crosslinked polymer network, and oxidation of the carbon, respectively. The thermal stability of these materials is found to be largely dependent on the amount of unreacted free oil molecules present in the bulk polymers. The CFO polymers have higher moduli and thermal stability than the FO polymers due to the lower amount of free oil present in the CFO bulk polymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fish oil polymers; Cationic copolymerization; Thermosets

1. Introduction

The environment is being overwhelmed by non-biodegradable, petroleum-based polymeric materials [1,2]. The increasing demands for such materials have increased the dependence on crude oil and left the highways, beaches and landfills overflowing with these non-renewable, indestructible materials. In contrast, current interest in cheap, biodegradable polymeric materials has recently encouraged the development of such materials from readily available, renewable, inexpensive natural sources, such as carbohydrates, starch, and proteins. However, relatively little work has been done on the conversion of fats and oils to high molecular weight polymers [3,4].

Fish oil is biodegradable, and is readily available as a by-product in the production of fish meal. Typically, fish oil has a triglyceride structure with a high percentage of polyunsaturated ω-3 fatty acid side chains, which can contain as many as $5 \sim 6$ non-conjugated carbon–carbon double bonds per ester side chain. These double bonds in the fatty acid chains of the fish oil triglyceride have *cis*-stereochemistry [5–7]. Currently, fish oil is used industrially to produce protective coatings, lubricants, sealants, inks, animal feeds and surfactants [6]. The high degree of unsaturation just mentioned has prompted researchers to examine fish oil as a potential monomer for polymerization or co-polymerization into useful polymers. The work in this area, which has appeared mostly in patents, has recently been reviewed [8]. The homopolymerization of fish oil, facilitated by the carbon–carbon double bonds present in the oil, can be effected at temperatures near 300°C in closed "kettles" under an inert atmosphere or a vacuum. The resulting viscous oil has been used in varnish, detergents, and

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materials for the canning industry [8]. Fish oil has also been copolymerized with maleic anhydride to produce maleated fish oils, which have been used industrially as drying oils, heat-resistant varnishes, and as plasticizers in poly(vinyl chloride). Fish oil has also been modified through reactions with dienes, such as butadiene, isoprene and cyclopentadiene, to produce Diels–Alder adducts with interesting industrial applications. There are several other reports on fish oil copolymerization by free radical initiators and base [8]. However, all of the reports that have appeared in the literature so far have been concerned with the production of viscous oils from the polymerization or copolymerization of fish oil [8].

The work described here is part of a long-range research program that deals with the conversion of fish oil to useful solid plastics. This paper reports our progress in understanding the synthesis–structure–property relationships of some new fish oil plastics [9]. These new polymers have been prepared from both native and conjugated fish oil (FO and CFO) [8]. Boron trifluoride diethyl etherate has been used as the initiator. Divinylbenzene (DVB), norbornadiene (NBD) and dicyclopentadiene (DCP) have been employed as comonomers. The advantages of these plastics include low cost and the renewable nature of the fish oil. These beneficial features are likely to encourage renewed research interests in fish oil and other natural fats and oils as sources for useful polymers.

2. Experimental

2.1. Materials

The FO used in this study was Norwegian Pronova EPAX 5500 EE Lot no. 60301 fish oil, which was supplied by Pronova Biocare, Bergen, Norway. The CFO was prepared in our laboratory by using Wilkinson's catalyst [$RhCl(PPh_3)_3$]. The procedure for conjugation of the fish oil is described elsewhere [8]. The degree of conjugation was calculated to be about 90%. The DVB, NBD and DCP comonomers were analytical reagents, purchased from Aldrich Chemical Company and used as received. The boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$ distilled grade) was also supplied by Aldrich and used as received. The properties of the fish oil polymers were compared with those of some commercial polymers, such as polystyrene (PS210, Huntsman Corp.), polyethylene (Paxon 3205, Paxon Polymer Co.) and epoxy resin.

2.2. Cationic copolymerization

The desired amounts of comonomers and initiator were added to FO or CFO at room temperature. The reaction mixture was vigorously stirred, and heated for a given time at the appropriate temperatures, usually at 60°C for 24 h and then 110°C for additional 24 h. The relative compositions of the reactants are listed in Table 1. The nomenclature adopted in this study for the samples is as follows: FO and CFO represent fish oil and conjugated fish oil, respectively; DVB, NBD, and DCP denote divinylbenzene, norbornadiene and dicyclopentadiene comonomers, respectively. For example, CFO–DVB–DCP-38 corresponds to a polymer sample prepared from conjugated fish oil, the divinylbenzene and dicyclopentadiene comonomers; the mole percent of CFO is 38%. The relative concentration of the initiators in the starting materials was maintained at 7.7 mol% for all the reactions reported in this study (Table 1). When two comonomers have been used as in the above example, the weight ratio of DVB to NBD or DCP was maintained at 2:1. P-DVB represents DVB homopolymer in Table 1.

2.3. Soxhlet extraction of the polymers by methylene chloride

A 2 g sample of the bulk polymer was extracted with 100 ml of refluxing solvent (methylene chloride) using a Soxhlet extractor in air for 24 h. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble oils were isolated for further characterization. The insoluble solid was dried under vacuum for several hours before weighing.

2.4. Characterizations

The densities of the plastics were measured at room temperature according to ASTM D-792. Differential scanning calorimetry (DSC) thermograms of the test samples were recorded over the temperature range from 30 to 300°C using a Perkin–Elmer Pyris DSC-7 under a nitrogen atmosphere. The DSC scans were conducted at a heating rate of 20°C/min. Indium was used as a standard for temperature calibration. The sample weight used was about 10 mg.

Dynamic mechanical data were obtained using a Perkin–Elmer dynamic mechanical analyzer Pyris DMA-7e in a three-point bending mode. Thin rectangular specimens of 1 mm thickness and 2.5 mm depth were used, and the span to depth ratio was maintained at around 5.0. The measurements were performed at a heating rate of 3°C/min and a frequency of 1 Hz.

A Perkin–Elmer Pyris-7 thermogravimetric analyzer was used to measure the weight loss of the polymeric materials. The test samples were heated from 30 to 900°C at a heating rate of 20°C/min in an atmosphere of air or nitrogen.

The ^1H and ^{13}C NMR spectra were recorded in deuterated chloroform using a Varian Unity spectrometer at 300 and 75.5 MHz, respectively. Solid state cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR spectroscopy was performed on solid polymer samples using a Bruker MSL 300 spectrometer. Samples were examined at two spinning frequencies (2.5 and 3.0 kHz) to differentiate between actual signals and spinning side-bands.

Table 1
Relative compositions of the FO or CFO copolymerizations with DVB, NBD or DCP initiated by boron trifluoride diethyl etherate

Samples	FO		CFO		DVB		NBD		DCP		Initiator		Observations	%Yield
	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%		
FO-92	92.3	96.9									7.7	3.1	Fluid	
CFO-92			92.3	96.9							7.7	3.1	Soft solid	~100
P-DVB					92.3	92.0					7.7	8.0	Explosion	
P-DVB–NBD					54.1	60.7	38.2	30.3			7.7	9.0	Explosion	
P-DVB–DCP					61.5	61.0			30.8	31.0	7.7	8.0	Explosion	
FO–DVB-38	37.7	62.5			54.6	32.7					7.7	4.8	Hard solid	~100
FO–DVB-56	55.8	77.6			36.5	18.4					7.7	4.0	Soft solid	~100
FO–DVB-66	66.3	84.3			26.0	12.0					7.7	3.7	Fluid	
FO–DVB–NBD-38	37.7	65.0			32.0	20.0	22.6	10.0			7.7	5.0	Hard solid	~100
FO–DVB–NBD-56	55.9	79.4			21.1	10.9	15.3	5.6			7.7	4.1	Soft solid	~100
FO–DVB–NBD-66	66.3	85.6			15.2	7.1	10.8	3.6			7.7	3.7	Fluid	
FO–DVB–DCP-38	37.7	62.4			36.6	21.9			18.0	10.9	7.7	4.8	Hard solid	~100
FO–DVB–DCP-56	55.9	77.6			24.4	12.3			12.0	6.1	7.7	4.0	Soft solid	~100
FO–DVB–DCP-66	66.3	84.3			17.3	8.0			8.7	4.0	7.7	3.7	Fluid	
CFO–DVB-38			37.7	62.5	54.6	32.7					7.7	4.8	Hard solid	~100
CFO–DVB-56			55.8	77.6	36.5	18.4					7.7	4.0	Hard solid	~100
CFO–DVB-66			66.3	84.3	26.0	12.0					7.7	3.7	Soft solid	~100
CFO–DVB–NBD-38			37.7	65.0	32.0	20.0	22.6	10.0			7.7	5.0	Hard solid	~100
CFO–DVB–NBD-56			55.9	79.4	21.1	10.9	15.3	5.6			7.7	4.1	Hard solid	~100
CFO–DVB–NBD-66			66.3	85.6	15.2	7.1	10.8	3.6			7.7	3.7	Soft solid	~100
CFO–DVB–DCP-38			37.7	62.4	36.6	21.9			18.0	10.9	7.7	4.8	Hard solid	~100
CFO–DVB–DCP-56			55.9	77.6	24.4	12.3			12.0	6.1	7.7	4.0	Hard solid	~100
CFO–DVB–DCP-66			66.3	84.3	17.3	8.0			8.7	4.0	7.7	3.7	Soft solid	~100

3. Results and discussion

3.1. Structures of FO and CFO and their cationic copolymerization

Generally, fish oil has a triglyceride structure with saturated, mono-unsaturated and multi-unsaturated fatty acid side chains [5–7]. The ^{1}H NMR spectrum (Fig. 1a) shows that the FO used in this study has a high degree of unsaturation with approximately 3.7 carbon–carbon double bonds per molecule. Additional analysis [10] from the supplier of the FO confirmed that the FO is a mixture of various structures, which are predominantly composed of ω-3 fatty acids (esters), such as docosa-4,7,10,13,16,19-hexaenoic acid (DHA, 24.72%), eicosa-5,8,11,14,17-pentaenoic acid (EPA, 31.68%) and docosa-7,10,13,16,19-pentaenoic acid (DPA, 4.27%). Fig. 1b shows the ^{1}H NMR spectrum of the CFO. Compared with the spectrum of the FO, it can be seen that the methylene hydrogen between two carbon–carbon double bonds have disappeared and additional vinylic hydrogens have appeared at $\delta = 5.65$–6.60 ppm upon conjugation. The degree of conjugation, estimated at ~90%, was calculated from the integration ratio of the vinylic hydrogens ($\delta = 5.36/\delta = 5.65$–$6.60$) in the CFO and the known fatty acid composition of the oil. Fig. 2 shows the ^{13}C NMR spectra of both the FO and CFO. After conjugation, the peaks due to the sp^2 carbons in the alkene region ($\delta = 120$–140 ppm) of the CFO spectrum become relatively scattered. This is consistent with the fact that conjugation increases the number of different sp^2 carbons present in the molecule.

The high unsaturation in the FO structure is expected to provide reactive sites for the cationic polymerization of the FO molecules. Complexes of boron trifluoride with an ether have been shown to be particularly effective initiators for cationic polymerization [11,12]. However, the simple homopolymerization of FO by boron trifluoride diethyl etherate does not lead to solid polymeric materials. The reactivity of the fish oil might be expected to increase by conjugating the carbon–carbon double bonds. The conjugated FO (i.e. CFO) used in this study had about 90% conjugation, but even this material failed to afford solid products with viable stiffness and strength upon homopolymerization. While pure FO or CFO can be initiated even at room temperature due to the low activation energy of the cationic initiation [11,12], the low mobility of the fish oil apparently impedes chain propagation of the active centers. The resulting products are, therefore, viscous fluids or rubbers with poor stiffness and strength. In contrast, DVB, NBD or DCP have lower molecular weights, but a higher density of carbon–carbon double bonds. These monomers are known to be suitable for cationic polymerization [11,12]. In fact, each of them has been observed to react almost explosively once the initiator is added. Therefore, the addition of small amounts of these reactive dienes to the FO or CFO has been found to result in moderate reactions that can be controlled to yield useful products as shown in Table 1.

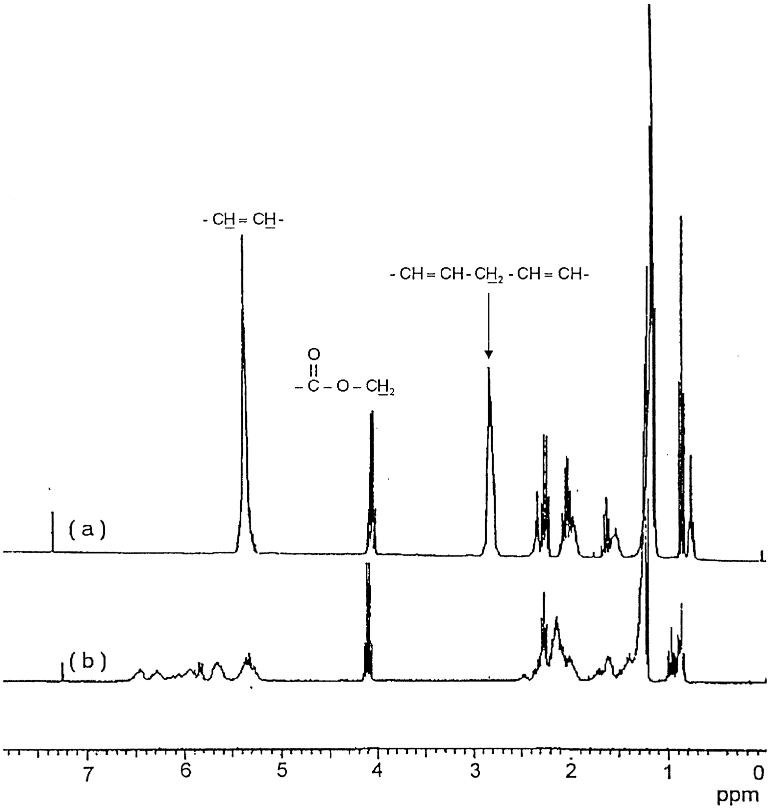

Fig. 1. ^{1}H NMR spectra of (a) FO and (b) CFO.

In this study, dark brown colored products ranging from soft rubbers to hard plastics have been obtained, and the yields of bulk polymer are approximately 100 wt%. The relationship between the reaction rate, which is monitored by the gel time, and the original compositions of the reactants at room temperature is shown in Fig. 3. Fig. 3 shows that no solid products were observed when more than 90 wt% FO was mixed with DVB comonomer in the

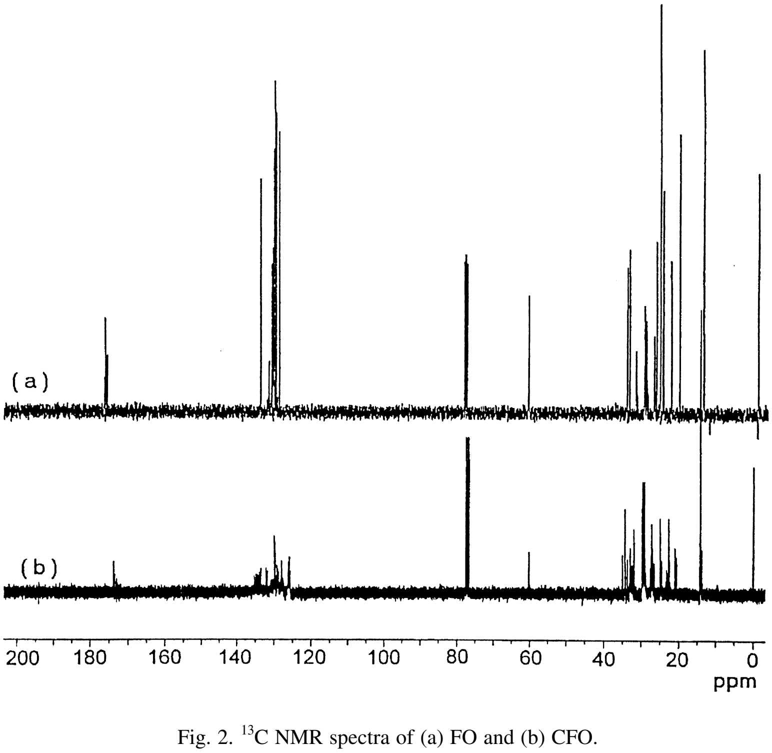

Fig. 2. ^{13}C NMR spectra of (a) FO and (b) CFO.

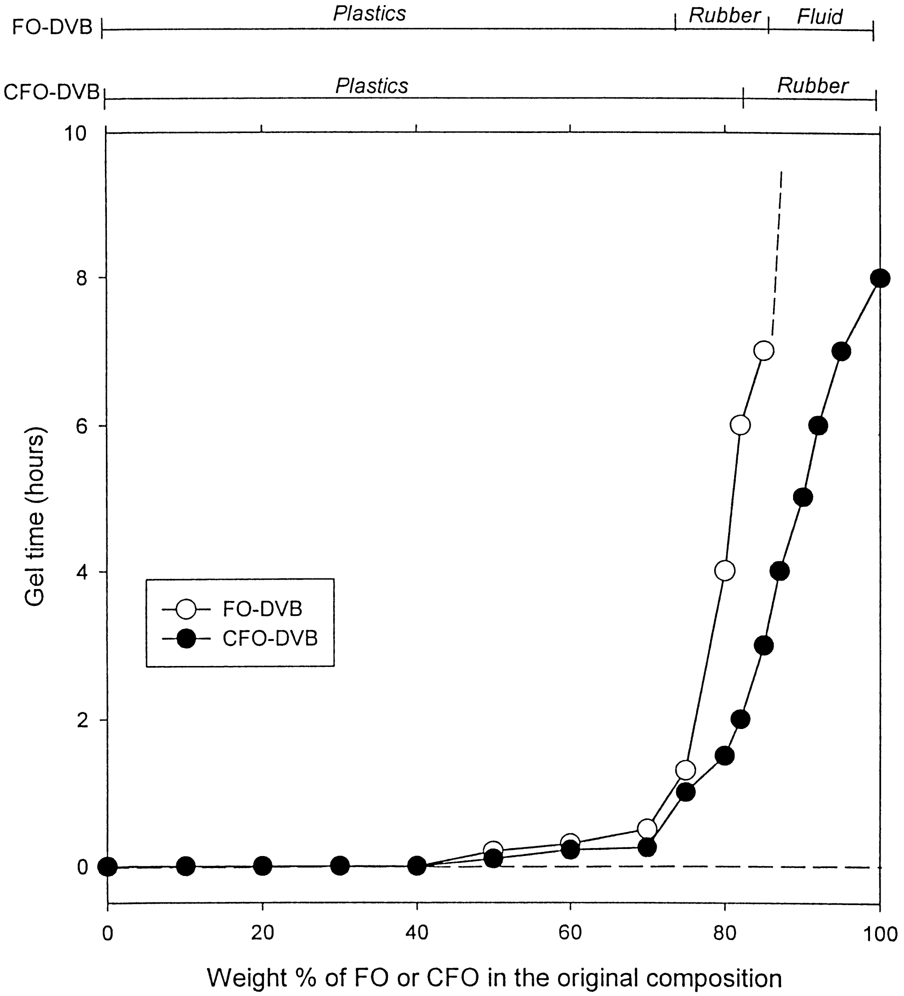

Fig. 3. The oil composition dependencies of copolymerization rates (gel time) and the resulting polymer morphologies.

original composition. The products were dark-brown fluids of low to moderate viscosities. However, pure DVB comonomer or its mixtures with less than 50 wt% FO resulted in very fast or explosive reactions. The gel time in each case was just a few seconds. Although solid products were obtained in this case, the reactions were difficult to control, the resulting polymers were generally full of voids and irregular in shape. Fortunately, there exists a composition range, within which solid plastics and rubbers are obtained from reactions with controllable reaction rates. This composition range for FO reactions is approximately 50–90 wt% FO in the original composition. Good rigid plastics, however, could be obtained only when the FO was less than 75 wt% within the above composition region. When the FO concentration is very high in the original composition, the resulting polymers are found to be soft and weak rubbers with limited use. However, CFO is more reactive than FO. Thus, the homopolymerization of CFO into a soft rubber can be initiated without any comonomers (Fig. 3). Solid plastics and rubbers can be obtained from controllable reactions over a significantly wide composition range, i.e. 50–100 wt% CFO in the original composition. The composition window for producing good rigid CFO polymers is also much wider than that of the FO polymers (Fig. 3).

DSC was used to confirm the completion of the reactions. Fig. 4 shows the DSC thermograms of the CFO–DVB polymers. The curves show a broad shoulder between 100 and 150°C (see the arrows in the figure), indicating the glass transition region of polystyrene segments in the polymer materials (which will be discussed in Section 3.4). The DSC thermograms did not show any evidence of post-curing behavior. The lack of post-curing suggests that the reactions go to completion under the conditions used.

3.2. Density

The densities of the FO and CFO polymers are listed in Table 2. Generally these materials have densities of approximately 1000 kg/m^3. The density values of the polymers in this study have been found to be similar to those of conventional plastics [13]. The low density of the materials is expected to facilitate easy handling, cheap transportation and their utilization in materials designs that have weight

Table 2
Physical properties and structure of the fish oil and conjugated fish oil polymeric materials

Samples	Densities (kg/m^3)	M_c (g/mol)	T_g (°C)	Soxhlet extraction (wt%)	
				Insoluble	Soluble
FO-92	–	–	–	–	–
CFO-92	–	–	–	–	–
P-DVB	–	–	–	–	–
P-DVB–NBD	–	–	–	–	–
P-DVB–DCP	–	–	–	–	–
FO–DVB-38	1001	~220	66	75	25
FO–DVB-56	1016	–	–	60	40
FO–DVB-66	–	–	–	42	58
FO–DVB–NBD-38	1012	~200	79	75	25
FO–DVB–NBD-56	1040	–	–	56	44
FO–DVB–NBD-66	–	–	–	–	–
FO–DVB–DCP-38	1016	~230	62	68	32
FO–DVB–DCP-56	1007	–	–	41	59
FO–DVB–DCP-66	–	–	–	–	–
CFO–DVB-38	1005	~100	114	84	16
CFO–DVB-56	1001	~200	68	82	18
CFO–DVB-66	1002	~300	52	79	21
CFO–DVB–NBD-38	1024	~120	108	85	15
CFO–DVB–NBD-56	1001	~220	68	80	20
CFO–DVB–NBD-66	1008	–	45	74	26
CFO–DVB–DCP-38	1020	~130	113	84	16
CFO–DVB–DCP-56	1003	~260	79	77	23
CFO–DVB–DCP-66	1006	–	60	73	27

limitations. Our results show that the type of fish oil used (i.e. FO and CFO) did not have any observable effect on the densities of the polymeric materials. Further, there was no clear relationship between the densities of the materials and their compositions.

3.3. Microstructure of the polymers

The polymer materials in this study are expected to be thermosets due to the multiple carbon–carbon double bonds present in the fish oil and in the comonomers [14]. Soxhlet extraction using methylene chloride as the refluxing solvent was used to study the structure of these polymer materials. Table 2 lists the extraction results for all of the FO and CFO polymer samples. Generally, 50–85 wt% of insoluble substances were obtained. These insoluble substances are highly crosslinked polymers that cannot be melted and are not soluble or even swellable in common solvents, such as THF and CH_2Cl_2.

Solid state ^{13}C NMR spectroscopy provides valuable information on the insoluble materials. Fig. 5a is the solid state ^{13}C NMR spectrum of the insoluble material obtained

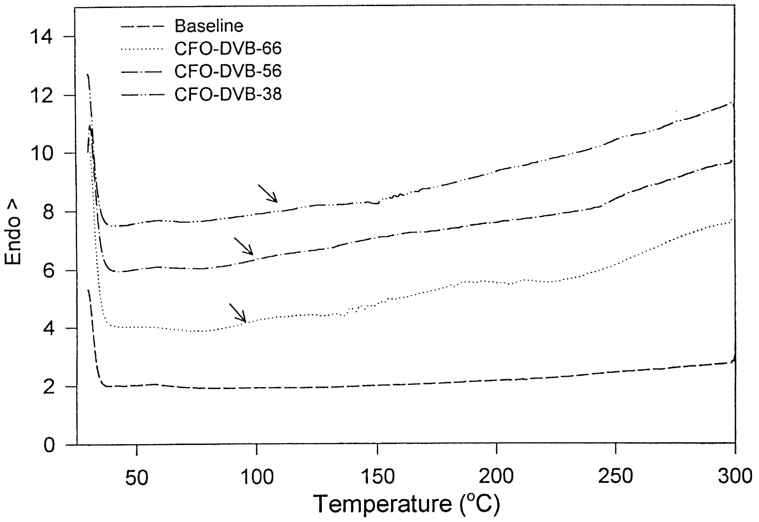

Fig. 4. DSC thermograms of the CFO–DVB polymers (arrows denote glass transition region).

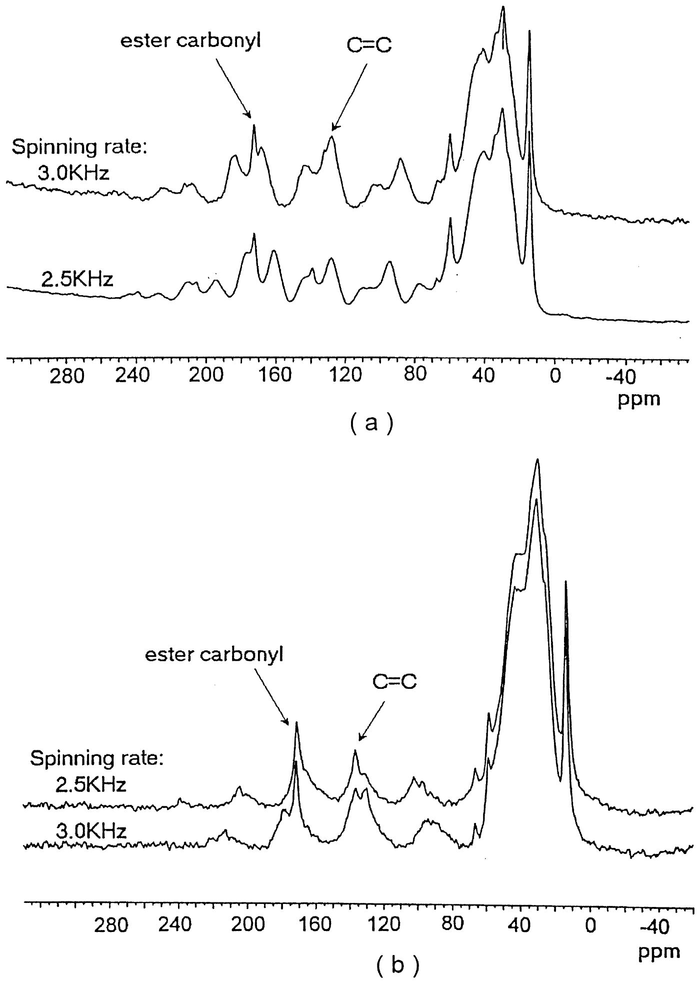

Fig. 5. Solid-state ^{13}C NMR spectra of the insoluble substances extracted from (a) CFO–DVB-38 and (b) CFO–DCP-38 samples.

after the extraction of CFO–DVB-38. The spectrum clearly shows the presence of ester carbonyls ($\delta = 165$–175 ppm) and carbon–carbon double bonds ($\delta = 120$–140 ppm). It follows that some amount of fish oil was incorporated into the crosslinked polymer network. Here, the detected double bonds may be largely due to the DVB segments present in the copolymers, as well as the residual double bonds of the incorporated fish oil segments in the crosslinked polymer network. To test this hypothesis, the insoluble substance from a sample of CFO–DCP-38 was studied in a similar manner (Fig. 5b). This figure still shows the presence of carbon–carbon double bonds in this insoluble substance. After reaction, the double bonds in the DCP segments in the crosslinked polymer network have disappeared. Therefore, the detected double bonds are ascribed to the unreacted ones in the incorporated fish oil segments in the crosslinked polymer network. In other words, after one double bond is reacted, others nearby in the FO or CFO molecules are less likely to participate in subsequent reactions.

The soluble substances extracted from the bulk polymers, which range from 15 to 50 wt%, are oils at ambient temperature. Fig. 6 shows the ^{1}H and ^{13}C NMR spectra for the oils extracted from the sample CFO–DCP-38. The results show that the extracted oil has a structure similar to that of the native fish oil, except that a substantial number of the carbon–carbon double bonds have disappeared. The ^{1}H NMR spectrum (Fig. 6a) shows very few vinylic hydrogens ($\delta = 5.2$–5.5 ppm), and the ^{13}C NMR spectrum (Fig. 6b) shows a limited number of sp^{2} carbons in the alkene region ($\delta = 120$–140 ppm). This indicates that the unreacted free oils contain very few carbon–carbon double bonds. The preceding discussion implies that the materials are composed of crosslinked polymer networks plasticized by a certain amount of unreacted free oil. The fish oil segments incorporated into the crosslinked networks still have some unreacted carbon–carbon double bonds however.

Fig. 7 shows the wt% of oil extracted from the bulk polymers as a function of the original compositions. The composition range used was in the region where good plastics and rubbers were obtained at a moderate reaction rate (see Fig. 3). The results in Fig. 7 indicate that the amounts of unreacted free oils present in the bulk polymers steadily increase with increasing fish oil concentrations in the original compositions. As expected, more unreacted free oil

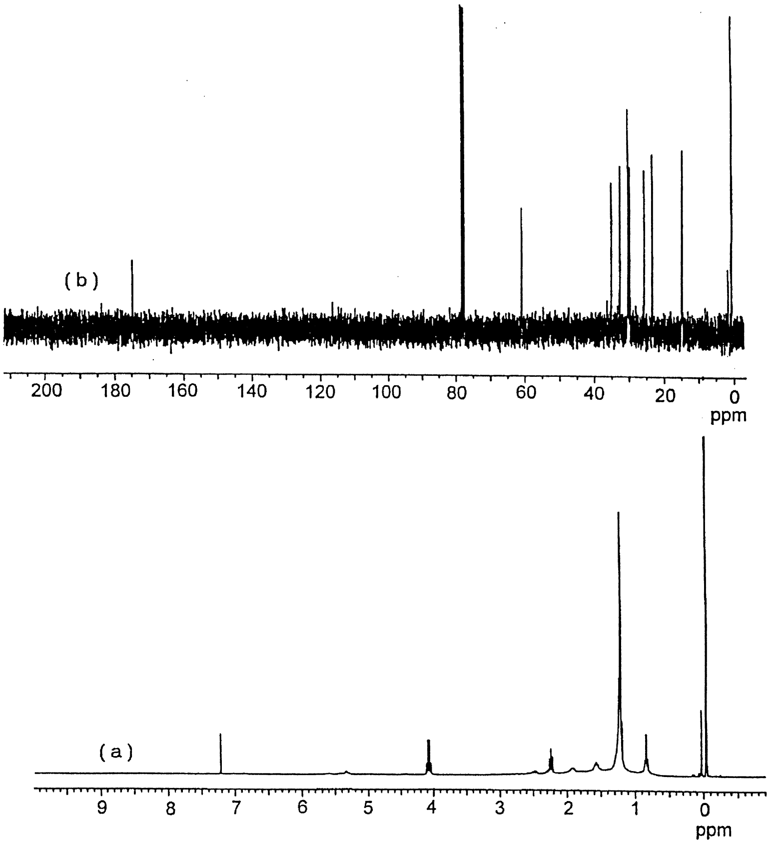

Fig. 6. (a) ^{1}H NMR spectrum and (b) ^{13}C NMR spectrum of the unreacted free oils extracted from the sample CFO–DCP-38.

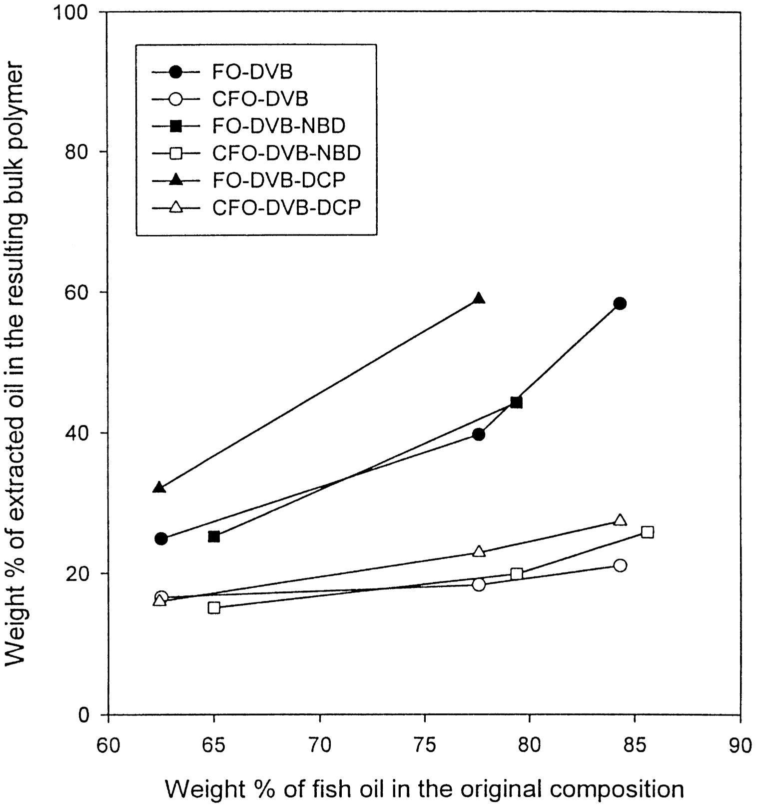

Fig. 7. The dependence of the unreacted free oils present in the bulk polymer on the fish oil concentration in the original composition.

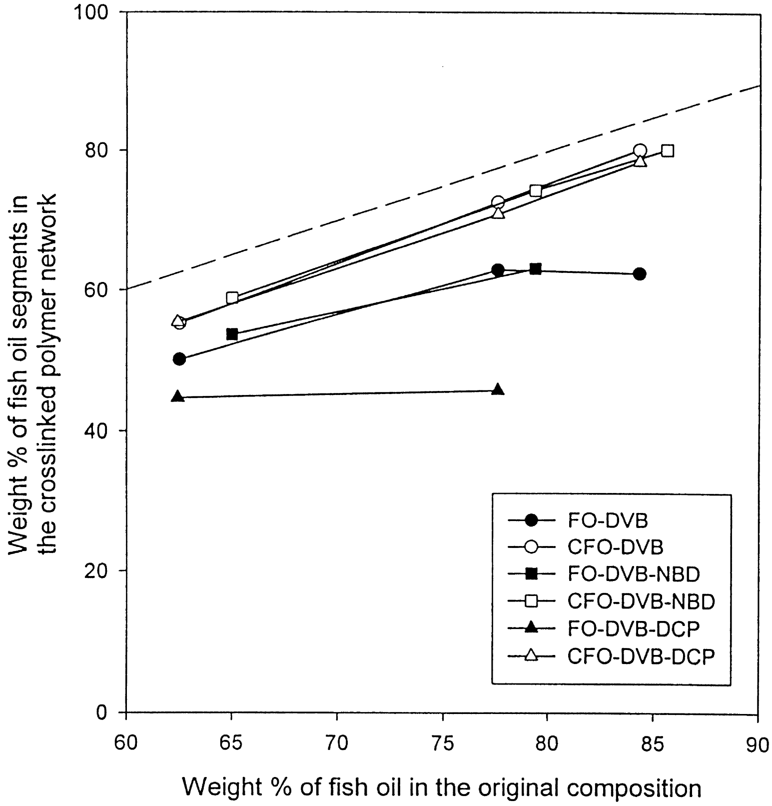

Fig. 8. Variation of wt% of fish oil segments in the crosslinked polymer network as a function of wt% of fish oil concentration in the original composition. The dashed line represents ideal copolymerization where the original composition of the reactants is equivalent to that of the resulting crosslinked polymer network.

appears in the FO polymers than in the CFO polymers due to the higher reactivity of CFO. This difference is very significant with high FO or CFO concentrations in the original compositions. When more comonomers are used in the original composition, the difference in the amounts of the unreacted free oil between the resulting FO and CFO polymers becomes smaller.

Fig. 8 shows the wt% of the fish oil segments incorporated

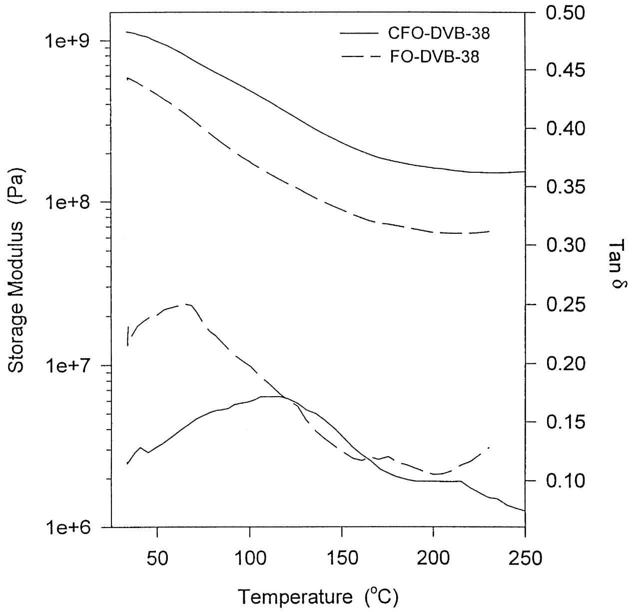

Fig. 9. Temperature dependencies of the storage modulus E' and loss factor tan δ for the FO and CFO polymers.

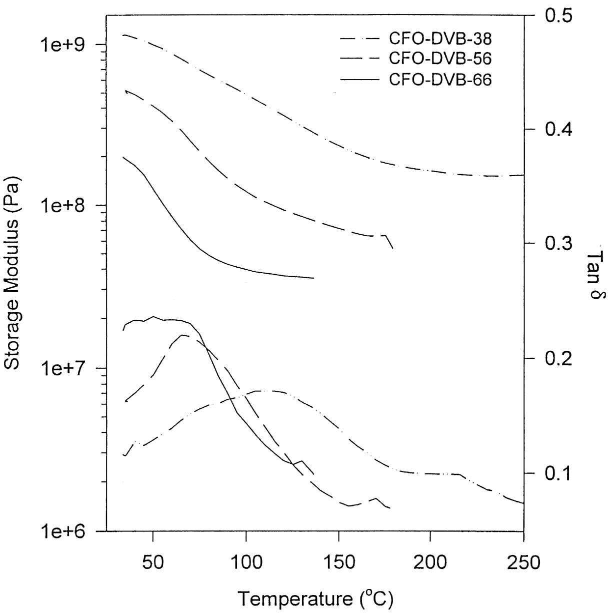

Fig. 10. Temperature dependencies of the storage modulus E' and loss factor tan δ for the CFO polymers with various comonomer concentrations.

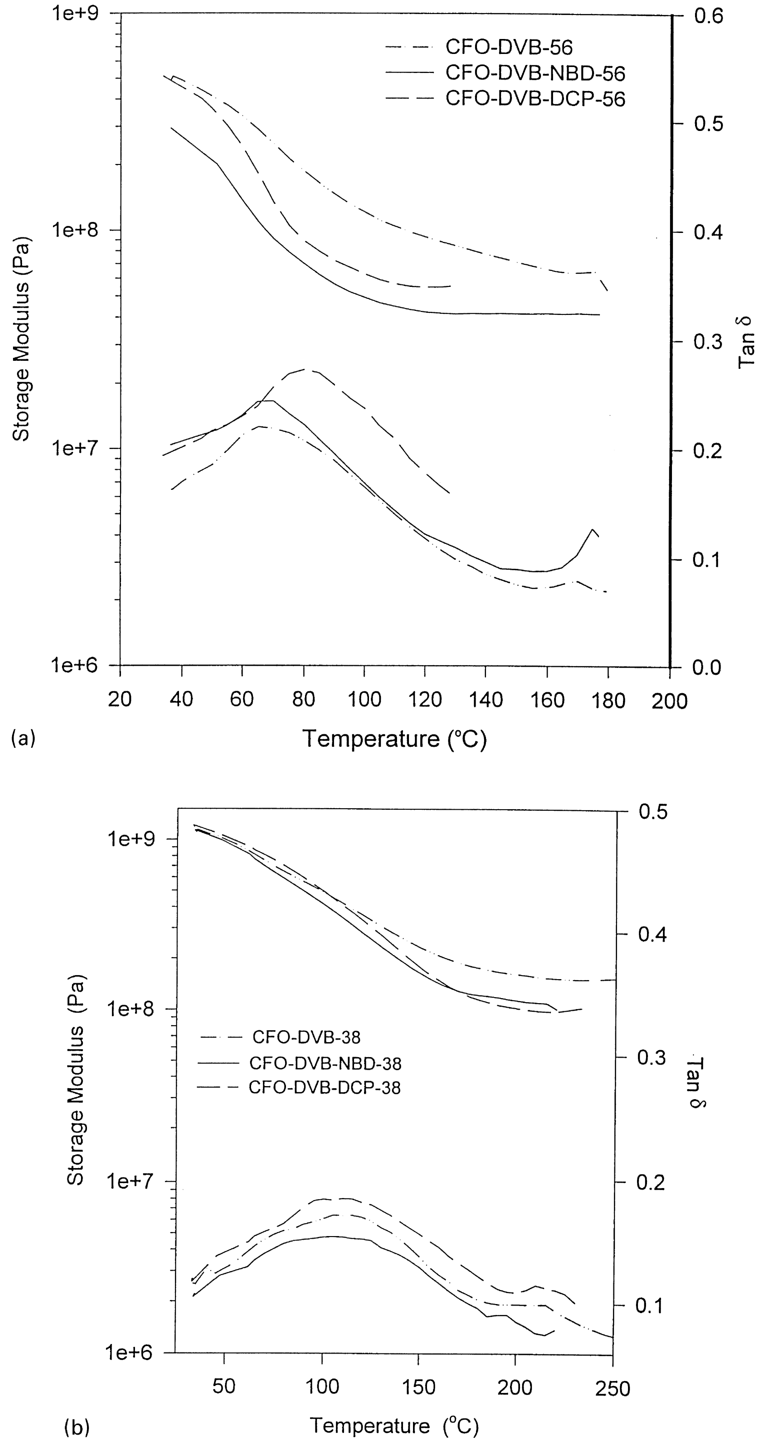

Fig. 11. Temperature dependencies of the storage modulus E' and loss factor tan δ for the CFO polymers with a second comonomer: (a) 56 mol% CFO and (b) 38 mol% CFO.

in the crosslinked polymer network as a function of fish oil concentration in the original composition. The wt% of fish oil segments incorporated in the crosslinked polymer network was calculated based on the assumption that all of the comonomers participated in the copolymerization, a reasonable assumption, which was confirmed by the ^{1}H NMR spectral analysis discussed earlier. The amounts of fish oil segments incorporated in the crosslinked polymer networks are found to be expectedly lower than the fish oil concentration in the starting materials. A linear relationship between them was observed within this composition region, which is almost parallel to the ideal copolymerization line (dashed line in Fig. 8) where the original composition of the reactants is equivalent to that of the resulting crosslinked

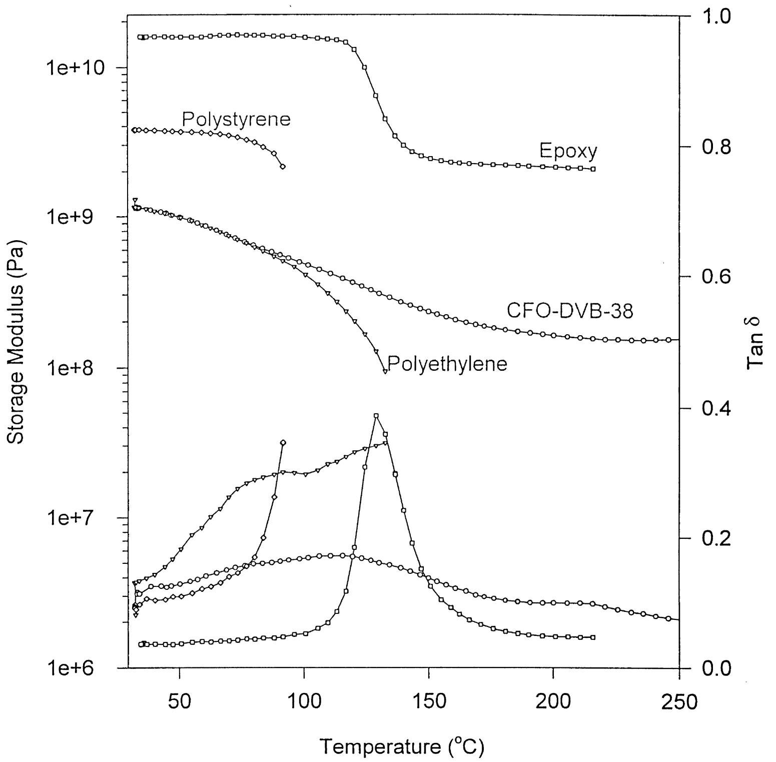

Fig. 12. Temperature dependencies of the storage modulus E' and loss factor tan δ for a typical CFO polymer and some commercial polymers.

polymer networks. Because of the higher reactivity of CFO, the concentration of CFO incorporated is evidently higher than that of the FO incorporated in the resulting crosslinked polymer networks. It follows that the structure of the resulting polymers is mainly determined by their original compositions.

3.4. Dynamic mechanical analysis (DMA)

Fig. 9 shows the temperature dependence of the storage modulus E' and the loss factor tan δ for the FO and CFO polymers. In general, the DMA curves of the FO and CFO polymers are similar. But the modulus of the CFO polymer is evidently higher than that of the FO polymer over the whole temperature range studied. The figure shows that the storage moduli of the FO and CFO polymers at room temperature are approximately 7.5×10^8 and 1.1×10^9 Pa, respectively. As expected, the modulus decreases gradually with increasing temperature until the elastic plateaus appear at high temperatures above 180°C. The elastic plateaus in the DMA curves indicate the existence of crosslinked network structures in the bulk polymers. The broad glass transition regions observed from the loss factor curves are due primarily to the extensive motion of chain segments diversified by crosslinking in these polymeric systems. The glass transition temperature, the temperature corresponding to the maximum tan δ peak, of the CFO polymer is approximately 110°C, about 30–50°C higher than that of the FO polymer.

Fig. 10 shows the DMA curves of the CFO polymer samples with various amounts of DVB comonomer in the original composition. Clearly, the comonomer improves the thermomechanical properties of the resulting bulk polymers. The degree of crosslinking of the polymers is significantly improved when more comonomer is employed in the original composition as evidenced by the increase in E' in the DMA curves. The higher the comonomer concentration in the original composition is, the higher is the glass transition temperature of the resulting polymer and broader is the related glass transition region.

Fig. 11a shows the effect on the DMA behavior of the resulting CFO polymers of adding a second comonomer to the original compositions (56 mol% CFO). Polymers produced with the different comonomers have different storage moduli at room temperature, but their tan δ behavior is similar. It appears that the addition of a second comonomer to the original composition does not improve the thermomechanical properties of the resulting polymers, and the materials appear to be poorer than that without a second comonomer. When the concentration of the CFO used in the original composition is low (~38 mol% CFO), the difference in the DMA curves of the polymers is almost negligible as shown in Fig. 11b.

Based on the above discussion, it is clear that the CFO polymers have better thermomechanical properties than the FO polymers. Of the comonomers studied, DVB was found to give polymers with the best thermomechanical properties. The specimen CFO–DVB-38 has the highest storage

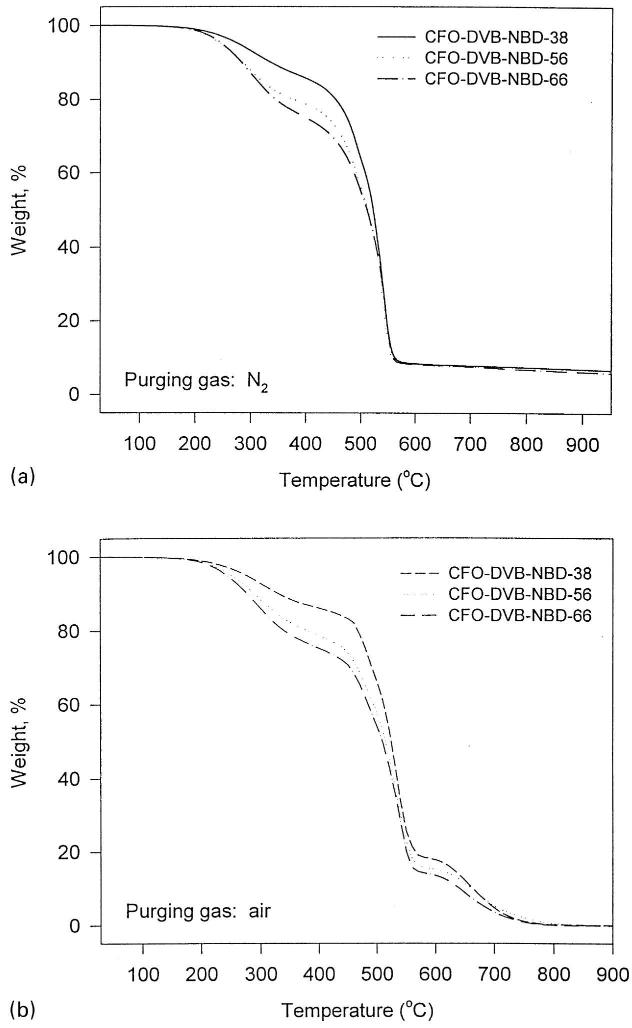

Fig. 13. TGA thermograms of the CFO polymers in (a) nitrogen and (b) air atmospheres.

modulus and glass transition temperature among all of the samples tested. Fig. 12 provides a comparison between this CFO polymer and some commercial polymers. The glass transition temperature of this CFO polymer is approximately 110°C, which is slightly higher than that of the polystyrene, but lower than that of the epoxy used in this study. The modulus of the CFO polymer at room temperature is about 1.1×10^9 Pa, which is the same order of magnitude as that of polyethylene. Due to its thermosetting nature, the CFO polymer material has significantly better properties at higher temperatures ($T > 200$°C) than those of the thermoplastic polymers tested.

The observed variations in the properties of the fish oil plastics are mainly attributed to the structures of these thermosetting polymers as discussed in the previous sections. More free oil exists in the FO polymers than in their CFO counterparts as shown in Fig. 7. This free oil reduces the properties of the bulk polymers due to their plastisizing effect. The amount of free oil decreases when more comonomer is added to the reaction mixture, thereby resulting in plastics with improved properties. The fish oil segments incorporated in the crosslinked polymer networks are also closely related to the original composition as shown in Fig. 8. These fish oil segments in the crosslinked polymer network are expected to influence the physical properties of the bulk polymers. But, the fish oil segments contribute only 10–20 mol% to the crosslinked polymer network. The mobility of the oil segments is severely restricted upon crosslinking. Therefore, their effect on the physical properties of the bulk polymers is negligible in contrast with the amount of free oil in the bulk polymer. The average molecular weights between two adjacent crosslinks, M_c, were calculated from the elastic modulus in the rubbery state of the FO and CFO polymers based on the above DMA curves following standard procedures described elsewhere [14]. The M_c results are listed in Table 2. Although the crosslinked structure in the FO and CFO polymers is not ideally identical, the calculated M_c results, which vary from 100 to 300 g/mol, indicate that the crosslinking density in the bulk polymers is very high.

3.5. Thermal stability and phase decomposition transitions

Thermogravimetric analysis (TGA) was used to investigate the thermal decomposition behavior of the polymers in air and nitrogen atmospheres. Fig. 13a shows the TGA curves of the CFO–DVB–NBD polymers under nitrogen. Two distinct temperature regions are observed where the samples experienced significant weight loss (200–400°C and 400–560°C). When the samples were tested under an O_2 atmosphere, an additional temperature region (560–800°C) was observed as shown in Fig. 13b. The other FO and CFO polymers showed decomposition behavior similar to those reported in Fig. 13a and b. To understand the origins of the observed multi-stage thermal decomposition process in the FO and CFO polymers, we performed TGA analysis on the bulk polymer (FO–DVB–NBD-38), the insoluble substances and the unreacted free oils extracted from this bulk polymer. The results are shown in Fig. 14. It is clear from Fig. 14 that most of the unreacted free oil disappears at temperatures between 200 and 400°C, corresponding to the same temperature region of the first decomposition stage of the polymers as shown in Fig. 13. Careful examination of the TGA measurements revealed that decomposition stage-I was due primarily to evaporation of the unreacted oil in the bulk polymer, which was confirmed by the ^{1}H NMR analysis of the condensed evaporated oils. On the other hand, the insoluble substances were found to be highly crosslinked thermosets that decompose at temperatures greater than 400°C (Stage-II, Fig. 14). This decomposition stage is ascribed to carbonization of the crosslinked polymer network. Stage-III corresponds to the oxidation of the carbons, which occurs above 560°C in air.

From the preceding results, it is clear that the thermal stability of the FO and CFO polymers is limited by the

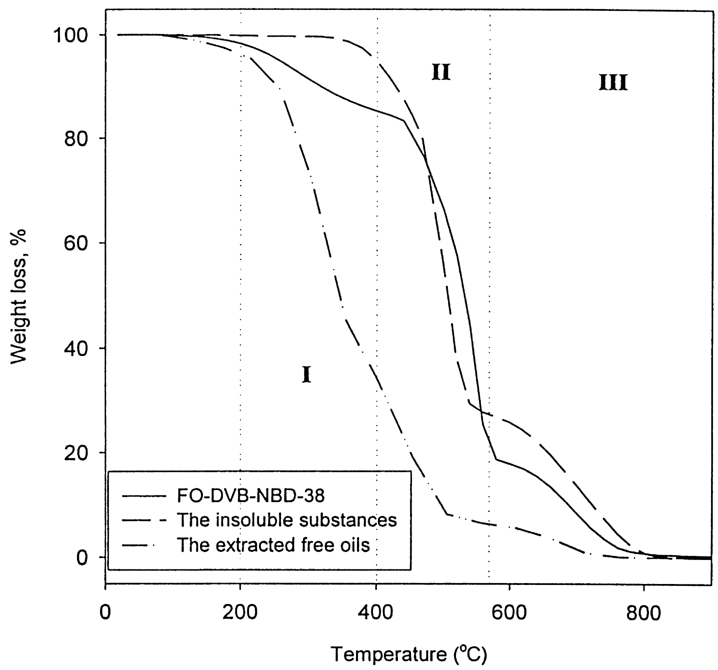

Fig. 14. TGA thermograms of the bulk polymer FO-DVB-NBD-38, the insoluble substances and unreacted free oils extracted from the bulk polymer.

first decomposition stage in the TGA thermograms, which is directly related to the amount of unreacted free oil in the bulk polymer. In this study, the temperature at 10% weight loss was selected as a reference for evaluating the thermal stability of each polymer material. Fig. 15a and b shows the temperatures at 10% weight loss for the FO and CFO polymers, respectively. It can be seen from these figures that the characteristic decomposition temperatures of CFO polymers are higher than those of the FO polymers. This finding is consistent with the earlier observation that CFO polymers contain less free oils than the FO polymers. As shown earlier in Fig. 7, increasing fish oil concentration in the original composition results in a steady increase in the amount of the unreacted free oil in the resulting bulk polymer, and a decrease in thermal stability. Fig. 15a and b also shows that the thermal stability of the bulk polymers from the same type of fish oil (i.e. FO or CFO) is reduced by increasing the fish oil concentration in the original composition, a consequence of the increase in the unreacted free oil present in the resulting polymer. At high oil concentration in the original composition, the temperatures at 10% weight loss of the resulting polymers appear to be relatively independent of the oil concentration (see Fig. 15). This observation may be rationalized in the following way. Stage-I in the TGA curves involves two major steps, i.e. diffusion of the free oil to the surface of the bulk polymer and subsequent evaporation. The diffusion of the free oil is retarded by highly crosslinked materials, but the evaporation of the free oils from the polymer surface occurs rather rapidly at high temperatures. The temperatures at 10% weight loss are therefore predominantly determined by the diffusion process, rather than the subsequent evaporation. However, when the amount of unreacted free oil present in the bulk polymer is very high, diffusion of the free oil to the polymer surface occurs rapidly, minimizing the difference in the temperatures of 10% weight loss at these relatively high oil concentrations.

4. Conclusion

1. Polymers ranging from rubbers to hard plastics have been produced by copolymerizing FO or CFO with DVB, NBD or DCP comonomers. Viable polymers can be obtained from a range of reactant composition under controllable, moderate reaction rates.
2. The polymers are found to be typical thermosetting materials. They have glass transition temperatures ranging from 50 to 110°C, to an extent that depends on the original composition of the reactants. The modulus at ambient temperature of the CFO polymers can be as high as 1.1×10^9 Pa, which is comparable to those of conventional polymers, such as polyolefins.
3. Three distinct decomposition stages are found upon thermogravimetric analysis, which correspond to evaporation of the unreacted free oil present in the bulk polymer, carbonization of the crosslinked polymer, and subsequent oxidation of the carbons. The thermal stability of the polymers is mainly determined by the amount of the unreacted free oil present in the bulk polymer.
4. CFO bulk polymers have lower amount of unreacted free oil than the FO polymers. The dynamic mechanical properties and thermal stability of the CFO polymers are found to be higher than those of the FO polymers.

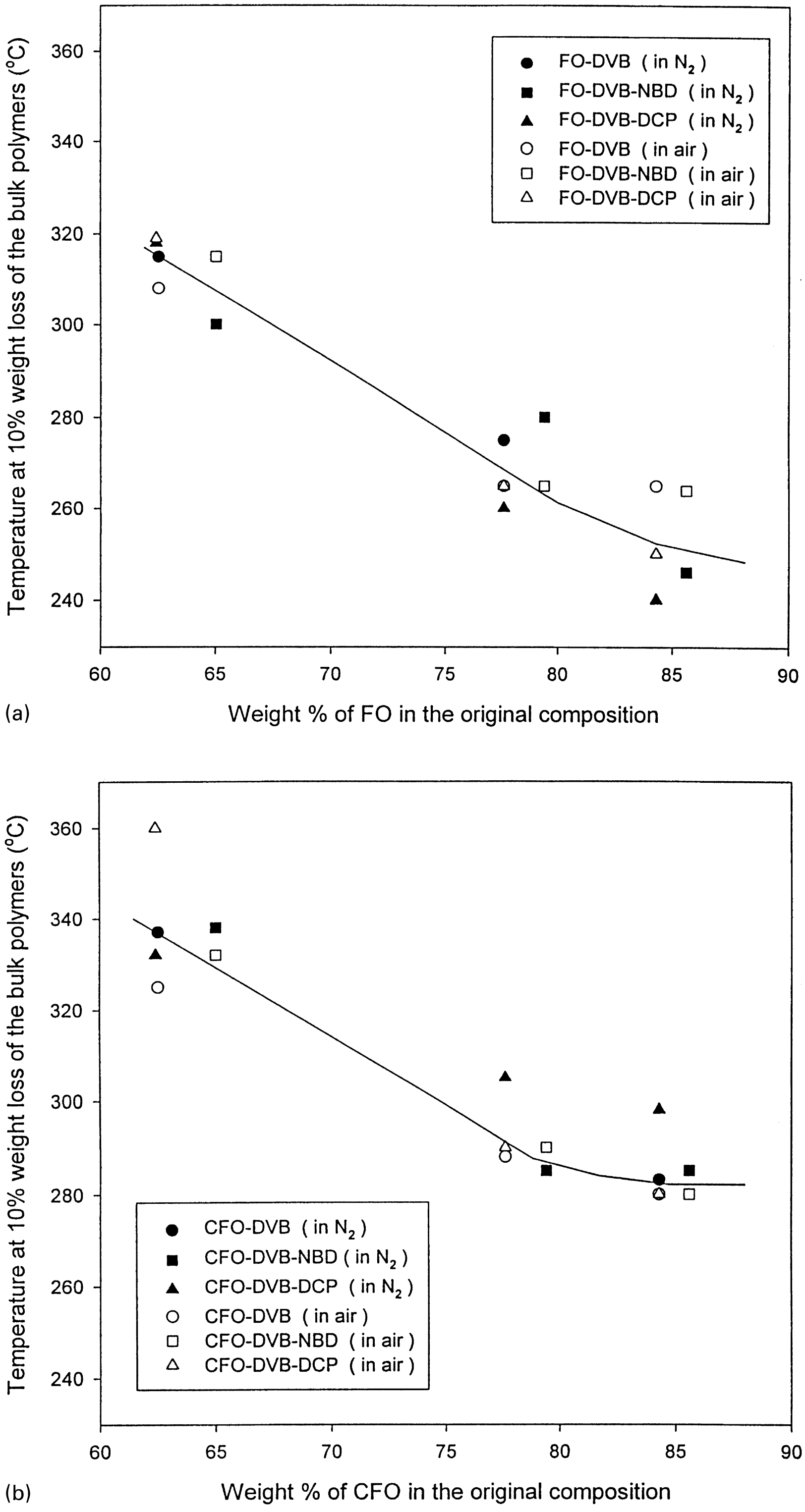

Fig. 15. Temperatures at 10% weight loss for both (a) FO and (b) CFO polymers.

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