Journal of Fluorine Chemistry 132 (2011) 348–355

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Mechanical and thermal properties of perfluoroalkyl ethyl methacrylate–methyl methacrylate statistical copolymers synthesized in supercritical carbon dioxide

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ARTICLE INFO

Article history:
Received 17 November 2010
Received in revised form 7 March 2011
Accepted 10 March 2011
Available online 17 March 2011

Keywords:
Supercritical carbondioxide
Mechanical properties
Fluomethacrylate copolymers
Free volume
Young's modulus
Glass transition

ABSTRACT

Poly(methyl methacrylate-ran-perfluoroalkyl ethyl methacrylate) copolymers having varying perfluoroalkyl ethyl methacrylate ester (Zonyl-TM) contents were synthesized in supercritical CO_2. Complete amorphous structures of the copolymers were verified by XRD. Young's modulus (Y_{mod}) of the copolymers was decreased linearly from 1.57 to 1.08 GPa and T_g values from 102 to 77 °C with the increase of Zonyl-TM content. A linear relationship between the Y_{mod} and the T_g values of the copolymer was also found. The increase of the large branched pendant groups resulted in the increase of the free volume and a corresponding decrease in Y_{mod} and T_g of the copolymers. A good fit was found when the Schneider equation was used. Negative deviation from the Gordon–Taylor equation was observed when Zonyl-TM content was lower than 14% due to rapid increase in free volume and then a positive deviation was found due to the dipole–dipole interactions between the methyl ester and fluoroalkyl ester groups.

1. Introduction

Polymeric materials are used in many areas ranging from construction materials to microelectronic processing [1,2]. Some characteristics of polymer properties can be effectively modified through the introduction of fluorinated groups. The presence of highly stable C–F bonds can substantially improve the chemical, thermal and photochemical stabilities of polymers [3]. In general, fluoropolymers are categorized as main-chain and side-chain fluoropolymers, and most of the side-chain fluoropolymers are synthesized from the polymerization reaction of the fluorinated methacrylate monomers [4]. The introduction of the pendant fluorinated groups through the acrylic monomers which have perfluoroalkyl side groups, decreases the surface tension of the obtained copolymer films [5,6]. Fluoro methacrylate (FMA) copolymers have been used increasingly in a wide range of applications including surface coatings for textile, paper and leather industries, biomaterials, microelectronics and antifouling [7,8]. Some of statistical FMA copolymers with methyl methacrylate (MMA) were synthesized by using bulk copolymerization [9], solution copolymerization in $scCO_2$ [10] and in polar solvent mixtures such as α,α,α-trifluorotoluene/1,1,2-trichlorotrifluoroethane [11].

Polymers generally exhibit three different types of strain–stress behaviors with respect to their structures and types: brittle, plastic and highly elastomeric. For brittle polymers, stress increases rapidly with a small increase in strain, and the strain–stress plot is generally linear. For plastics, two different types of behaviors are exhibited in the plot. Stress initially increases rapidly in response to a slight increase in strain, but it does not change significantly afterwards [12,13]. Y_{mod} is the most important mechanical property of polymers to affect their industrial usage [12–14]. It can be calculated by taking the slope of the linear part in the strain–stress plot where Y_{mod} value changes 5% or less in most cases [15]. Y_{mod} values change from 0.007 GPa for an elastic polymer to 4 GPa for a hard and brittle polymer, and this value is between 48 and 410 GPa for metals [12]. Mechanical properties are highly sensitive to environmental factors such as temperature, the amount of available oxygen, the moisture content and the presence of an organic solvent in the medium [12,16–18]. The change in the Y_{mod} value of polymethylmethacrylate (PMMA) was reported as between 2.24 and 3.24 GPa at room temperature [12]. Y_{mod} value is considerably sensitive to the relative humidity. Ishiyama and Higo measured the Y_{mod} of PMMA homopolymer at a constant temperature with a different strain ratio under various relative humidity of the environment (up to 98%) [16]. They indicated that, the Y_{mod} of PMMA decreased linearly from 3.23 to 2.88 GPa, when the relative humidity was increased from 11% to 98% [16]. Another important parameter affecting the Y_{mod} of polymers is the free volume of the copolymer. This property also alters the T_g of the copolymer [6,9,18–21]. Choi et al., synthesized MMA-trifluoro

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doi:10.1016/j.jfluchem.2011.03.010

ethyl methacrylate and MMA-fluoroacrylate (FA) copolymers by bulk polymerization, and the differential scanning calorimeter (DSC) thermograms of the copolymers indicated that introducing FA monomer increases the free volume of the copolymer, which resulted from the long side chain of the perfluoro ethyl acrylate [9]. Generally, the mechanical properties of polymers diminish proportionally with the decrease of the T_g value [18,22–26]. From the structural point of view, the free volume of the polymer depends on the length and the size of the pendant groups in the polymer chain [9,24,25].

1.1. Free volume theory and the prediction of the T_g values of copolymers

The Gordon–Taylor equation is the first study to derive the relationship between the weight fraction of a comonomer (w) and the T_g of the copolymer, as given in Eq. (1) [27].

$$T_g = \frac{w_1 T_{g1} + l w_2 T_{g2}}{w_1 + k w_2} \tag{1}$$

where k is a fitting constant, w_i is the weight fraction of the monomer i of the copolymer, T_{g1} and T_{g2} represents the corresponding glass-transition temperatures of the homopolymers in this equation. Monomer 2 is assigned to the monomer whose homopolymer having the higher T_g. When a copolymer having a strong inter- and/or intra-molecular interaction, its T_g value cannot be predicted by fitting in the Gordon–Taylor equation [28].

Schneider et al. suggested a viral like third power equation which better fits the experimental results (Eq. (2)) [29].

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = (1 + K_1)\phi_2 - (K_1 + K_2)\phi_2^2 + K_2\phi_2^3 \tag{2}$$

$$\phi_2 = \frac{k w_2}{w_1 + k w_2} \tag{3}$$

where Φ_2 is the volume fraction of the component having the higher T_g and the two fitting parameters, K_1 and K_2, of this power equation characterize the contributions to the copolymer from monomer 1 and monomer 2. Schneider et al., indicated that if the K_1 value is higher than zero and the $(K_1 - K_2)$ value is lower than zero, then the T_g vs. composition curve can exhibit both positive and negative deviation. The curve show positive deviation when monomer 1 which has the lower T_g is the dominant composition and negative deviation when monomer 2 which has the higher T_g is the dominant composition [28]. Zhou et al., synthesized the fluorinated alkyl methacrylate copolymers consisting of monomers containing different number of –CF_3 end group and methyl methacrylate, and they indicated that the presence of the bulky CF_3-containing groups caused a positive deviation from the Gordon–Taylor equation due to the dipole–dipole interaction between the $CF_3(CF_2)_nCH_2CH_2O$– and the C=O groups [30]. When 2,2,2-trifluoroethyl methacrylate containing only one –CF_3 group was used in the copolymer, then it had a good fit with the Gordon–Taylor equation, however when perfluoro t-butyl methacrylate containing three –CF_3 groups was used in the copolymer, then it had a positive deviation from the Gordon–Taylor equation [30,31].

The free volume of the copolymers can be measured by the positron annihilation lifetime spectroscopy (PALS) as reported in the literature [21,32–36]. Bamford et al., characterized the free volume of the fluorinated copolymers of MMA and butyl methacrylate (BMA) and their homopolymers [21]. The free volume of the hole, V_f is calculated by using the hole radius R_H,

$$V_f = 4/3\,\pi {R_H}^3 \tag{4}$$

The fractional free volume content (F_v) of the system can then be estimated as follows [32,37]:

$$F_v = C V_f I_3 \tag{5}$$

where C is a fitting constant and the values of C range from 0.001 to 0.002 Å^{-3} for the common polymers and Hill et al. [37] have proposed to use an arbitrary average value of 0.0015 Å^{-3}. It was reported that the increase in the FMA content having long and dense side chains caused a large free volume fraction in the copolymer [21]. However, the relationship of the increase of the free volume of the copolymers by introducing the Zonyl-TM content and the values of Y_{mod} and the T_g is not well studied.

In this study, we determined the Y_{mod} and the T_g of statistical copolymers of methyl methacrylate and Zonyl-TM, which were synthesized in $scCO_2$. We choose $scCO_2$ as a polymerization medium due to its environmental and industrial advantages such as non-toxic, non-flammable, easily separation and recycling properties, inertness to chain transfer reactions during polymerization, and the ease of tuning of its properties because of its accessible critical point. Emulsion copolymerization of MMA and fluoroacrylates are also possible and reported in the literature [11,38] but the resultant copolymers contain emulsifiers as undesired impurities affecting both surface and mechanical properties adversely. We kept the Zonyl-TM contents of the copolymers in the range of 2.6–35.4 wt%. Amorphous percentage of the copolymer was examined by XRD and DSC. The free volumes of the copolymers were calculated using Bamford PALS fluorinated copolymer data [21] by assuming that their copolymer structures were similar to our synthesized copolymers as an approximation. The experimental results of the T_g values were correlated with the FMA monomer weight fraction by the Gordon Taylor and the Schneider equations. In addition, the Y_{mod} of the prepared films were measured after dissolving the copolymers in chloroform and solution casting was applied to obtain a 400 μm thick films. The change in the Y_{mod} and the T_g values was observed to decrease linearly with the increase of the Zonyl-TM ratio in the copolymers. The reasons for this decrease are discussed in the text.

2. Results and discussions

2.1. Copolymer characterization

It is well-known that the molecular weights of the perfluoro acrylic copolymers synthesized in CO_2 medium were higher than the copolymers obtained in polar organic solvents [6,10,39]. DeSimone et al. reported that the copolymer molecular weight of FOA with MMA in $scCO_2$ were more than 270,000 g/mol [10], whereas other researchers reported that the solution copolymerization of perfluoro alkyl methacrylate with MMA in MEK [39] and in BuOAc [6] resulted in much lower molecular weights which were in the range of 20,000–25,000 g/mol. The copolymers synthesized in CO_2 resulted in high M_w due to the low surface tension, low viscosity, high diffusivity and less chain transfer properties of CO_2. Besides its environmentally advantageous properties over the conventional organic solvents, copolymerizations in CO_2 result in longer macromolecular chains which are another useful property in chemical industry.

The number average molecular weight, M_w of the copolymers decreased from 115,000 down to 42,000 with the increase of the Zonyl TM content as seen in Table 1. The GPC traces of the copolymers were shown in Fig. 1S-a and b in Supporting Information section. The bimodal molecular weight distribution was observed in Fig. 1S-a for $TM_{2.5}$ copolymer sample which has the highest molecular weight and all of the other samples showed

Table 1
Copolymer composition and GPC results of MMA–Zonyl-TM copolymers.

Copolymer code	Copolymer composition[a] F_1	M_w[b] (g/mol)	M_n[b] (g/mol)	$[\eta]$[c] (mL/g)	Yield[d] (%)
$TM_{2.5}$	2.6	115,000	32,000	35.1	83
$TM_{5.0}$	7.6	70,000	28,000	26.6	87
$TM_{10.0}$	13.4	69,000	28,000	24.4	84
$TM_{20.0}$	24.5	66,000	28,000	21.1	81
$TM_{25.0}$	29.1	53,000	21,000	20.4	86
$TM_{30.0}$	35.4	42,000	19,000	14.3	90

$TM_{2.5}$ means the feed weight ratio of Zonly-TM = 2.5 wt% and MMA = 97.5 wt%.

[a] Determined from H-NMR.

[b] Determined from GPC.

[c] Determined from Ubbelohde-type viscometer.

[d] From gravimetric calculation.

monomodal distribution. Mueller et al. investigated the modality of precipitation polymerization of the vinylidene fluoride polymerization in $scCO_2$ and reported that the bimodality was observed especially for high monomer conversion [40]. Ahmed et al. reported kinetic models of solution, surface and interior polymerization methods giving precipitated polymers in $scCO_2$ [41]. They found that the solution polymerization reaction occurred only in fluid phase while surface and interior polymerization reactions occurred in both of polymer and fluid phases. It was proposed that the radicals grow in the fluid phase until precipitation takes place, and then the radicals continue growing in the polymer phase so that both phases can be important loci of polymerization [41].

The state of CO_2 phases in a polymerization reaction is important. There are two possibilities: homogeneous or heterogeneous polymerizations. In general, copolymerizations in CO_2 were carried out at high pressures in a homogeneous $scCO_2$ medium. Lora and Mchugh reported that the MMA (28.9%)–PMMA (5.1%)–CO_2 (66%) by weight ternary system was in a single homogeneous phase when the pressure and temperature was 930 bar and 85.6 °C, respectively [42]. On the other hand, Shin et al. showed that the polymerization medium of the random copolymer of heptadeca fluorodecyl methacrylate–MMA was homogeneous until the MMA ratio reaches up to 18.7 wt% at 300 bar and 70 °C. Above this MMA content ratio, the copolymerization medium changed from homogenous to heterogeneous [43]. Wang et al. indicated that vinyl monomer polymerization like MMA conversion and M_w of the PMMA were increased at the pressure decreasing MMA–CO_2 mixture at vapor–liquid equilibrium pressure including CO_2 and MMA liquids and vapors [44]. They suggested that this phenomena was related to the presence of MMA monomer in the liquid CO_2 phase with higher concentration than that of the homogenous phase, so the polymerization rate in liquid CO_2 phase was faster than the homogenous phase [44]. In our study, it is possible that the copolymerization occurs both in $scCO_2$ and liquid CO_2 phases due to low polymerization pressure of 130 bar. The increase of the M_w of the copolymer with the decrease in the Zonyl-TM content is related to the fact that the polymerization took place in liquid CO_2 medium when MMA monomer content in the monomer feed ratio increases. Copolymerization was started in a homogenous $scCO_2$ medium, but when the conversion increased sufficiently in a short period of time, the copolymerization medium was changed into a heterogeneous system consisting of $scCO_2$ and liquid CO_2, especially for the copolymerizations containing high MMA content. Thus, the increase in the Zonly-TM content in the feed resulted in the increase in the duration of the homogeneous polymerization in $scCO_2$ causing the decrease of the copolymer M_w consistent with the literature [44].

Monomer feed ratios are given in Table 1 and Zonyl-TM monomer feed ratio (by weight) was shown in the subscript of the copolymer code in this table. It was clearly seen in this table that the monomer to copolymer conversion of Zonyl-TM is larger than the CO_2–phobic MMA monomer indicating that the reactivity ratio of Zonyl-TM is larger than the reactivity ratio of MMA [r(Zonyl-TM) > r(MMA)] due to the CO_2-philic nature of Zonyl-TM monomer. The compositions of the copolymers were characterized by means of ^1H NMR spectroscopy. The weight ratio of Zonyl-TM in the copolymer, F_1, the yield and the molecular weight results obtained from the GPC are given in Table 1. The representative ^1H NMR spectrum of the copolymer TM_{30} was shown in Fig. 1. The amount of the MMA and the Zonyl-TM monomers in the synthesized copolymers were calculated from the integral ratio of the methyl protons ($-COOCH_3$) and the methylene protons ($-CH_2R_f$) corresponding to PMMA and PFMA, respectively. The peak domains of the methyl and the methylene protons agreed with the values reported in the literature [9]. The structure of the copolymers was also characterized with the FTIR-ATR spectrum of the films. The representative FTIR-ATR spectrum of the TM_{30} copolymer sample was shown in Fig. 2. The peak at 1726 cm^{-1} in the spectrum signifies the C=O stretching vibration relating to the methacrylate segments [45] and the peak at 1142 cm^{-1} corresponded to the CF_2 stretching belonging to the fluoro methacrylate segments [46]. X-ray diffraction (XRD) measurements give the percentage of the amorphous or the crystalline regions. The XRD measurements indicated that, the Zonyl-TM-ran-MMA copolymers are completely amorphous as they were expected to be. Fig. 3 shows XRD results of the $TM_{2.5}$, TM_{10}, TM_{20}, and TM_{30} copolymers and no crystalline peak is seen in this figures which is in concordance with the report of Choi et al. who showed the floroacrylate side chains are more rigid than the hydrocarbon chains and no crystalline structure was observed for the MMA–floroacrylate copolymers when the MMA content of the copolymers increased up to 50 wt% [9].

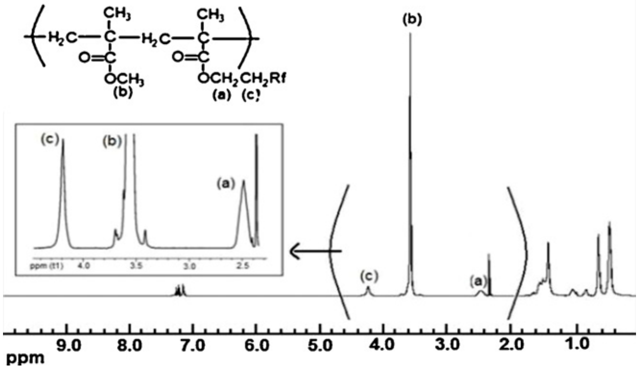

Fig. 1. Representative ^1H NMR spectrum of TM_{30} sample.

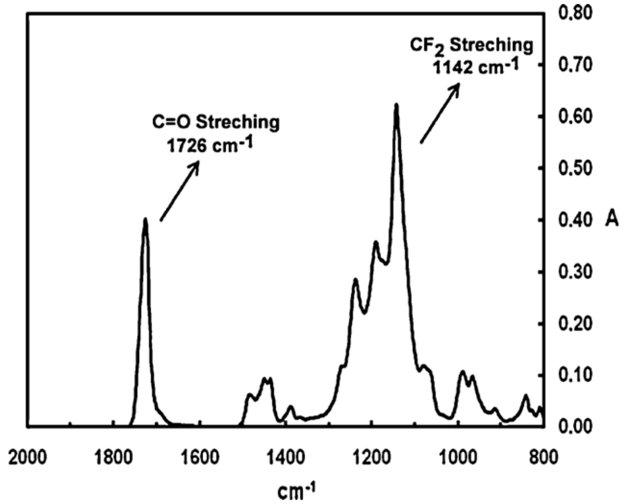

Fig. 2. Representative FTIR-ATR spectrum of TM_{30} sample.

2.2. Young's modulus results

DMA results of the MMA–Zonyl-TM copolymers were given in Table 2. The change in the Y_{mod} with the variation of the Zonyl-TM content of the copolymer is given in Fig. 4. Strain ranges of the copolymers were measured under 2% as shown in Fig. 2S in Supporting Information section. It was observed that, when the Zonyl-TM content increases to 2.6 wt%, the Y_{mod} value of the copolymer was found to be 1.57 GPa, which is approximately half of that of PMMA homopolymer. The increase in the Zonyl-TM ratio from 2.6 to 35.4 wt% cause the decrease of the Y_{mod} values linearly from 1.57 to 1.08 GPa. This behavior can be explained by the fact that the free volume of the copolymer increased with the increase of the Zonyl-TM content, and this is the reason of the decrease of the Y_{mod} values of the copolymers [25]. In literature, most of the fluoropolymer Y_{mod} values were reported to be between 0.001 and 2 GPa depending on the type of the fluoropolymer. For example, Xu et al., reported the Y_{mod} value of a hyperbranched fluoropolymer (HBFP) poly(ethylene glycol) (PEG) polymer network (HBFP-PEG) containing 30, 45, 55 and 63 PEG (wt%) were 0.28, 1.44, 11.9 and 12.6 MPa, respectively [25]. On the other hand, Velweire et al., synthesized the PFM-P75 (containing 75 mol% octafluoropentyl- and 25 mol% 2-ethylhexylacrylate side chain) copolymer having two different side chains. One side chain was fluoro methacrylate and the other side chain was ethylhexylacrylate and both of them were long and dense. They reported a low Y_{mod} value, around 1 MPa [47]. Brady et al., investigated the mechanical properties of some main chain fluoropolymers such as poly(hexafluoropropylene) (PHFP), poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) and they found that, the Y_{mod} values of the fluoropolymers are in the range of 0.5–1.2 GPa [26]. They also reported the Y_{mod} values of the PMMA was 2.8 GPA [26]. There is no report on the Y_{mod} values of the methyl methacrylate-fluoro methacrylate (Zonyl-TM)

Table 2
DSC and DMA results of MMA–Zonyl-TM copolymers.

Copolymer code	Y_{mod}[a] (GPa)	T_g[b] (°C)	T_g[c] (°C)	T_g[d] (°C)
$TM_{2.5}$	1.57	102	101.0	100.0
$TM_{5.0}$	1.49	92	94.0	93.5
$TM_{10.0}$	1.50	89	87.1	89.0
$TM_{20.0}$	1.30	87	76.1	83.9
$TM_{25.0}$	1.22	82	72.3	82.1
$TM_{30.0}$	1.08	77	67.6	79.5

[a] Determined from DMA.
[b] Determined from DSC.
[c] Calculated from Gordon–Taylor equation.
[d] Calculated from Schneider equation ($k = 0.405$, $K_1 = 1.6$ and $K_2 = 2.0$).

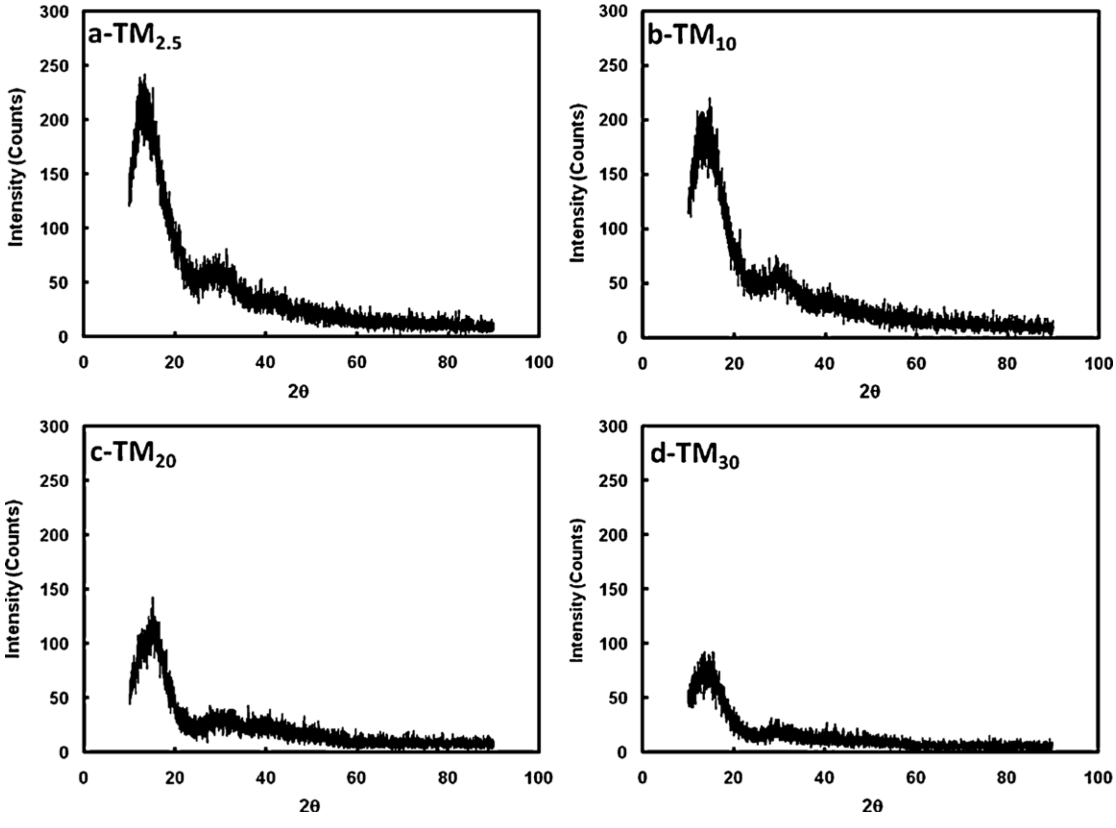

Fig. 3. XRD spectra of $TM_{2.5}$, TM_{10}, TM_{20}, and TM_{30} copolymers.

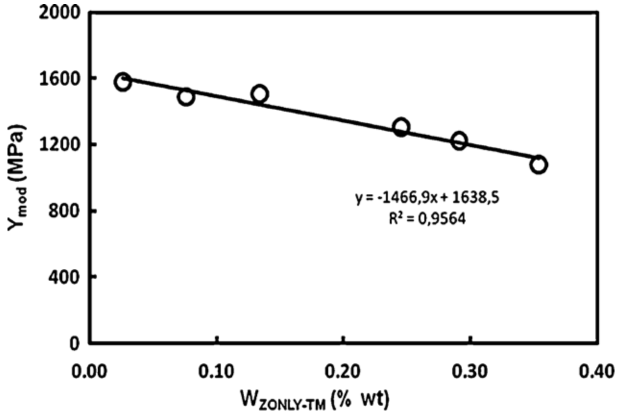

Fig. 4. Change of Y_{mod} results with the change in Zonyl-TM wt% of copolymers.

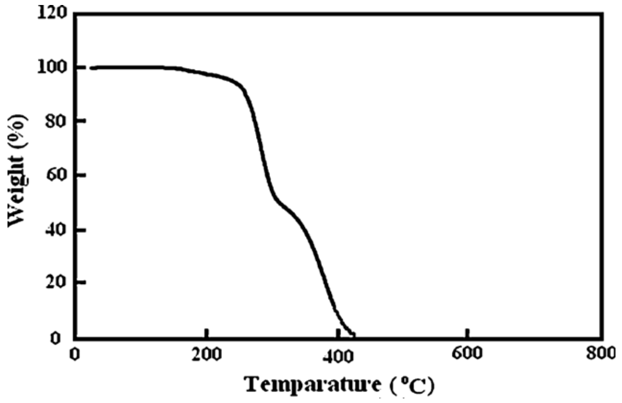

Fig. 5. Representative TGA spectrum of the TM_{30} sample.

copolymer as a function of the FMA content in the literature to the best of our knowledge.

2.3. T_g results and comparison with the theoretical models

TGA thermograms of the representative copolymer TM_{30} was shown in Fig. 5. It is seen that the decomposition of the copolymer takes places in three steps: the first step was the initial decomposition at 171 °C and 2.9 wt% of the copolymer was decomposed in this step. Later, 48.3 wt% of the copolymer was decomposed at the second step at 282 °C. The residual copolymer (47.8 wt%) was decomposed in the third step at 381 °C. The copolymers were random as seen in Fig. 6 showing the DSC thermograms of the all copolymers. Park et al. [11] reported that the homopolymers and the random copolymers of perfluoromethacrylate with MMA gave a single peak in their DSC thermograms like our random copolymers, but the graft copolymer and mixture of the homopolymers shows double peaks [11]. Thus, our DSC thermogram results showed that our copolymers were random. The T_g results of the copolymers are given in Table 2 which was calculated from DSC. In this table, it is realized that the increase of the perfluoroalkyl ethyl methacrylate content in the copolymers caused a decrease in the T_g values due to the increase in the number of $–CF_2–$ group in the $CF_3(CF_2)_x–$ side chain. In the literature, T_g value of PMMA homopolymer was reported to be 105 °C [30] and T_g value of the poly(perfluoroalkyl ethyl methacrylate) homopolymer having $x = 5$ were reported as 21.2 [48], 49.1 [6] and 52 °C [11] and T_g value was found to be 90.8 °C when $x = 0$ [6]. We determined $T_g = 40$ °C for Zonyl-TM homopolymer which was synthesized in the heterogeneous CO_2 medium and this value was within the range of T_g values reported in the literature.

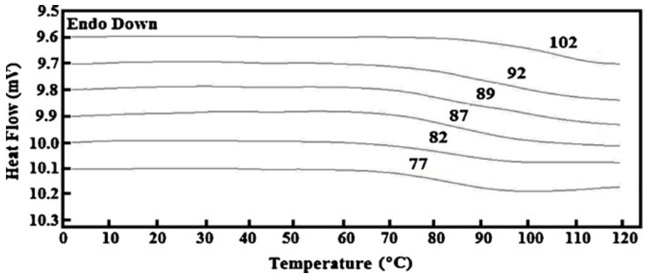

Fig. 6. DSC thermograms of the copolymers.

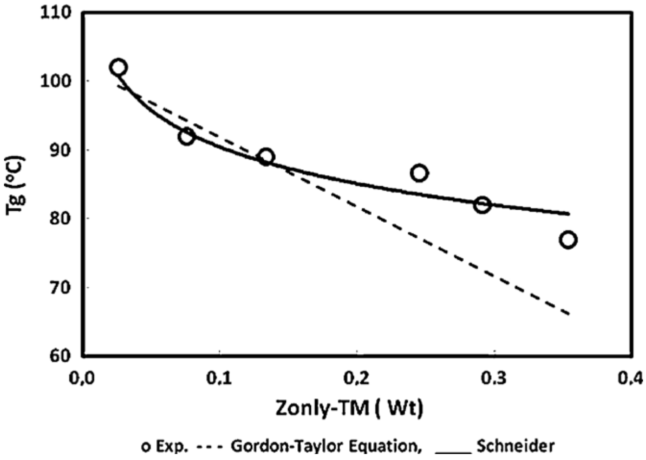

Fig. 7. Change of T_g results with the change in Zonyl-TM wt% of copolymers and fitting equations of Gordon–Taylor and Schneider.

We tried to estimate the T_g values of copolymers according to the Zonyl-TM content by using the Gordon–Taylor (Eq. (1)) and also the Schneider (Eq. (2)) equations and the resultant plot is given in Fig. 7. As seen in this figure, T_g data points calculated by the Gordon–Taylor equation decreased linearly with the increase in the Zonyl-TM weight percent (w_1), giving a regression coefficient R^2 value of 0.9907. For this calculation, six Gordon–Taylor fitting constants and the k values were determined by using the experimental T_g value of each copolymer in Eq. (1), and then we calculated the mean k value of 0.405 for the six copolymers. On the other hand, when the Schneider equation was used, most of the T_g values of the copolymers were found to fit the experimental data as shown in Fig. 7. The volume fraction of the higher T_g value component, Φ_2 was calculated from Eq. (3), where the k value was taken from the Gordon–Taylor equation as being equal to 0.405. The fitting parameters K_1 and K_2 for all the systems were calculated by using numerical iteration as 1.6 and 2.0, respectively and the R^2 values were 0.99 as shown in Fig. 7. Experimental T_g values shown the negative deviation from the Gordon–Taylor equation due to the high PMMA content (high T_g) until the Zonyl-TM content of copolymer weight fraction is 0.14. However, when the Zonyl-TM weight fraction was higher than 0.14, T_g values showed a positive deviation from Gordon–Taylor equation due to the high Zonyl-TM content (low T_g) as seen in Fig. 7. An inversion of the initial negative deviation of T_g to positive were due to the competition between the effect of the free volume and dipole–dipole interactions. The increase in the Zonyl-TM content of the copolymer caused an increase in not only the dipole–dipole interactions but also the free volume of the copolymer. When Zonyl-TM weight fraction of the copolymer was lower than 0.14, the free volume effect was more dominant than the dipole–dipole interaction effect, so the decrease of the T_g value was more steeper and the negative deviation from the Gordon–Taylor was observed. However, when Zonyl-TM weight fraction was higher than 0.14, then the dipole–dipole interactions which occurred between $CF_3(CF_2)_nCH_2CH_2O$– and C=O groups became more dominant. The rate of decrease in the T_g of the copolymers was slowed down by the increase in the dipole–dipole interactions due to the decrease in the chain mobility, and thus the positive deviation from the Gordon–Taylor equation started afterwards as shown in Fig. 7.

In general, other than the polymer free volume, the T_g values of the copolymers were also affected by the molecular weight, chemical structure, intermolecular forces, symmetry and chain stiffness [13]. Decreasing the molecular weight of a copolymer usually resulted in a decrease in the T_g value of that copolymer [13,49]. However, the most important factor to affect the T_g value is the free rotation ability along the polymer chain which is related with the presence of the long side groups [6,50]. van de Grampal et al. reported that there were no systematic relation between the T_g values of the copolymers with their molecular weights when perfluoro ethyl methacrylate–MMA copolymers were used. The main effect on the T_g values of the copolymers was the increase of the perfluoro methacrylate content [6]. Fernandez-Garcia et al. reported that the T_g value of the random copolymer of MMA with butyl acrylate (BA) and indicated that the influence of M_n on T_g is not very important, since the increase in molecular weight may be compensated by the decrease in T_g due to the increasing the free volume by the enrichment of BA in the polymer chain [50]. According literature results, it can be concluded that if the copolymer has a long and dense side chain like Zonyl-TM, T_g values were mostly affected with the change of the free volume.

2.4. Free volume calculations

The free volume fractions of the copolymers were calculated by using the Bamford experimental PALS data of a fluorinated copolymer [21], assuming that the hepta-fluoro-butyl-methacrylate (HFBMA) and the Zonyl-TM behave similarly as a function of the fraction of the number of fluorine (F) atoms in the copolymer. The calculation results of the fraction of the number of the F atoms for all the copolymers were presented in Table 3. The R_H value of the HFMBA and the MMA was reported as 3.981 Å and 2.95 Å, respectively [21]. The R_H value of the Zonyl-TM was predicted as 4.015 Å depending on the fraction of its F atoms and the R_H value of the MMA taken from in the literature was 2.95 Å [21]. It was a reasonable estimation that the R_H value of the Zonly-TM is larger than that of the HFBMA due to its longer and denser side chains. All copolymer R_H values were then calculated as a function of the fraction of the F atoms.

The free volume size (V_f) and the free volume fraction (F_v) of the copolymer were calculated using Eqs. (4) and (5), respectively. The I_3 values of the copolymer were also estimated to be similar to R_H. The fitting constant, c, was taken as 0.0015 reported by Hill et al. [37]. The calculated data of the fraction of the number of F atoms, V_f, f_v, and the predicted data of the I_3 and the R_H were shown in Table 3. It is clearly seen that the free volume fraction of the copolymer increased as a function of the Zonly-TM content due to the introduction of the dense and the long side chain. In summary, when the Zonyl-TM content, which has a longer side chain than the methyl methacrylate in polymer was increased, the free volume of the copolymers rises from 116.2 to 196.1 Å^3. Thus, the Y_{mod} and the T_g values of the copolymer reduced (Figs. 4 and 7) in a similar trend with the data reported in references [9,30,34,39,51]. In addition, the relationship between the Y_{mod} and the T_g values of the copolymer is shown in Fig. 8. In this figure, it can be seen that the increase in the T_g value of the copolymer resulted in a linear increase of the Y_{mod} [52]. It is possible that this linearity is due to similar effect of free volume of the copolymers on the Y_{mod} and T_g parameters.

Table 3
PALS data and free volume fraction of Zonyl-TM–MMA copolymers.

Copolymer	Fraction of F^a	I_3^{b}	R_H (Å)^b	V_f (Å^3)^c	F_v^{d}
MMA	0.0	0.3000	2.9500	107.5	0.0484
TM$_{2.5}$	0.032	0.2974	3.0275	116.2	0.0519
TM$_{5.0}$	0.084	0.29332	3.1561	131.7	0.0579
TM$_{10.0}$	0.135	0.2891	3.2807	147.9	0.0641
TM$_{20.0}$	0.211	0.2829	3.4680	174.7	0.0741
TM$_{25.0}$	0.236	0.2809	3.5298	184.2	0.0776
TM$_{30.0}$	0.266	0.2784	3.6041	196.1	0.0819
Zonyl-TM	0.432	0.2650	4.0150	271.1	0.1078

[a] Calculated using Zonyl-TM–MMA copolymer atom number.
[b] Prediction of Bamford et al. [21] experimental data using fraction of F atom of the copolymers.
[c] Calculated from Eq. (4).
[d] Calculated from Eq. (5).

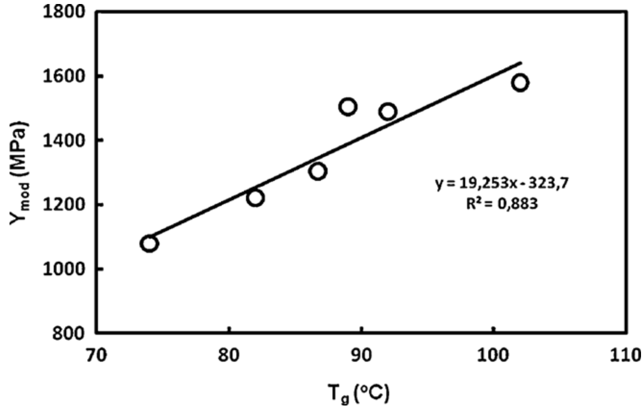

Fig. 8. Change of Y_{mod} results with the change in T_g of copolymers.

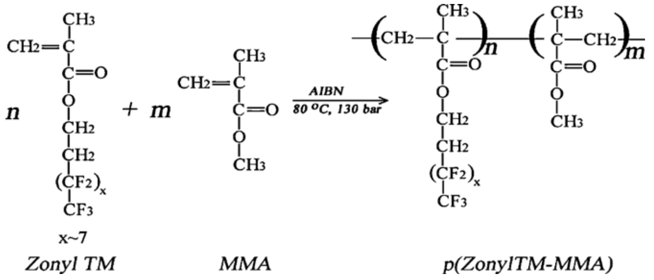

Fig. 9. Sketch of the copolymerization reaction of Zonyl-TM with MMA in $scCO_2$.

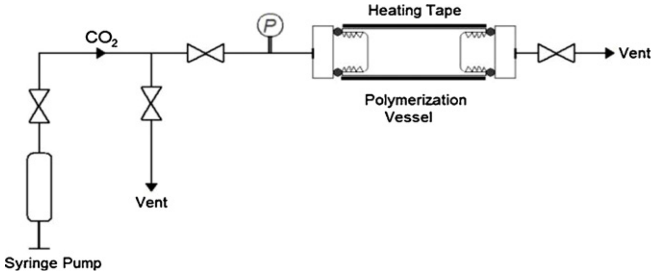

Fig. 10. The schematic of the polymerization apparatus.

3. Conclusion

Fluorinated methacrylate copolymers were successfully synthesized by free radical polymerization of Zonyl-TM and MMA in a supercritical CO_2 medium. The mechanical, thermal and chemical properties of the statistical copolymers were investigated. XRD measurements indicated that the Zonyl-TM-ran-MMA copolymers were completely amorphous. It was determined that the T_g and Y_{mod} values of the copolymers were decreased as a function of the Zonyl-TM content which increases the free volume of the copolymers due to its long side chain. Experimental T_g values of the copolymers were compared with those calculated by the Gordon–Taylor and the Schneider equations, and a good fit was found when the Schneider equation was used. Negative deviation from the Gordon–Taylor equation was observed when the Zonyl-TM content in the copolymer was between 0 and 14 wt% due to rapid increase in the free volume. However after the Zonyl-TM content was larger than 14 wt%, then the positive deviation was found due to the effect of dipole–dipole interactions between the methyl ester group and the fluoroalkyl ester group of the monomer units in the copolymers. In addition, a linear relationship between the Y_{mod} and the T_g values of the copolymer was found due to similar effect of free volume of the copolymers on these parameters.

4. Experimental

4.1. Materials

Methyl methacrylate monomer (MMA), chloroform and the initiator 2, 2′-azobis(2-methylpropionitrile) (AIBN) were purchased from Aldrich. High-purity carbon dioxide was obtained from Linde Gas A.S. Turkey. Zonyl-TM (perfluoroalkyl ethyl methacrylate monomer, Fig. 9) was purchased from DuPont-Turkey and used directly. Zonyl-TM is a commercial fluoromonomer mixture containing homologous fluoroalkyl ethyl methacrylates having varying side-chain. The specification of Zonyl-TM shows that it consists of 90–95% of perfluoroalkyl ethyl methacrylates containing different $(CF_2)_x$ groups ranging from $(CF_2)_4$ to $(CF_2)_{20}$. Approximately 85% of the mixture is composed of $(CF_2)_6$, $(CF_2)_8$ and $(CF_2)_{10}$ [53]. Other compounds present in ZONYL-TM as impurities are perfluoroalkyl ethyl alcohols (2–3%), fluoropolymers (2–3%), methyl methacrylates (0.9–1%), cyclohexane (0.5–1%) and water (0.07–0.5%) [53].

4.2. Copolymer synthesis

The experimental set-up is shown in Fig. 10. High-pressure reactions were carried out in a stainless steel vessel (diameter: 28.7 mm, height: 160 mm and vessel volume: 104 mL). $ScCO_2$ was delivered to the reactor with an Isco automatic syringe pump (Model 260 D). The pressure in the reactor was measured with a pressure gauge that was controlled with a syringe pump pressure transducer having a digital display of sensitivity ±0.1 bar. The vessel was heated through a heating-tape containing a J type thermocouple with PID controlled units of sensitivity ±0.1 °C. The thermocouple was inserted directly into the heating-tape. A heating system calibration was performed to maintain an accurate fluid temperature.

In a typical copolymerization, Zonyl-TM and AIBN (1 wt% of the total amount of the monomers) initiator were dissolved in liquid MMA. The mixture was injected into the vessel by means of a syringe-needle, and the vessel was charged with $scCO_2$ at 50 °C via the syringe pump and after the removal of air from the vessel, the valve was closed and then the reactor was heated to 80 °C and kept at this temperature for 16 h. At the end of the reaction, CO_2 was vented slowly and the vessel was cooled down to room temperature. The white solid copolymer was collected and the product was dissolved in toluene and was precipitated into methanol to separate the unreacted monomers. The purified copolymer product was filtered through milipore and was dried in a vacuum oven and the yield was measured gravimetrically. Copolymerizations were performed at a constant temperature of 80 °C and at a pressure of 130 bar.

4.3. Copolymer characterization

The monomer ratios in the copolymer were determined by ^1H NMR spectra using an Inova-500 MHz spectrometer with $CDCl_3$ as a solvent. The values on the spectrometer were recorded as ppm relative to the internal standard (TMS). The spectrophotometric examination of the perfluoro ethly methacrylate copolymers was carried out by the Fourier Transform Infrared Spectroscopy (FTIR-ATR) reflectance (PerkinElmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal). The number (M_n) and the weight (M_w) molecular averages were determined by dissolving the copolymers in ultra pure THF solvent in the gel permeation chromatography (GPC, Agilent 1100 GPC with Waters Styragel HR4E and HR5E columns) instrument. The calibration was carried out with the poly (methyl methacrylate) standard, and the solvent flow rate was 0.3 ml/min. In addition, the intrinsic viscosity of the copolymer's chloroform solution was determined using an Ubbelohde-type viscometer (radius of 3.15×10^{-4} m, No: 50110). The viscosity measurements were carried out with a flow time of 43 s for chloroform at 25 ± 0.1 °C. The copolymer concentrations were in the range of 1×10^{-1} to 1.67×10^{-2} g/cm^3. The measurements were repeated 3 times for each concentration with deviations less than 0.1 s. The DSC measurements were carried out on a PerkinElmer DSC Cade100 calibrated with indium. Each sample was scanned at a heating rate of 10 °C min^{-1}. The T_g values were determined on the second scan to ensure identical thermal histories. The TGA measurement of the representative copolymer TM_{30} was scanned using a Mettler Toledo TGA 851 instrument. 5.3 mg of copolymer was used under a dry nitrogen purge and with ramping at a rate of 10 °C/min, starting from 25 up to 700 °C. The XRD measurements were carried out using a Rigaku D-Max Rint-2200 series X-Ray Diffractometer.

4.4. Preparation of the thick film

The copolymer films with a thickness of 400 μm were prepared via the solution casting method. These films were obtained by pouring the chloroform solution of the sample copolymer with a concentration of 20.0 mg/ml (w/v) into a Petri dish at room temperature and dried in an oven at room temperature under vacuum overnight.

4.5. Young's modulus measurements

The tensile testing of samples, having dimensions of 400 μm × 5 mm × 10 mm, are performed using the TA Instruments Dynamic Mechanical Analysis (DMA) Q800 at 30 °C in a medium of approximately 50% relative humidity. The samples were placed between two clamps and force was applied from the direction of the lower clamp while keeping the upper clamp fixed. The forces were increased with a ramp rate of 1 N/min from 0 to 18 N and the Y_{mod} calculations are performed with the software of the equipment, TA Instruments Universal Analysis 2000.

Acknowledgments

This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) under the project "Development of Environmentally Benign Processes for the Fabrication of Self-Cleaning and Self-Healing Superhydrophobic Surfaces" (Project No: MAG-104M360). The authors would like to thank Dr. Ferda Hacivelioglu for useful discussion on DSC data and Mr. Adem Sen for obtaining XRD data in the Material Science and Engineering Department of Gebze Institute of Technology for the XRD facility.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.03.010.

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