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Analysis of the interaction using FTIR within the components of OREC composite GPE based on the synthesized copolymer matrix of P(MMA-MAh)

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Abstract

Poly(methyl methacrylate-maleic anhydride) (P(MMA-MAh)) has been synthesized from methyl methacrylate (MMA) and maleic anhydride (MAh) monomers. The molar ratio of monomers was found to be 1MAh:8MMA. The molecular weight of copolymer was determined in the order 10^4 (g/mol).

Rectorite modified with dodecyl benzyl dimethyl ammonium chloride (OREC) was used as a filler additive to modify gel polymer electrolytes (GPEs) which consisted of P(MMA-MAh) used as polymer matrix, propylene carbonate (PC) as a plasticizer and $LiClO_4$ as lithium ion producer. Characterization of interaction of C═O in PC and copolymer with Li^+ and OH group on OREC surface has been thoroughly examined using FTIR. The quantitative analysis of FTIR shows that the absorptivity coefficient a of copolymer/$LiClO_4$, PC/$LiClO_4$, PC/OREC and copolymer/OREC is 0.756, 0.113, 0.430 and 0.602, respectively, which means that the Li^+ or OH bonded C═O is more sensitive than free C═O in FTIR spectra. The limit value of bonded C═O equivalent fraction of copolymer/$LiClO_4$, PC/$LiClO_4$, PC/OREC and copolymer/OREC is 55, 94, 57 and 26%, respectively, which implies that all the interaction within the components is reversible and the intensity of interaction is ordered as PC/$LiClO_4$, PC/OREC, copolymer/OREC and copolymer/$LiClO_4$.

Keywords: Rectorite; Gel polymer electrolytes; FTIR

1. Introduction

Gel polymer electrolytes (GPEs) are reported to be suitable for electrochemical devices since their transport properties are quite exceptional and they have an ionic conductivity in the order of 10^{-3} S/cm, an electrochemical stability window exceeding 4.5 V and lithium-ion transference numbers averaging 0.9 [1–9]. In GPEs, the addition of plasticizer to the polymer electrolyte results in high segmental motion and thus increases the ionic conductivity. It is well recognized that the addition of inorganic fillers such as ceramic powder, alumina or silica to GPEs based on the polyether matrix will not only enhance its ionic conductivity but also improve dimensional mechanical stability [10–14].

Rectorite (REC) is a type of layered clay with specific texture similar to that of montmorillonite (MMT). It is a regularly interstratified clay mineral of dioctahedral mica-like layer (non-expansible) and dioctahedral smectite-like layer (expansible) in a 1:1 ratio. The smectite layer has the capability of cation exchange. However, REC is also hydrophilic. To render it more hydrophobic, the hydrated cations between the silicate layers need to be exchanged with cationic surfactants such as organic quaternary ammonium salts.

Maleic anhydride (MAh) is a unique comonomer because it does not readily undergo homopolymerization, but forms copolymers without difficulty [15]. As the numbers of polar, rigid or cyclic groups in the backbone of polymers increased [16,17], the chain elasticity of polymer decreased. On the

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other side interactions of the electron accepting maleic anhydride groups with the charge carriers are expected, which should reduce the ionic association and should restrict the mobility of the anions.

The application of Fourier transform infrared (FTIR) spectroscopic techniques to assess polymer science has been conducted for many years [18–24]. FTIR is a particularly suitable technique for investigating the specific intermolecular interaction [25–28]. The changes of interaction behavior can be characterized through the identification of the IR spectral features in intensity, bandwidth and position with which it allows to quantitatively study the interaction. Digar et al. [29] quantitatively studied the interaction of Li^+ with segments of PUA with FTIR, and found that the deconvoluted FTIR spectra show three kinds of C=O in PUA/$LiClO_4$ system. In addition, with the addition of lithium, three peaks were shifted to lower wave number, and the area of three peaks also changed. Wu and Chang [28] also used FTIR to quantitatively study the interaction within polyester/$LiClO_4$ system, which clearly clarifies the Li^+ status in the polymer electrolyte. But until now, there have not been reports about FTIR quantitative research of GPE. In GPE systems, there are more components, so it is more necessary and important to quantitatively study the interaction between components.

In the present work, we will focus on the interaction between the components of copolymer of poly(methyl methacrylate-maleic anhydride) (P(MMA-MAh)), filler additive of rectorite modified with dodecyl benzyl dimethyl ammonium chloride (OREC), propylene carbonate (PC) and $LiClO_4$ with FTIR spectra, which will help us to understand the micro-interaction of OREC modified GPEs. In addition, the quantitative measurement method mentioned in the present work can be widely used in a variety of polymer science.

2. Experimental section

2.1. Materials

The plasticizer was propylene carbonate (PC) from Shangshi Reagent Co. and acetone from Xi'an Chemical Reagent Co. was used as solvent. PC and acetone were stored over molecular sieves (4 Å) in order to remove residual water traces. $LiClO_4$ was obtained from Xi'an Chemical Reagent Co. Sodium rectorite (Na-REC) was refined from clay minerals in Wuhan, China. The CEC is 45 meq/100 g and the *d*-space is 2.22 nm. The natural rectorite (REC) was modified with surfactant of dodecyl benzyl dimethyl ammonium chloride in our lab. The amount of surfactant exchanged into OREC was determined as 0.27 mmol g^{-1} and the *d*-spacing of organic modified clay was 2.99 nm [30].

2.2. Synthesis of copolymer

To a 500 ml four-necked reactor equipped with mechanical stirrer and condenser, toluene (200 ml), MMA (18.0 g), MAh (17.7 g) and AIBN (0.026 g) as catalyzer were added sequentially. The reaction was carried out at 80 °C under nitrogen atmosphere for 8 h. Solvent in the reaction mixture was then removed by filtration method. The crude product was washed by diethyl ether until the unreacted monomers were removed completely. The purified product was dried in a vacuum oven to remove the trapped solvent at 100 °C for 24 h.

2.3. Beer–Lambert's law

A single optical path was used to study the interaction within the GPE. All samples in the absorption range would obey Beer–Lambert's law.

$$\left|\frac{I}{cl}\right|\lim_{c\to 0} = \varepsilon \tag{1}$$

where I is the intensity of absorption; ε is the absorptivity coefficient; l is the thickness of sample; and c is the concentration.

2.4. Characterization

The molar ratio of MAh and MMA was determined as follows.

The hydrolysis of copolymer was carried out with a 2 M NaOH solution at 25 °C under argon atmosphere for 1 h. The copolymer solution was precipitated in 2 M HCl solution; then the sample was isolated by filtration and washed several times with water to remove the traces of NaCl and then dried in vacuum at 50 °C. Titration of dicarboxylic groups was carried out using a 0.1 M NaOH solution in the presence of phenolphthalein. The percentage of sodium uptake is given by the relationship

$$\%\mathrm{Na} = \frac{V_{\mathrm{NaOH}} \times n_{\mathrm{NaOH}} \times 40}{a \times 1000} \times 100 \tag{2}$$

where V_{NaOH} is the volume of NaOH solution (ml); n_{NaOH} is the normality of solution (mol/l); a is the sample weight (g).

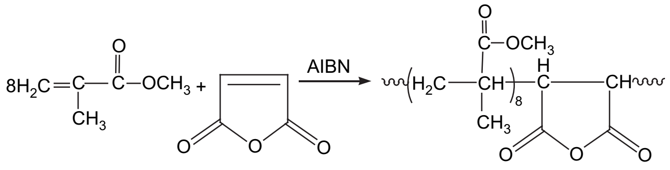
The total neutralized dicarboxylic content (%) can be calculated using the relationship

$$\%\mathrm{Dicarboxylic} = \frac{\%\mathrm{NaOH} \times a \times 45}{40 \times 2} \tag{3}$$

where 40 and 45 are the chemical equivalents of NaOH and carboxylic group, respectively.

^{1}H NMR spectra of polymers were recorded with a 500 MHz BRUKE NMR spectrometer in $CDCl_3$, using TMS as the internal standard. The molecular weight of the copolymer was determined by gel permeation chromatography (GPC) with laser scattering detector, ultrastyragel column with pore sizes of 10^3–10^5 Å. The eluent used was THF at a flow rate of 0.5 ml min^{-1}. Samples for ^{1}H NMR determination were typically scanned 64 times between δ values of 0–10 ppm.

FTIR was performed on an infrared spectroscopy of WQF-310 in the wave number range 4000–400 cm^{-1}. The sample dispersed in acetone was casted on KBr pellets. Until acetone



Scheme 1. Synthesis of copolymer of MMA-MAh.

was completely dropped out from the thin film, the KBr pellet with sample was placed in the meter for measurement. All infrared spectra were obtained at 16 scans with a resolution of 0.1 cm^{-1} at room temperature.

3. Results and discussion

3.1. Characterization of copolymer

Based on the method of hydrolysis of maleic anhydride copolymer and according to Eqs. (2) and (3), the molar ratio was found to be 1MAh:8MMA, as shown in Scheme 1. Fig. 1 indicates the very low molecular weight distribution for the copolymer. Table 1 shows the molecular weights and the radius moments of the synthesized copolymer.

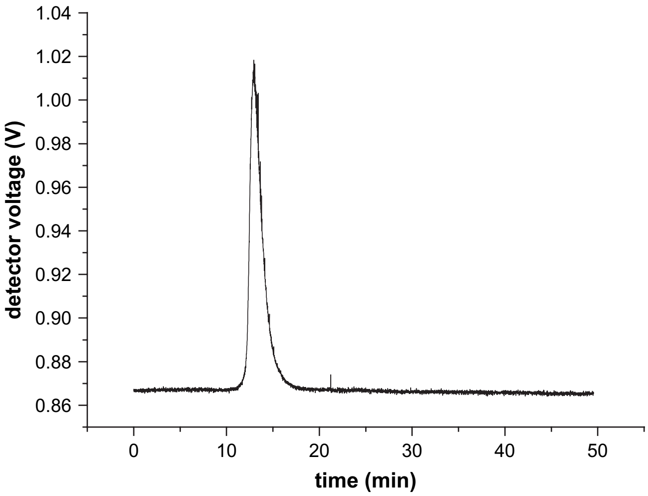


Fig. 1. GPC analysis of copolymer.

Table 1
Molecular weights and radius moments of the synthesized copolymer

Copolymer	Molar mass moments (g/mol) × 10^4			Radius moments (nm)		
	M_n	M_w	M_z	R_n	R_w	R_z
P(MMA$_8$-MAh)	6.402	6.675	7.299	8.4	9.0	9.5

Fig. 2 shows the FTIR spectrum of the copolymer. The FTIR spectra of the copolymer product show bands at 1851 and 1786 cm^{-1} corresponding to the antisymmetric and symmetric stretches of C=O in anhydride, and at 952–909 cm^{-1} due to the ring stretching vibrations of a saturated cyclic five-membered anhydride. The band at 1731 cm^{-1} corresponds the stretch of C=O in MMA. The peak from the free carboxylic acid groups was absent, which meant that there was no hydrolysis reaction of anhydride in the product (bands at 1640 and 1500 cm^{-1}are assigned to carboxylate (COO$^-$) ion). Therefore, the resulted copolymer contains all the characteristic groups of methyl methacrylate and maleic anhydride and is successfully synthesized.

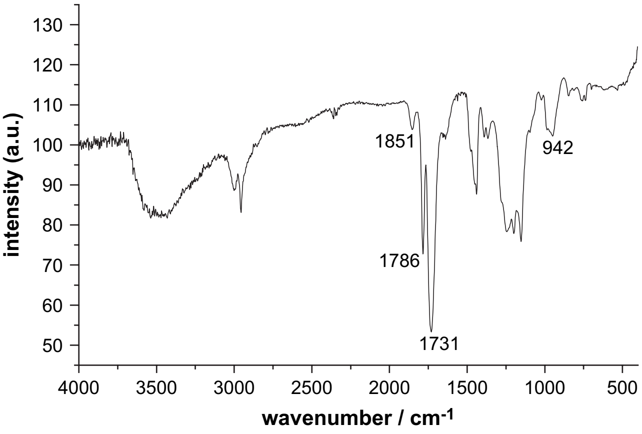


Fig. 2. FTIR spectra of the synthesized copolymer.

The chemical structure of the prepared copolymer was characterized by ^{1}H NMR analysis, as shown in Fig. 3. The ^{1}H NMR characteristic spectra of copolymer contain at 1.03 ppm a signal for the $-CH_3$ group, at 2.0 ppm for the $-CH_2-$ group, at 3.7 ppm for the $-COOCH_3$ group and at 2.8 ppm for the methine (=CH−) group.

The X-ray diffraction pattern of copolymer at room temperature from $2\theta = 2°$ to $50°$ is shown in Fig. 4, in which the diffraction pattern for the synthesized copolymer is broad, without any resolved peaks, indicating it is amorphous.

3.2. Quantitative measurement of interactions between components

The C=O absorption from 1800 to 1650 cm^{-1} is highly sensitive to interaction behavior, such as hydrogen bonding.

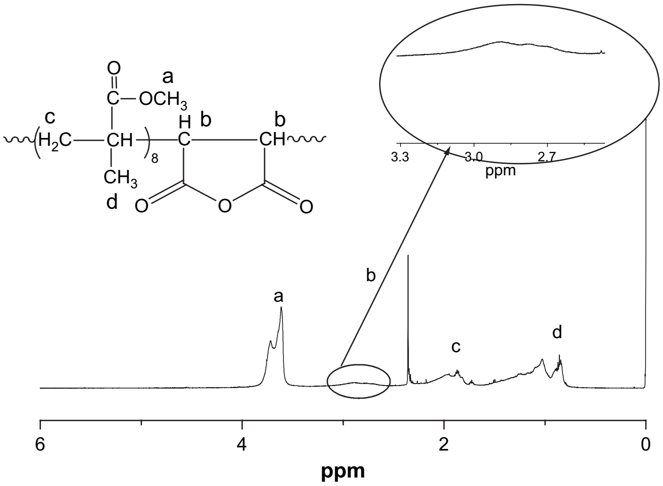


Fig. 3. ^{1}H NMR of copolymer.

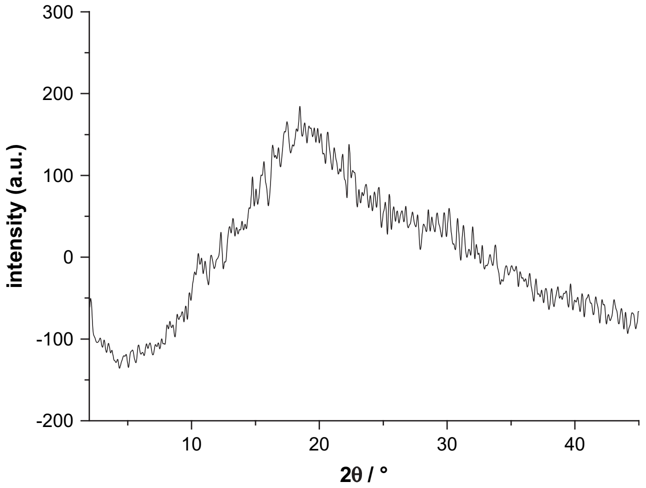


Fig. 4. XRD of copolymer.

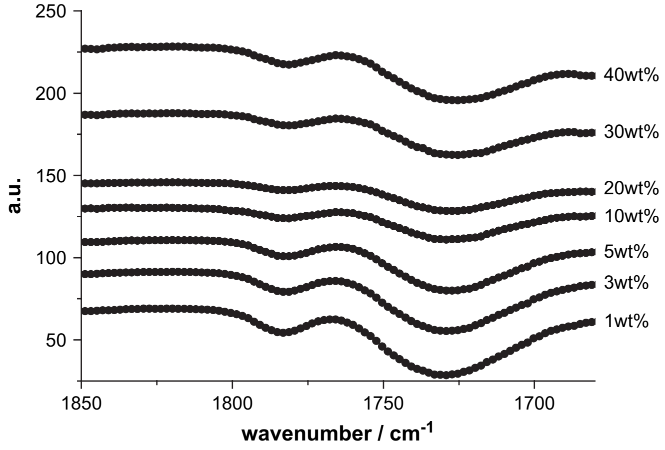


Fig. 5. FTIR spectra of copolymer/$LiClO_4$ blends from 1850 to 1650 cm^{-1} with varying the content of $LiClO_4$ from 5 to 50 wt%.

The absorption of C═O group in IR spectroscopy can be separated into two bands: free and hydrogen bonded when the C═O group interacts with other proton donating groups such as −OH, −NH, etc. The newly formed band corresponding to the absorption of hydrogen-bonded C═O appears at relatively lower wave number position from that of the free C═O in FTIR spectroscopy [21]. The behavior of Li^+ bonded C═O absorption formation is similar to the hydrogen-bonded C═O absorption formation.

A problem which arises in the quantitative analysis of FTIR spectra is the partial overlapping of both kinds of C═O stretching bands. A quantitative analysis of the observed profiles, including deconvolution and curve fitting, is then really helpful in order to clarify the nature of both kinds of C═O. In order to separate both bands, we choose to fit the spectra with all the fitting parameters left free to vary upon iteration until converging solution is reached. Although the spectral decomposition procedures have no unique solution, we remark that the one we adopted here uses the minimum number of parameters and, at the same time, it furnishes extremely good fits to the data. The best fit is, in fact, characterized by $r^2 \sim 0.9999$ for all the investigated systems.

3.2.1. Quantitative measurement of interactions for copolymer/$LiClO_4$ solid blends

Fig. 5 shows the FTIR spectra from 1850 to 1650 cm^{-1} of copolymer/$LiClO_4$ blends with various lithium salt contents. It was obvious that with the increase of lithium salt content, the position of C═O in both MMA and MAh shifted down to lower wave number, which was the results of interaction between C═O group and lithium ion of Li^+.

By adding lithium salt, portion of the C═O group is able to interact with Li^+ ion to form the Li^+ ion bonded C═O. Therefore, the Li^+ ion bonded C═O group of copolymer is increased, while the free C═O group is decreased. Curve fitting for C═O in MMA and MAh between 1800 and 1770 cm^{-1} and between 1760 and 1670 cm^{-1} shows two

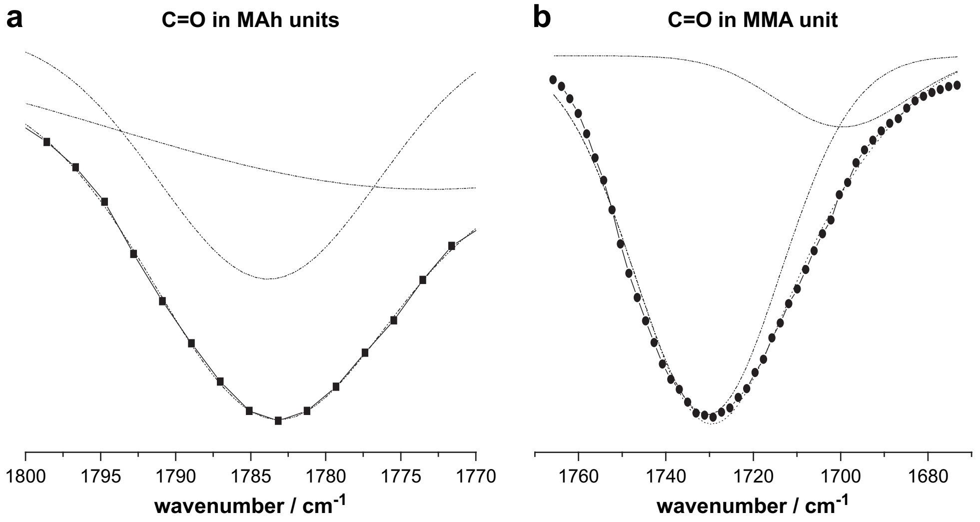


Fig. 6. Curve fitting for peaks of C═O group in copolymer/$LiClO_4$ blend (5 wt%).

Table 2
Results of copolymer/$LiClO_4$ blends with various lithium salt contents

Samples	C=O in MMA units		C=O in MAh units		F_1	F_2	F_3	Abs. a	$1-f$
	A_1 (1730 cm^{-1})	A_2 (1706 cm^{-1})	A_3 (1786 cm^{-1})	A_4 (1772 cm^{-1})					
1 wt%	0.876	0.002	0.112	0.010	0.881	0.110	0.009	0.754	1.58
3 wt%	0.859	0.013	0.102	0.026	0.863	0.108	0.029	0.758	5.09
Ave.								0.756	
5 wt%	0.835	0.021	0.091	0.063	0.847	0.106	0.047		10.71
10 wt%	0.788	0.071	0.065	0.076	0.805	0.100	0.095		18.56
20 wt%	0.584	0.273	0.033	0.120	0.718	0.090	0.192		45.73
30 wt%	0.529	0.322	0.011	0.138	0.632	0.079	0.289		53.98
40 wt%	0.510	0.337	0.008	0.145	0.545	0.068	0.387		55.17

A_1 and A_2 represent the area fractions of free and bonded C=O in MMA units, respectively, A_3 and A_4 represent the area fractions of free and bonded C=O in MAh units, respectively; F_1 and F_2 represent the equivalent fractions of C=O in MMA and MAh, respectively; F_3 represents the equivalent fraction of Li^+; a is the absorptivity coefficient of C=O group. $1-f$ is the equivalent fraction of the lithium-ion bonded C=O.

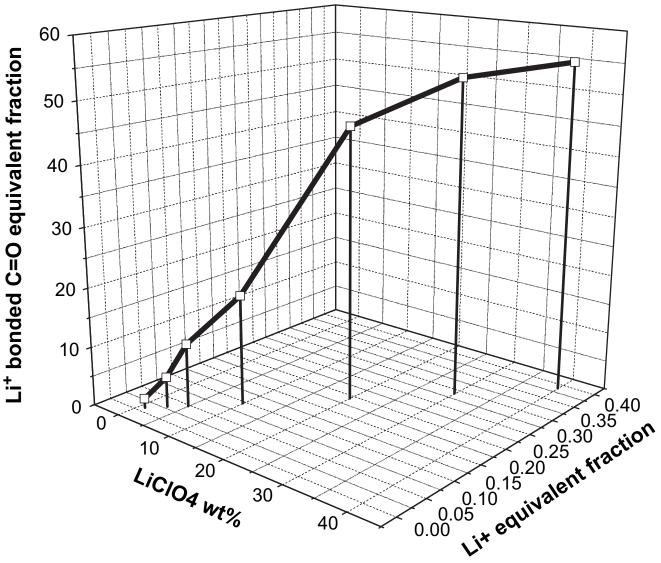


Fig. 7. The relation between Li^+ bonded C=O equivalent fraction and $LiClO_4$ content for copolymer/$LiClO_4$ blends.

Gaussian peaks, respectively, for example, Fig. 6 provides an adequate fit for the copolymer/$LiClO_4$ (5 wt%) blend as dashed line.

Curve fitting shows two Gaussian peaks for C=O in MMA unit at 1730 and 1706 cm^{-1}, as well as C=O in MAh unit at 1786 and 1772 cm^{-1}. The results of area fractions (A_1, A_2, A_3 and A_4) of peak obtained from the curve-fitting procedure are displayed in Table 2. The following equation can be used to determine the absorptivity coefficient of C=O in copolymer.

$$a = \frac{(A_1 + A_3) \times F_3}{(A_2 + A_4) \times (F_1 + F_2 - F_3)} \tag{4}$$

where a is the absorptivity coefficient of C=O group in copolymer. A_1 and A_2 represent the area fractions of free and bonded C=O in MMA units, respectively; A_3 and A_4 represent the area fractions of free and bonded C=O in MAh units, respectively. F_1 and F_2 represent the equivalent fractions of C=O in MMA and MAh, respectively. F_3 represents the equivalent fraction of Li^+. The calculated equivalent fractions (F_1, F_2 and F_3) are also displayed in Table 2.

The absorptivity coefficient a of C=O group in copolymer was calculated for copolymer/$LiClO_4$ blends with low lithium salt concentration. It is reasonable to assume that only simple interaction between lithium ion and C=O group is presented and obeys Beer's law in low lithium salt concentration blends. So according to Eq. (4), the absorptivity coefficient a determined from the 1 and 3% lithium salt blends is given in Table 2. The average value of absorptivity coefficient of copolymer/$LiClO_4$ is 0.756, which implies that the absorptivity sensitivity of the lithium-ion bonded C=O at 1706 and 1772 cm^{-1} is larger than that of free C=O at 1730 and 1786 cm^{-1}.

Table 2 also summarizes the curve-fitting results of absorbance area fractions of free and bonded C=O group in MMA and MAh units of copolymer with varying lithium salt content from 5 to 40 wt%. The equivalent fraction of

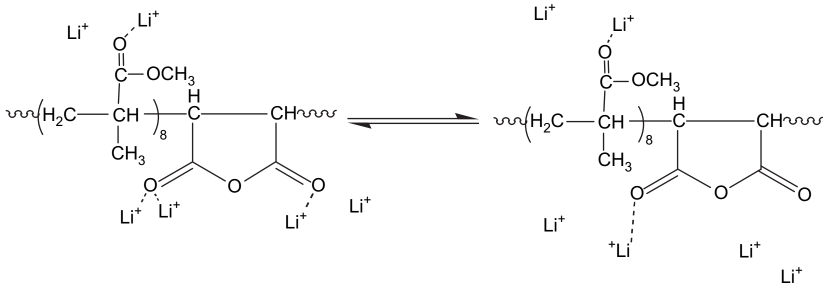


Fig. 8. The reversible interaction between C=O in copolymer and Li^+.

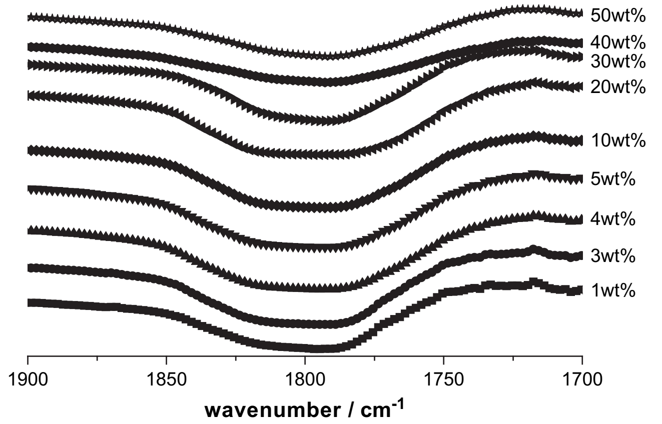


Fig. 9. FTIR spectra of PC/LiClO$_4$ solutions from 1900 to 1700 cm^{-1} with varying the content of LiClO$_4$ from 1 to 50 wt%.

bonded C=O group in the solid blends can be obtained from the following equation

$$1-f=\left[1-\frac{(A_1+A_3)\times a}{(A_1+A_3)\times a+A_2+A_4}\right]\times 100\% \tag{5}$$

where f is the equivalent fraction of the free C=O in the solid blends and $1-f$ is the equivalent fraction of the lithium-ion bonded C=O. The calculated results are also displayed in Table 2.

Fig. 7 shows the relation of Li$^+$ bonded C=O equivalent fraction and LiClO$_4$ content of the copolymer/LiClO$_4$ blends, based on the results shown in Table 2. As would be expected, the Li$^+$ bonded C=O equivalent fraction increased with increasing LiClO$_4$ content. It implies that the interaction between Li$^+$ and C=O increases with the increase of lithium salt content for copolymer/LiClO$_4$ blends. It also apparently shows that the efficiency of Li$^+$ interacting with C=O in lower concentration is greater than that in higher concentration. The equivalent fraction of Li$^+$ bonded C=O closes to 50% when the lithium salt weight content is 30 wt% (Li$^+$ equivalent fraction around 0.289). There is a limit value of 55% Li$^+$ bonded C=O equivalent fraction as shown in Fig. 7. So the turning point occurs at Li$^+$ equivalent fraction around 0.289 and the Li$^+$ bonded C=O equivalent is around 53.98%, which means that the coordination behavior of Li$^+$ with C=O group would not be hindered until the equivalent fraction is more than 0.289. But if the Li$^+$ equivalent fraction is more than 0.289, the Li$^+$ bonded C=O equivalent fraction only increases to 55.17%, which is the result of reversible coordination between Li$^+$ and C=O group in the copolymer, as shown in Fig. 8.

Table 3
Results of PC/LiClO$_4$ solution with various lithium salt contents

Samples	C=O in PC		F_1	F_2	Abs. a	$1-f$
	A_1 (1793 cm^{-1})	A_2 (1776 cm^{-1})				
1 wt%	0.924	0.076	0.991	0.009	0.111	41.13
3 wt%	0.789	0.211	0.971	0.029	0.115	70.30
Ave.					0.113	
4 wt%	0.675	0.365	0.962	0.038		82.71
5 wt%	0.583	0.427	0.952	0.048		86.63
10 wt%	0.437	0.563	0.904	0.096		91.94
20 wt%	0.402	0.598	0.806	0.194		92.94
30 wt%	0.371	0.629	0.708	0.292		93.75
40 wt%	0.368	0.632	0.609	0.391		93.84
50 wt%	0.377	0.623	0.509	0.491		93.60

A_1 and A_2 represent the area fractions of free and bonded C=O in PC, respectively; F_1 represents the equivalent fraction of C=O group; F_2 represents the equivalent fraction of Li$^+$; a is the absorptivity coefficient of C=O group; $1-f$ is the equivalent fraction of the lithium-ion bonded C=O.

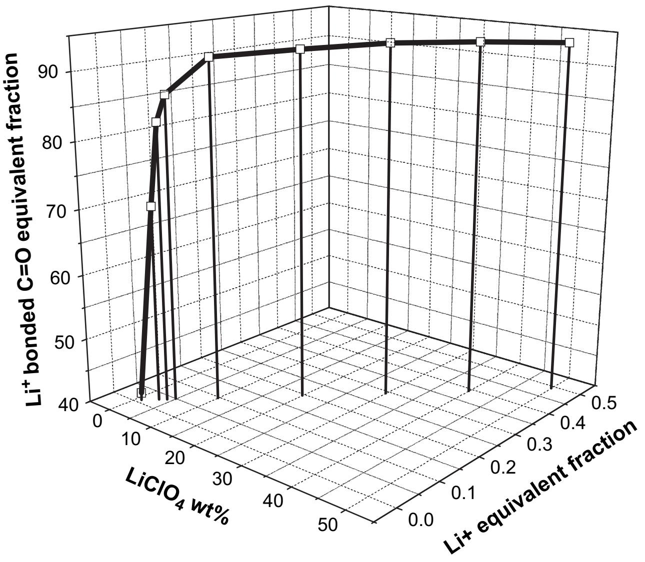


Fig. 10. The relation between Li$^+$ bonded C=O equivalent fraction and LiClO$_4$ content for PC/LiClO$_4$ solution.

3.2.2. Quantitative measurement of interactions for PC/LiClO$_4$ blends

Fig. 9 shows the FTIR spectra from 1900 to 1700 cm^{-1} of PC/LiClO$_4$ solution with various lithium salt contents. It was obvious that with the increase of lithium salt content, the position of C=O in PC obviously shifted down to lower wave number, which was the results of interaction between C=O group and Li$^+$.

There are two kinds of C=O groups in the PC/LiClO$_4$ solution, namely free and bonded C=O. The overlapped peaks also are separated with the curve-fitting method mentioned above. Curve fitting for C=O in PC ranging between 1850 and 1725 cm^{-1} shows two Gaussian peaks at 1793 and 1776 cm^{-1}, and the equivalent fractions (A_1, A_2) of two Gaussian peaks are calculated and displayed in Table 3.

For PC/LiClO$_4$ solution, the following equation can be used to calculate the absorptivity coefficient a.

$$a=\frac{A_1\times F_2}{A_2\times(F_1-F_2)} \tag{6}$$

where a is the absorptivity coefficient of C=O group in PC. A_1 and A_2 represent the area fractions of free and bonded

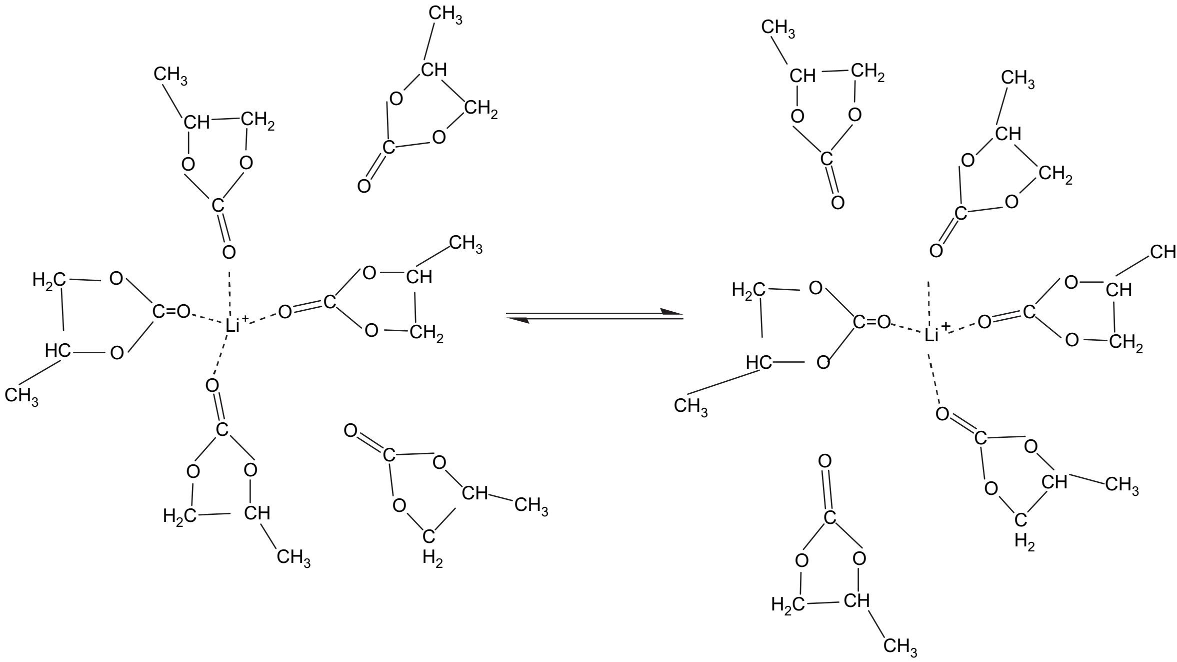


Fig. 11. The reversible interaction between C=O in PC and Li^+.

C=O in PC, respectively. F_1 and F_2 represent the equivalent fractions of C=O group and Li^+, respectively. The calculated equivalent fractions ($F_1$and F_2) of C=O and Li^+ are also displayed in Table 3.

The average value of absorptivity coefficient of PC/$LiClO_4$ is 0.113, which implies that the absorptivity sensitivity of the lithium-ion bonded C=O at 1776 cm^{-1} is significantly larger than that of free C=O at 1793 cm^{-1}. In addition, the value of absorptivity coefficient of PC/$LiClO_4$ is much smaller than that of copolymer/$LiClO_4$, which indicates that the intensity of interaction of C=O in PC with Li^+ is greatly larger than that of C=O in copolymer with Li^+.

The following equation can be used to calculate the Li^+ bonded C=O equivalent fraction in PC/$LiClO_4$ solution.

$$1-f=\left[1-\frac{A_1\times a}{A_1\times a+A_2}\right]\times 100\% \tag{7}$$

where f is the equivalent fraction of the free C=O in the solid blends and $1-f$ is the equivalent fraction of the lithium-ion bonded C=O.

The calculated results are displayed in Table 3 and are used to generate Fig. 10 from which it is obvious that the Li^+ bonded C=O equivalent fraction drastically increases when the lithium salt weight concentration is lower than 10 wt% (Li^+ equivalent fraction 0.096). There is a limit value of 94% Li^+ bonded C=O equivalent fraction as shown in Fig. 10. So the turning point occurs at Li^+ equivalent fraction around 0.096 and the Li^+ bonded C=O equivalent is around

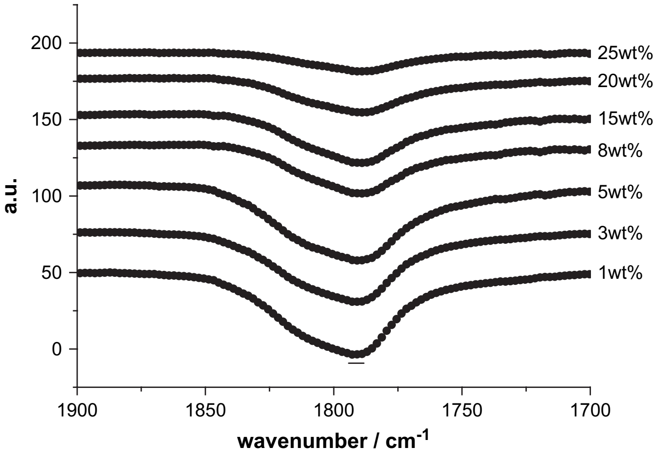


Fig. 12. FTIR spectra of PC/OREC blends from 1900 to 1700 cm^{-1} with varying the content of OREC from 5 to 25 wt%.

Table 4
Results of PC/OREC blends with various OREC contents

Samples	C=O in PC		F_1	F_2	Abs. a	$1-f$
	A_1 (1793 cm^{-1})	A_2 (1773 cm^{-1})				
1 wt%	0.993	0.007	0.997	0.003	0.428	1.61
3 wt%	0.977	0.023	0.990	0.010	0.432	5.19
Ave.					0.430	
5 wt%	0.925	0.075	0.984	0.016		15.86
8 wt%	0.817	0.183	0.973	0.027		34.25
12 wt%	0.722	0.278	0.959	0.041		47.24
15 wt%	0.637	0.363	0.947	0.053		57.00
20 wt%	0.619	0.381	0.927	0.073		58.87
25 wt%	0.604	0.396	0.905	0.095		60.39

A_1 and A_2 represent the area fractions of free and bonded C=O in PC, respectively; F_1 and F_2 represent the equivalent fractions of C=O group and the equivalent fraction of OH group on OREC surface, respectively; a is the absorptivity coefficient of C=O group; $1-f$ is the fraction of the OH group bonded C=O.

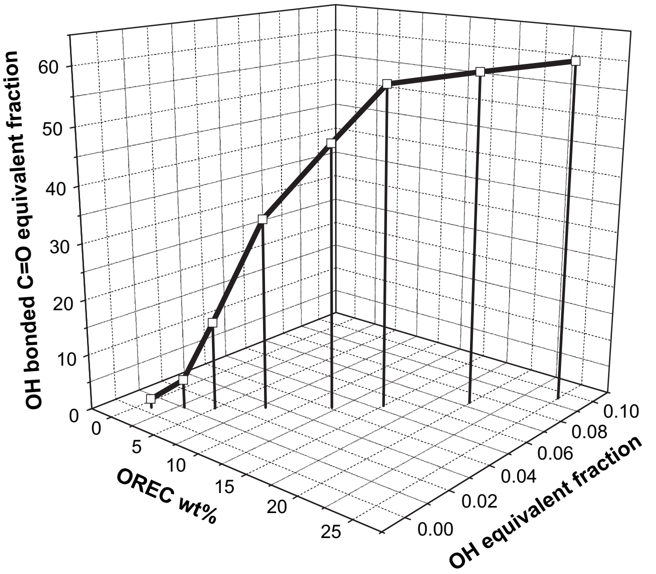


Fig. 13. The relation between OH bonded C═O equivalent fraction and OREC content for PC/OREC blends.

91.94%, which means that the coordination behavior of Li^+ with C═O group would not be hindered until the equivalent fraction is more than 0.096. But if the Li^+ equivalent fraction is more than 0.096, the Li^+ bonded C═O equivalent fraction increases little, which is the result of strong coordination interaction between Li^+ and C═O group in PC, as shown in Fig. 11.

3.2.3. Quantitative measurement of interactions for PC/OREC blends

Fig. 12 shows the FTIR spectra from 1900 to 1700 cm^{-1} of PC/OREC blends with various clay contents. It was obvious that with the increase of OREC content, the position of C═O in PC obviously shifted down to lower wave number, which was the results of interaction between C═O group and OH group on OREC surface.

There are two kinds of C═O group in the PC/OREC blends, namely free and bonded C═O. The overlapped peaks also are separated with the curve-fitting method. Curve fitting for C═O in PC ranging between 1850 and 1750 cm^{-1} shows two Gaussian peaks at 1793 and 1773 cm^{-1}, and the equivalent fractions (A_1, A_2) of two Gaussian peaks are calculated and displayed in Table 4.

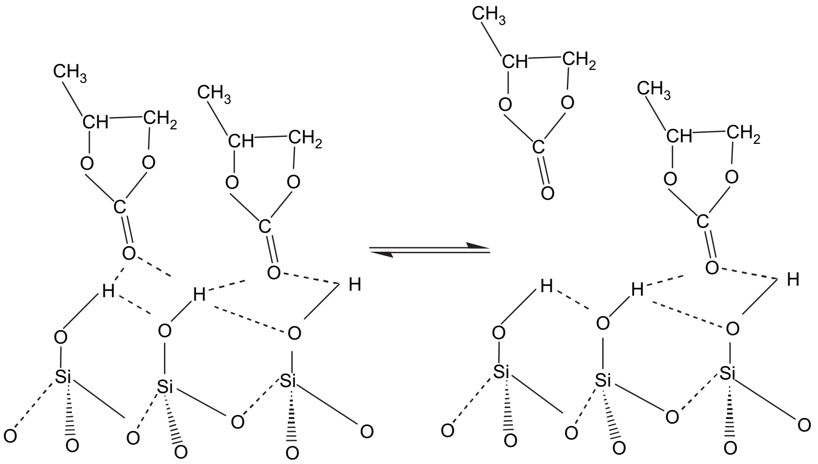


Fig. 14. The reversible interaction between C═O in PC and OH on OREC surface.

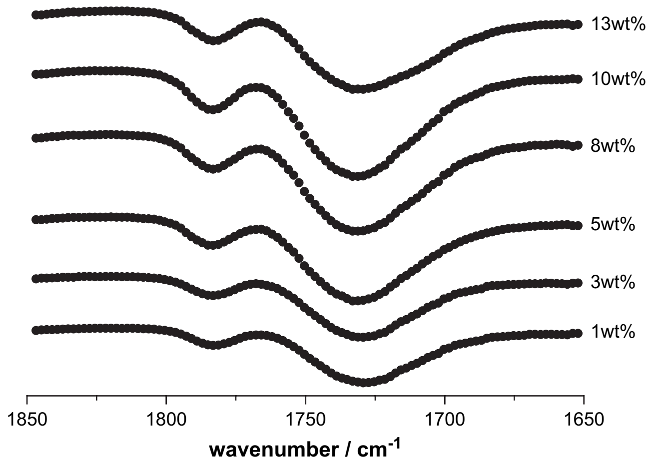


Fig. 15. FTIR spectra of copolymer/OREC blends from 1850 to 1650 cm^{-1} with varying the content of OREC from 1 to 13 wt%.

According to Eqs. (6) and (7), with the calculated value of F_1 and F_2 given in Table 4, the OH bonded C═O fraction was calculated and displayed in Table 4.

The average value of absorptivity coefficient of PC/OREC is 0.430, which implies that the absorptivity sensitivity of the OH bonded C═O at 1773 cm^{-1} is larger than that of free C═O at 1793 cm^{-1}. In addition, the value of absorptivity coefficient of PC/OREC is larger than that of PC/$LiClO_4$, which indicates that the C═O group in PC has more attraction to Li^+ than to OH group on OREC surface.

The OH bonded C═O equivalent fraction calculated is displayed in Table 4 and is used to generate Fig. 13. It is apparent that when the OREC content is lower, the OH bonded C═O equivalent greatly increases. The turning point occurs at

Table 5
Results of copolymer/OREC blends with various OREC contents

Samples	C=O in MMA units		C=O in MAh units		F_1	F_2	F_3	Abs. a	$1-f$
	A_1 (1730 cm^{-1})	A_2 (1703 cm^{-1})	A_3 (1786 cm^{-1})	A_4 (1772 cm^{-1})					
1 wt%	0.873	0.003	0.122	0.002	0.798	0.199	0.003	0.597	0.83
3 wt%	0.868	0.007	0.119	0.006	0.794	0.198	0.008	0.607	3.14
Ave.								0.602	
5 wt%	0.802	0.057	0.108	0.033	0.790	0.196	0.014		14.11
8 wt%	0.761	0.096	0.091	0.052	0.781	0.194	0.025		22.39
10 wt%	0.736	0.108	0.087	0.069	0.776	0.193	0.030		26.32
13 wt%	0.734	0.111	0.084	0.071	0.768	0.192	0.040		26.99

A_1 and A_2 represent the area fractions of free and bonded C=O in MMA units, respectively, A_3 and A_4 represent the area fractions of free and bonded C=O in MAh units, respectively; F_1 and F_2 represent the equivalent fractions of C=O in MMA and MAh, respectively; F_3 represents the equivalent fraction of OH group on OREC surface; a is the absorptivity coefficient of C=O group; $1-f$ is the fraction of the OH group bonded C=O.

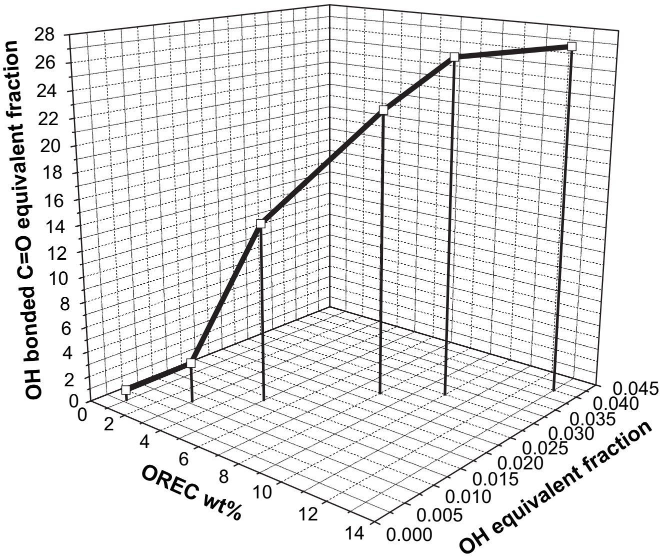


Fig. 16. The relation between OH bonded C=O equivalent fraction and OREC content for copolymer/OREC blends.

15 wt% OREC content (OH equivalent fraction around 0.053) and the OH bonded C=O equivalent is around 57%, which means that the coordination behavior of OH with C=O group would not be hindered until the equivalent fraction is more than 0.053. The interaction between C=O in PC and OH on OREC surface is shown in Fig. 14.

3.2.4. *Quantitative measurement of interactions for copolymer/OREC solid blends*

Fig. 15 shows the FTIR spectra ranging from 1850 to 1650 cm^{-1} of copolymer/OREC blends with various clay contents. It was obvious that with the increase of OREC content, the position of C=O in copolymer obviously shifted down to lower wave number, which was the results of interaction between C=O group in copolymer and OH group on OREC surface.

According to Eqs. (4) and (5), with the calculated value of F_1, F_2 and F_3 given in Table 5, the OH bonded C=O equivalent faction $(1-f)$ was calculated and is given in Table 5.

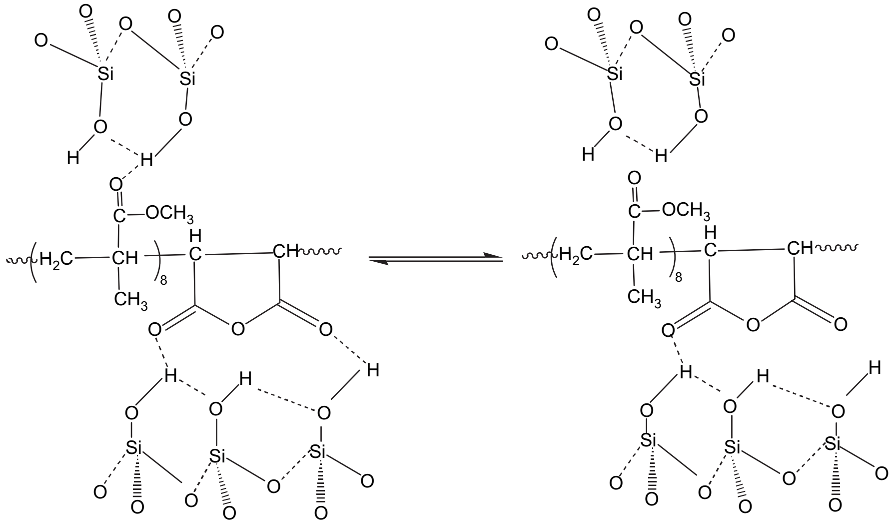


Fig. 17. The reversible interaction between C=O in copolymer and OH on OREC surface.

The average value of absorptivity coefficient of copolymer/OREC is 0.602, which implies that the absorptivity sensitivity of the OH bonded C=O at 1703 and 1772 cm^{-1} is significantly larger than that of free C=O at 1730 and 1786 cm^{-1}.

In addition, the value of absorptivity coefficient of PC/OREC is smaller than that of copolymer/OREC, which indicates that the stretching absorption of OH bonded C=O in PC is more sensitive than that of OH bonded C=O in copolymer, that is to say, the OH group on OREC surface is easier to intact with C=O in PC than to do with C=O in copolymer.

The relation between the calculated OH bonded C=O equivalent fraction and the OREC added content is shown in Fig. 16. It is apparent that when the OREC content is lower, the OH bonded C=O equivalent is greatly increases. The turning point occurs at 10 wt% OREC content (OH equivalent fraction around 0.030) and the OH bonded C=O equivalent is around 26%, which means that the coordination behavior of OH with C=O group would not be hindered until the equivalent fraction is more than 0.030. The interaction between C=O in copolymer and OH on OREC surface is shown in Fig. 17.

4. Conclusions

The copolymer of P(MMA-MAh) was successfully synthesized. The molar ratio of monomers of copolymer was found to be 1MAh:8MMA, while the molecular weight of copolymer was in the order 10^4 (g/mol).

Analysis of FTIR indicates that there is an interaction of C=O in PC and copolymer with Li^+ and OH group on OREC surface. The absorptivity coefficient a of copolymer/$\mathrm{LiClO_4}$, PC/$\mathrm{LiClO_4}$, PC/OREC and copolymer/OREC is 0.756, 0.113, 0.430 and 0.602, respectively, which means that the Li^+ or OH bonded C=O is more sensitive than free C=O. In addition, the limit value of bonded C=O equivalent fraction $(1-f)$ of copolymer/$\mathrm{LiClO_4}$, PC/$\mathrm{LiClO_4}$, PC/OREC and copolymer/OREC is 55, 94, 57 and 26%, which implies that all the interaction within the components is reversible and the intensity of interaction is ordered as PC/$\mathrm{LiClO_4}$, PC/OREC, copolymer/OREC and copolymer/$\mathrm{LiClO_4}$. So the polar group of C=O in PC and copolymer can promote the higher "dissolve" efficiency of lithium and increase the amount of Li^+ within the GPE system. The strong interaction between C=O in PC and OH on OREC surface can improve the solvent maintenance, and at the same time, the interaction of C=O in copolymer and OH on OREC is favorable for the dispersion of clay in GPE system.

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