

A PREDICTIVE MODEL FOR IN-SITU MONITORING OF MOLECULAR WEIGHT OF COPOLYMERS USING SPECTROSCOPIC METHODS

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Abstract

Acrylate-based polymers are commonly used across various industrial sectors. Consistent manufacturing of these polymers through the help of process analytical technology (PAT) is very desirable. The capability of monitoring the polymer molecular weight in real-time will help in reducing operation time and eliminating the frequent samplings needed to meet quality control specifications. Herein, we demonstrate the use of Fourier-transform infrared (FTIR) spectroscopy and develop a chemometric model to predict the molecular weight (M_w) of glycidyl methacrylate-co-methyl methacrylate copolymer. Furthermore, we show that acquiring highly correlated spectra enhances the robustness of the regression model. The developed model shows a satisfactory correlation with R^2 of $\sim 89\%$.

Keywords

Multivariate analysis, acrylate-based copolymer, FTIR spectroscopy, molecular weight prediction.

Introduction

Acrylate-based homo/copolymers are important materials with different physical and chemical properties and are used in many applications across various industrial sectors (Darvishi et al. 2013). For instance, the presence of glycidyl methacrylate (GMA) containing epoxy functional group in a polymer structure provides the possibility of tuning the polymer's surface chemistry. GMA-based polymers are used in various applications from coatings to finishes (Dhal, Ramakrishna, and Babu 1982). Hence, being able to determine the properties of acrylate-based homo/copolymers, in general, is valuable for many applications. The properties of polymers are mainly determined by their chemical structures as they

influence the morphology and characteristics of polymers. Molecular weight (M_w) is one of the most important characteristics of polymers, affecting polymer mechanical and thermal properties. Understanding the composition and properties of polymeric materials can help unravel the material failures and defects throughout the material and product's lifetime. In addition, this knowledge contributes to the development of new polymer-based materials. Several conventional methods exist for measuring M_w of polymers including gel permeation chromatography (GPC), viscometry, and light scattering (Podzimek 1994; Stein and Srinivasarao 1993). However, these methods are time consuming and do not have the capability of on-the-fly prediction of molecular weight. Spectroscopic methods, such as

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mid-infrared and Raman, are commonly used for analysis and characterization of polymeric materials (Chalmers and Everall 1999; Chalmers et al. 1992). For instance, Raman spectroscopy provides a significant amount of information, rendering data for determination of chemical and structural properties (Pelletier 2003). However, in several spectroscopic data, the complex and overlapping peaks make the extraction of detailed structural information difficult. The hidden information contained in the complex and overlapping peaks can be extracted using chemometrics, such as partial least square (PLS), where in-depth and quantitative information about the samples can be obtained. Herein, we monitor the molecular structure of Glycidyl Methacrylate-co-Methyl Methacrylate (GMA-co-MMA) copolymer using Attenuated Total Reflection-Fourier Transformed Infrared (ATR-FTIR) spectroscopy; not only does this provides us with a rich and full range of chemical bonds information, but its implementation and operation in industrial scales are simple, fast, and easy. In addition, Chemometrics are also utilized in this study to interpret and analyze ATR-FTIR data, to build appropriate regression models for the M_w prediction of Poly (GMA-co-MMA) based on M_w data attained by GPC. Finally, we optimize the predictive model by identifying highly-correlated spectra to the samples. This is very advantageous for real-time prediction of M_w .

Materials/Experimental Methods and Modellings

Chemicals & Instrumentations

Glycidyl methacrylate (GMA, ≥ 97 % purity containing 110 ppm monoethyl ether hydroquinone as inhibitor, CAS #607-123-00-4), 2,2'-azobis(2-isobutyronitrile) (AIBN, ≥ 98 % purity, CAS #78-67-1), and propylene glycol methyl ether acetate (PGMEA, ≥ 99.7 % purity, CAS #108-65-6) were obtained from Sigma-Aldrich Inc.; methyl methacrylate (MMA, ≥ 99.8 % purity, CAS #80-62-6) was purchased from TCI; tetrahydrofuran (THF, HPLC grade, CAS #109-99-9) was purchased from Fischer Inc. Nitrogen gas tank ($\geq 99.999\%$ purity) was purchased from Matheson Tri-Gas Inc.

The Mettler Toledo ReactIR 10 was equipped with the liquid N_2 MCT detector and apodization of Happ-Genzel. The Silver Halide (AgX) fiber conduit probe with a tip made of diamond (DiComp) was utilized to collect the ATR-FTIR spectra of copolymer solutions. A 750-mL jacketed reactor (vessel) equipped with a polytetrafluoroethylene (PTFE) anchor shaft and a Pt-100 PTFE temperature probe, which was utilized to control the temperature of the

copolymer solution, were purchased from Radley Inc. A refrigerated/heating circulator (Julabo Inc., DYNEO DD-200F) was employed to maintain the temperature of the jacketed reactor. The temperature was controlled in real time using LabVIEW, and a mass flow controller (Alicat Inc., MC-20SCCM-D/5M) was utilized to control N_2 flow rate.

Experimental Preparation and In-situ Data Collection

Copolymerization was performed by mixing MMA (10 mmol), GMA (10 mmol), and AIBN (0.5 mol% of total monomers) in PGMEA (20 wt.% of total monomers) in the 750-mL reactor, and the ReactIR probe was immersed into the polymerization solution. Before preparation of materials, the vessel was sealed and purged with N_2 gas to remove oxygen. Meanwhile, AIBN was mixed with ~ 20 % of the total PGMEA solution and purged with N_2 gas for 15-20 minutes. At the same time, GMA, MMA, and 90 % of the remaining PGMEA solution were sequentially added to the reactor, mixed at 310 rpm and room temperature. The 5-sccm N_2 flow rate was set for purging the reaction. Then, the temperature of the jacketed reactor was increased and maintained at a setpoint temperature (T_{sp}) of 76 ± 0.2 °C. When T_{sp} was reached, a mixture of AIBN and PGMEA was added to the reactor. The copolymerization reaction was conducted for six hours. After that, the temperature was set to 25 °C to cool down the reactor; ~ 200 mL of PGMEA solution was used for quenching.

The ATR-FTIR spectra of the copolymer solution was collected in the range of 3000-800 cm^{-1} using Mettler Toledo iC IR 7.0 software. The spectra were recorded every 15 seconds with 50 scans per sample and an 8 cm^{-1} spectra resolution. An air background was collected before the reaction started. For spectra stability and good spectra alignment, the ReactIR probe was connected to the vessel in a stable position. Then, the FTIR spectra were collected from the room temperature to the setpoint temperature, and the collection was continued until the end of the copolymerization reaction. For the GPC analysis, ~ 2 mL of the filtered PGMEA and copolymer mixture at a concentration of ~ 0.1 wt. % was prepared in THF.

Multivariate Models for the Molecular Weight Prediction

To develop a robust PLS model with an accurate polymer M_w prediction, it is important to select the ATR-FTIR spectral ranges that are correlated to the desired property of the polymer (Swierenga et al. 1998). There are many developed search-based selection methods, such as the Simulated Annealing (SA) and the Genetic Algorithm (GA) (Kalivas,

Roberts, and Sutter 1989; Lucasius and Kateman 1991), that are capable of efficiently identifying important wavelengths to predict a desired property; however, they still have limitations, such as slow convergence and only reaching a local minimum (Kalivas, Roberts, and Sutter 1989). Thus, it is necessary to test the different methods and identify the most appropriate model. In this study, we utilized different methods to predict M_w of copolymers and then evaluated the predictive capability of these methods. A manual wavelengths selection was the first method to build the PLS model. Here, we evaluated the spectra that were well-suited and strongly correlated to the production of copolymer; then we used them to build the PLS model for predicting the M_w of the copolymer.

The Simulated Annealing (SA) method was the second method to be employed in this study. Based on a concept of finding the most efficient solution to anneal hot materials from a heat bath by Bohachevsky et al. (Bohachevsky, Johnson, and Stein 1986), this method was developed and applied to find an optimal solution in the solution space of the thermal equilibrium of the cooling system (Kirkpatrick, Gelatt, and Vecchi 1983). This can be characterized and optimized by applying the Boltzmann distribution, which is shown in Equation (1).

$$P = \exp\left(\frac{C_1 - C_0}{-\beta}\right) \quad (1)$$

Where P , β , and C are the probability, annealing parameter, and evaluation metric value, respectively; 1 and 0 represent a new and current evaluation metric, respectively. Because of a strong connection between the behavior of the system with multiple degrees of freedom and the multivariate optimization problem, the SA is employed in the multivariate analysis problem. In this study, the SA was applied to find and select optimum wavelengths that are strongly correlated to the M_w of the copolymer. We started an experiment by randomly selecting bands from the spectral dataset, and these bands were evaluated. Depending on the correlation between selected bands and the predictive model, new bands were either added or replaced with the ones with a poor correlation, and an annealing parameter was updated based on an evaluation metric. The final selected bands were then used in the PLS model to find the optimal number of PCs, which results in the lowest evaluation metric value. After that, the selected bands and the optimum PC number were used in the PLS model for M_w prediction.

Furthermore, the Iterative Predictor Weighting Partial Least Square (IPW-PLS) method developed by Forina et al. (Forina, Casolino, and Pizarro Millan 1999), was also evaluated in this study. Unlike the SA,

this method was used to remove the noise and other factors that negatively impact the predictive capability of the PLS regression model. Thus, IPW-PLS can provide a stable and highly accurate prediction of the PLS model (Wu et al. 1995; Forina, Casolino, and Pizarro Millan 1999; Li et al. 2009). In the IPW-PLS, the product of the absolute value of the regression coefficient and the standard deviation of the predictor is computed and used to evaluate the regression model; more details of the IPW-PLS can be found elsewhere (Forina, Casolino, and Pizarro Millan 1999). Similar to the IPW-PLS method, we utilized the Large Regression Coefficient-Partial Least Square (LRC-PLS) model that selects the large absolute values of regression coefficient to evaluate the importance of wavelengths and uses that information in building the PLS model for the M_w prediction of the copolymer; lower values are excluded from the dataset. Then, we used the selected bands to find an optimal number of PCs and used both selected spectra and PCs to build the PLS model.

Training and Evaluation Metrics

For chemometrics analysis, we used the principal component analysis (PCA) and partial least square (PLS) models, and they were built and performed using Python language along with the SciPy and Sklearn libraries. Given that the copolymerization reaction is often operated at a high temperature and in an environment having IR light-absorbing solvents, gathering reliable data of M_w from ATR-FTIR in these conditions always comes with challenges and requires considerable analytical measurements. Thus, it is necessary to remove interferences from ATR-FTIR spectra before any further analysis. Here, the ATR-FTIR spectra were preprocessed by subtraction with an air spectrum and normalized by the maximum absorbance value of each sample. Then, the Savitzky-Golay filter with a window filter of 2, 1st derivative, and 2nd polynomial order and the Multiplicative Scatter Correction (MSC) were applied to further smooth and correct the spectra (Savitzky and Golay 1964; Dhanoa et al. 1994). For M_w , the value was first rescaled by applying the logarithm transformation and the standardized scaler. For the spectra selection, the 10-Fold cross-validation (CV) method was applied in the dataset, where a dataset was divided into 10 different folds, and one-fold was kept for an evaluation of the model. Once the potential wavelengths were selected, the dataset was split into an 80 and 20 % of train and test set, respectively, for building the PLS model. The principal component (PC), in which the lowest corresponding metric value was obtained in the PLS model, was utilized for the multivariate analysis.

To quantify the model performance, the root-mean-square error (RMSE) and the correlation coefficient of determination (R^2) are examined.

Results & Discussion

Before developing a multivariate model, we first needed to determine the sufficient number of collected samples and sample collection duration so that a full range of M_w of copolymer can be covered. Figure 1 illustrates the ATR-FTIR spectra and the corresponding M_w of Poly (GMA-co-MMA) as a function of time.

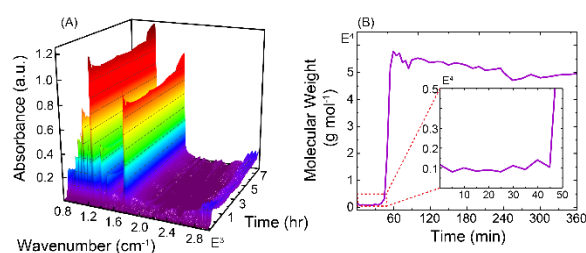


Figure 1. (A) 3D ATR-FTIR spectrum of Poly(GMA-co-MMA). (B) Molecular weight trajectory after 6 hours.

As shown in Figure 1B, the M_w of copolymer started to increase after 30 minutes and gradually approached plateau after ~ 5 hours. Afterward, we began to build the PLS model using a manual spectra region selection. The peaks assignment of the ATR-FTIR spectra of GMA, MMA, and PGMEA has been well-studied and can be found in the literature (Gulari, McKeigue, and Ng 1984). Figure 2 illustrates the main spectra region, which highlights a strong correlation of spectra to the M_w change of Poly(GMA-co-MMA).

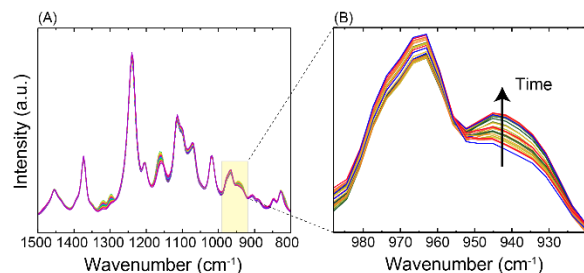


Figure 2. (A) Selected FTIR absorbance spectrum of Poly(GMA-co-MMA) solution. (B) FTIR absorbance spectra of the epoxy ring of Poly(GMA-co-MMA).

As shown in Figure 2A, there are several regions with a substantial intensity change (e.g., 1250-1350 cm^{-1}) that can be used for building the multivariate

model. The peak of the epoxy group, located at 940 cm^{-1} , can differentiate GMA from MMA and can show increase in M_w of the copolymer (Lipic, Bates, and Hillmyer 1998; Ishida and Allen 1996). This substantial feature can be explored with the multivariate model. Therefore, we first aimed to build the model by extracting a region ranging from 910 to 990 cm^{-1} , which includes the epoxy and -CH groups of GMA and MMA, as shown in Figure 2B. Prior to the multivariate model analysis, the selected FTIR spectra and M_w variation were preprocessed by applying the methods described in the “Training and Evaluation Metrics” section below. The selected processed FTIR spectra were then used to build a PCA model, which in turn was used to remove outliers and reduce the dimensionality of the spectral data that were necessary for the M_w prediction by using principal components (PCs) and scores (Hodge and Austin 2004). Figure 3A illustrates an explained variance plot with 10 PCs used in this study.

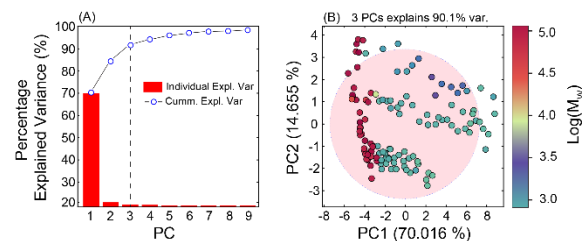


Figure 3. (A) Explained variance for the first 10 PCs from the PCA analysis. A dash line represents the selected PC components. (B) PCA plot in this study.

As can be seen, the explained variance and the cumulative explained variance reduces and increases, respectively, as the number of PCs increases. Based on Mahalanobis distance coupled with PCA analysis (De Maesschalck 2000), Figure 3A shows that three PCs were necessary to build the model using the manual spectra selection method. Outliers were also removed from the dataset by using the Hotelling T^2 and the squared prediction error (SPE/DmodX) detection methods. Any data point located either on or inside an ellipse is considered for the regression model. As illustrated in Figure 3B, most of the samples in the PCA plot were located inside an acceptable range and could be used for the further regression analysis. Finally, we built the PLS regression model using non-outlier spectra data to predict the M_w . Similar to building the PCA model, we identified the optimum number of PCs that produces the lowest MSE value, which is illustrated in Figure 4A. We found that the best result was obtained with two PCs and thus used them to build the PLS model. Figure 4B illustrates the

parity plot of the predicted and reported $\log(M_w)$ values. As can be seen, the result showed that a prediction of $\log(M_w)$ was poor with an R^2 value of $\sim 51.6\%$, suggesting that the method was unreliable, and an alternative method was recommended to improve the predictive capability of the PLS model.

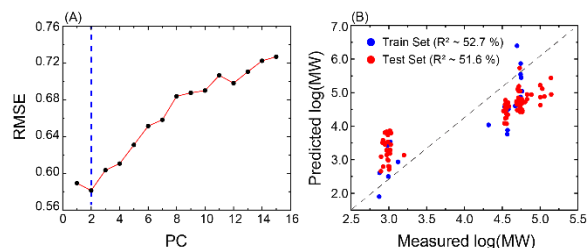


Figure 4. (A) RMSE of the PLS model as a function of PCs. A blue dash represents the selected PC. (B) Parity plot of predicted and reported $\log(M_w)$.

To further improve the $\log(M_w)$ prediction, we examined the goodness of SA and LRC-PLS models. For the SA method, we randomly selected wavelengths from the dataset. Figure 5A illustrates the selected spectra by the SA. As can be seen, the SA selected most of the notable functional groups contained in both GMA and MMA, such as C-H ($\sim 1480\text{ cm}^{-1}$) or ester group ($\sim 1732\text{ cm}^{-1}$), to improve the prediction of $\log(M_w)$. By using the SA method, R^2 of the M_w prediction was improved from ~ 51.6 to $\sim 72\%$. Furthermore, it was observed that the SA still selected the epoxy and CH groups similar to our manual wavelengths' selection. This indicates that the epoxy and CH group region truly has a high impact on the formation of the copolymer and leads to an increase of M_w of copolymer (Lipic, Bates, and Hillmyer 1998). We can observe that selecting more profound functional groups of Poly (GMA-co-MMA) can help the PLS model to distinguish wavelengths at different time steps and improve the M_w prediction.

Lastly, we evaluated the effectiveness of the LRC-PLS method. The wavelengths, selected by the LRC-PLS, are illustrated in Figure 5B. As shown in Figure 5A-B, most of the wavelengths selected by the LRC-PLS and SA are quite similar to each other; however, the range of selected spectra was reduced, and several new regions were defined. While the selected wavelengths of the SA mostly fall into the lower ($1000\text{-}1750\text{ cm}^{-1}$) and upper region ($2750\text{-}3000\text{ cm}^{-1}$), the LRC-PLS thoroughly explored an entire spectral space to select wavelengths.

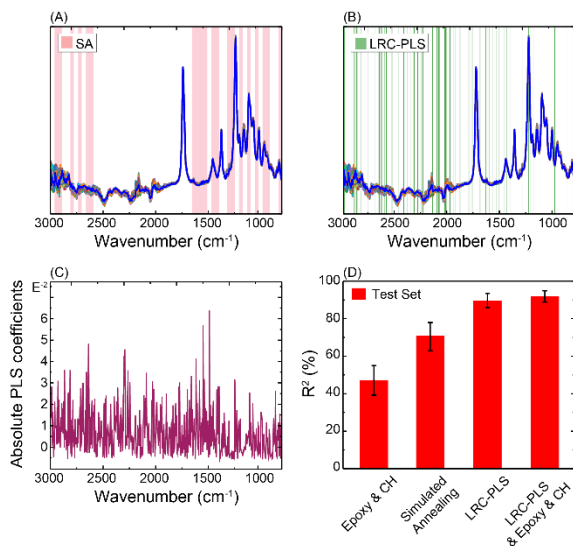


Figure 5. (A-B) Wavenumber selection comparison: (A) the Simulated Annealing (SA), and (B) LRC-PLS. (C) Absolute PLS coefficients plot obtained from the LRC-PLS. (D) Bar chart represents R^2 value of the testing set in this study. Data is averaged of 5 independent runs.

Thus, the LRC-PLS was proved to identify potential spectra that were more important to the predictive model and removed noise and low-correlated spectra. As a result, there is a significant improvement in the $\log(M_w)$ prediction of the PLS model with a higher R^2 -value when the LRC-PLS was applied. Nevertheless, the LRC-PLS still cannot identify crucial spectra regions that highlight the structure change of copolymer. For instance, epoxy was evaluated to have a less impact on the PLS model due to a low absolute model coefficient (Figure 5C) and thus discarded; however, this region showed a high impact upon the final product of Poly (GMA-co-MMA) as mentioned elsewhere. Thus, in the final step of this study, we evaluated the predictive capability of the PLS model by combining the LRC-PLS and “Epoxy & CH” spectra and then compared its result with other methods. As illustrated in Figure 5D, a combination of the LRC-PLS and the “Epoxy & CH” region gives the best predictive performance, followed by the LRC-PLS, the SA, and the “Epoxy & CH” region. The result shows that utilizing selective and profound function groups can help the PLS model to recognize the wavelengths distribution better and improve the predictive capability of the model, increasing the prediction of $\log(M_w)$ and surpassing the LRC-PLS method.

Conclusion

In this study, four methods were applied toward building a PLS model for predicting M_w of Poly (GMA-co-MMA). The results show that combining the LRC-PLS and highly-correlated spectra can enhance the robustness of the predictive model, which can be further applied to any other copolymers. Even though the results of the LRC-PLS and the combination method are quite similar, the results still point out the importance of selecting appropriate spectra regions as it improves the robustness of the PLS model.

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