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Synthesis and characterization of non-aromatic heat-resistant polymers

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1. Introduction

Heat-resistant polymer materials have been used in a wide range of industrial fields, from aerospace to construction, microelectronics, etc. There are several thermal criteria are considered for estimating the heat-resistance in various application. For instance, melting temperature, softening point, thermal decomposition temperature (T_d), and glass transition temperature (T_g).

The development of heat-resistant polymers began in the late 1950s and early 1960s. In the electronic field, most of polymer optical films would not maintain their optical and mechanical properties at such high processing temperatures. Hence, transparent, colorless heat-resistant polymers have attracted increasing interest over the last few decades.

The heat-resistance of polymers is influenced by physical and chemical aspects. From a physical point of view, there are several factors that weaken or enhance the heat-resistance of the polymer, such as the rigidity of the polymer chains. From a chemical point of view, the strength of the primary bonds in the macromolecular chain is an important parameter affecting the thermal resistance of a polymer. In short, the stronger the primary bond, the more thermally stable the polymers are[1].

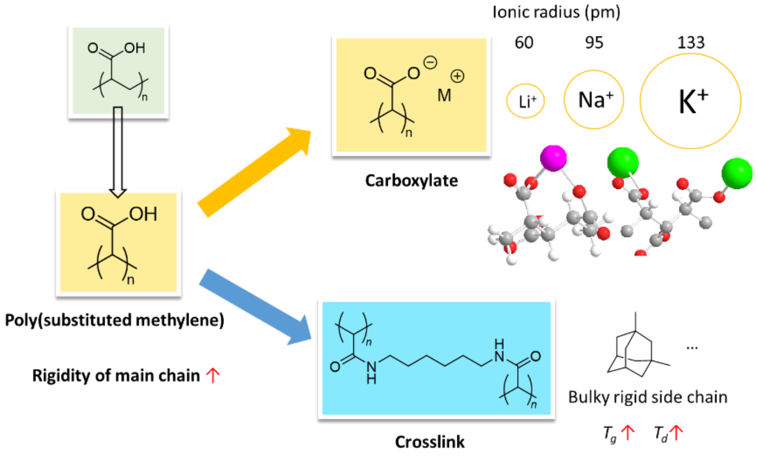

Figure 1. Two strategies for improving thermal properties of polymers

The primary motivation for this study is synthesis and characterization of transparent heat-resistant polymers. Since the current excellent heat-resistant polymer materials usually have darker color with aromatic ring structure, to synthesize a new transparent heat-resistant polymer, a rigid molecular structure that does not contain an aromatic structure is the best choice. Among the various polymers, polymethylene attracted my attention. Substituted polymethylene is the polymer with substituents on all their main chain carbon atoms, or we can call them poly(1,2-substituted ethylene). These polymers are expected to have unique properties because their main chain structure is rigid, and different from mono-substituted vinyl and 1,1-disubstituted vinylidene polymers, which have a methylene spacer in the main chain. Therefore, in this thesis, I designed polymers with rigid structures without aromatic rings from polyacrylic acid to poly(fumaric acid) (PFA) by reducing the methylene spacers in the repeating units. Based on this, there are two ideas to improve the thermal properties shown in Figure 1.

2. Syntheses of polymers

Salts of polymers are synthesized by neutralization of poly(fumaric acid) (PFA). And PFA is pyrolyzed from poly(di-tert-butyl fumarate) which is synthesized by free radical polymerization of di-tert-butyl fumarate monomer[2]. The composition and structure of the polymers were determined by NMR and IR spectroscopy. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were calibrated with PMMA standards by GPC. It is worth noting that different types of salt have different solubility in water.

Cross-linked polymers are synthesized by mixing condensation agent, polymer solution and cross-linking agent. Gels were also successfully synthesized by adjusting the ratio of cross-linking agent. Since cross-linked polymers are insoluble in any solvent, the characterizations of their structure and molecular weight is more difficult to perform, the measurements of their thermal properties is performed directly.

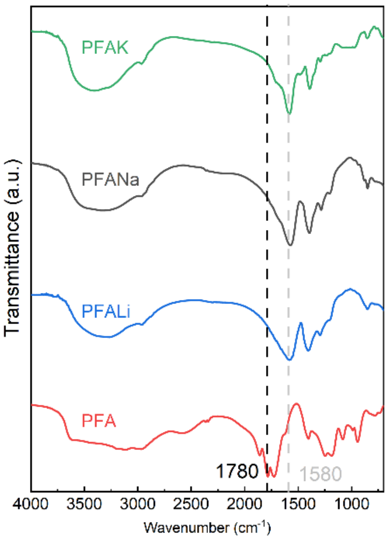

Figure 2. IR spectra of polymers

3. Characterizations of polymers

Thermal properties of polymers, including T_d and T_g, are performed by Thermal Gravimetric (TG) analysis and Differential Scanning Calorimetry (DSC). As the shown in Figure 3, the onset temperature of thermal decomposition for PFA salts is higher than PFA and cross-linked polymers. One of the reasons is thought to be the difficulty in purifying the cross-linked polymer and the lack of assurance that all cross-linking agents and condensation agents are removed. Their T_d is shown in Table 1, among the salts with monovalent ion, sodium salt has the beat thermal stability with the highest T_d. And they have different residual weight percentage because of metal ions do not change into gaseous substances to leave at the measurement temperature.

As shown in Figure 4, thermal stability of PFA sodium salt in different degree of neutralization has been investigated, since the sodium salt has the highest T_d and the worst solubility. Experiments show that the thermal decomposition temperature increases with the proportion of sodium salt, while the polymer does not form the film well at a proportion greater than 80%.

Table 1. Thermal decomposition temperatures of polymers

Polymers	T_d /°C
PFA	276
PFA-Li	343
PFA-Na	384
PFA-K	298
PFA-CHDM	252
PFA-HMDA	249
PFA-ADA	249

As the results of T_g, polymers synthesized in this study do not show a glass transition temperature. This is most likely because their T_g is higher than the T_d . However, we can also consider that their physical and mechanical properties will not change until thermal decomposition temperature.

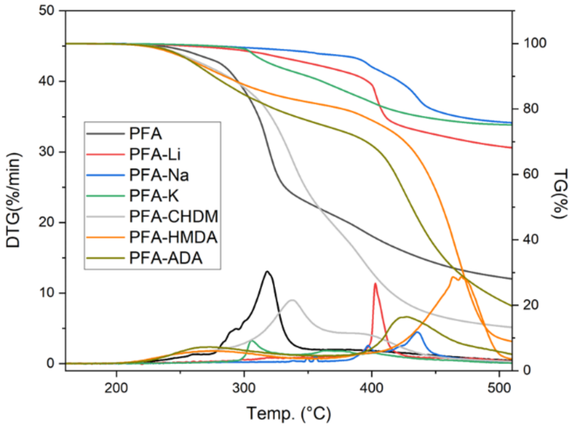

Figure 3. TG curves of polymers

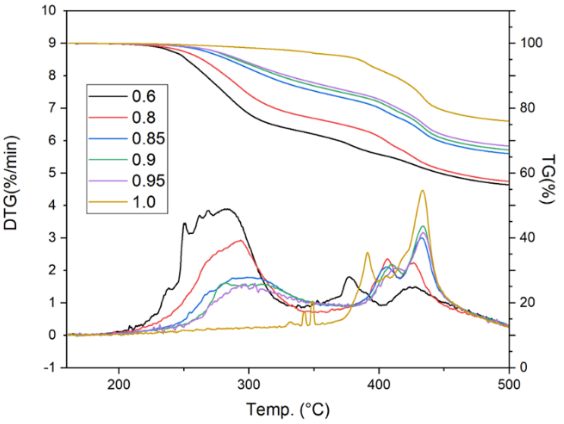

Figure 4. TG curves of PFA-Na in different degree of neutralization

Transmittance are measured by UV-Visible spectroscopy and Haze meter. UV-Visible spectra show that the PFA salts with good thermal stability have no significant absorption in the visible band, but the scattering of light is occurred by the inability of the sodium and lithium salts to form a nice polymeric film. Thus, the haze meter measures total transmittance to determine that these polymers are indeed colorless and transparent.

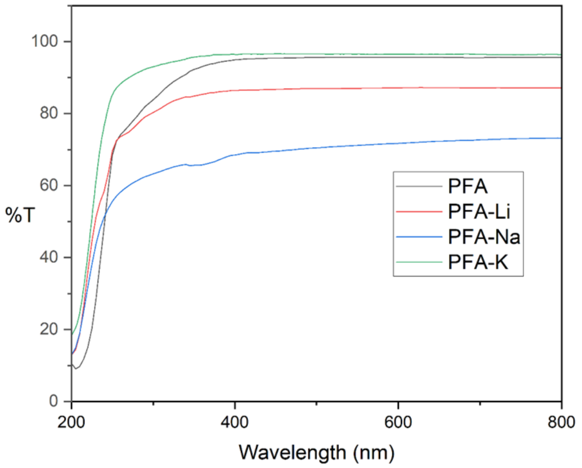

Figure 5. UV-Vis spectra of polymers

Table 2. Total transmittance and Haze of PFA and poly(di-metal fumarate)

	T.T	Haze	P.T.	Dif.
Air ref.	100	0.00	100	0.00
Glass ref.	91.1	0.19	90.9	0.17
PFA	91.6	0.34	91.3	0.31
PFA-Li	90.8	0.92	90.0	0.84
PFA-Na	90.4	19.6	72.7	17.7
PFA-K	90.9	0.59	90.3	0.54

4. Conclusion

The salts of PFA and cross-linked PFA were synthesized and characterized successfully. Among them, sodium salt of PFA shows excellent thermal stability as well as light transmittance. And its heat-resistance and solubility can be adjusted by different degrees of neutralization. Theses group of polymers with a rigid main chain structure can be developed for additional applications through other modifications in the future.

5. References

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