

# Gamma Radiation-Induced Synthesis of Thermostable Polymers for Enhanced Oil Recovery Applications

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In this study, a thermally stable copolymer based on polyvinylpyrrolidone (PVP) and acrylamide (AM) was successfully synthesized via gamma irradiation. The polymerization proceeded via a free-radical mechanism, enabling the formation of a high-purity product without the use of chemical initiators. The optimal irradiation condition was determined to be a dose of 20 kGy for 7 h. The optimal polymerization conditions were achieved at a reaction time of 7.46 h and an AM monomer concentration of 19.92 wt%, yielding a maximum reaction efficiency of 85.77%. The physicochemical properties of the copolymer were characterized by FT-IR, SEM and TGA, confirming successful copolymer formation and excellent thermal stability with a decomposition temperature above 200 °C. The rheological behavior and thermal stability of the polymer solution were evaluated under simulated reservoir conditions. At a concentration of 0.3 wt%, the P(AM–PVP) solution exhibited a stable viscosity of approximately 5.86 cP and remained nearly unchanged after 30 days of thermal aging at 128 °C. These results demonstrate the potential of the gamma-irradiated PVP–AM copolymer for enhanced oil recovery in high-temperature, high-salinity offshore reservoirs.

## 1. Introduction

Enhanced oil recovery (EOR) is an important technique for improving oil production after conventional recovery methods become inefficient (Mohd et al., 2018). Among various EOR methods, polymer flooding is widely applied because it increases the viscosity of injected water, improves the mobility ratio, and enhances sweep efficiency (Zeynalli et al., 2022). However, conventional polymers such as partially hydrolyzed polyacrylamide (HPAM) exhibit poor thermal and salt resistance, limiting their application in offshore reservoirs with high temperature and salinity, including the Bach Ho oil field in Vietnam, where reservoir temperatures exceed 120 °C (Mohsenatabar Firozjahi and Saghafi, 2020). Therefore, the development of thermally stable polymers is essential for high-temperature EOR applications.

Recent studies have incorporated N-vinylpyrrolidone (NVP) or polyvinylpyrrolidone (PVP) into acrylamide (AM)-based polymers to improve thermal stability through the pyrrolidone ring structure (Li et al., 2013; Xu et al., 2014). Most reported copolymers, however, are synthesized using chemical initiators, which require additional purification to remove residual initiators (Antonopoulou et al., 2024). Gamma irradiation-induced polymerization provides a cleaner alternative by generating free radicals directly without chemical initiators, enabling the preparation of high-purity polymers (Kamlangmak et al., 2024).

Previous studies demonstrated that gamma-irradiated AM–NVP copolymers possess potential for EOR applications (Nguyen et al., 2021). Nevertheless, direct irradiation of AM–NVP mixtures often results in excessive crosslinking and insoluble gels at high irradiation doses, whereas lower doses produce polymers with insufficient thermal stability. In addition, the low monomer concentration required during irradiation increases transportation costs for offshore applications. To overcome these limitations, this study employs a  $\gamma$ -ray pre-irradiation strategy in which PVP is first activated by gamma irradiation and subsequently grafted with AM. This approach suppresses excessive crosslinking while promoting controlled graft polymerization.

The objective of this study is to synthesize a thermally stable P(AM–PVP) copolymer using pre-irradiated PVP and to evaluate its physicochemical characteristics and rheological performance under simulated reservoir

conditions (128 °C, high salinity) for potential application in offshore enhanced oil recovery.

## 2. Materials and Methods

### 2.1 Materials

Acrylamide (AM, 99%) and polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich and used as received. Acetone (99%) and deionized water were used as the solvent and reaction medium, respectively. Polymer solutions were prepared using simulated seawater, whose chemical composition and physicochemical properties are summarized in Table 1.

*Table 1: Chemical composition and physicochemical properties of simulated seawater.*

| Composition (mg/L) |                |                  |                  |                               |                 | Physicochemical properties    |      |                  |              |
|--------------------|----------------|------------------|------------------|-------------------------------|-----------------|-------------------------------|------|------------------|--------------|
| Na <sup>+</sup>    | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | HCO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | pH   | Specific gravity | Salinity (‰) |
| 11421              | 296            | 1162             | 956              | 151.3                         | 21942           | 1025                          | 7.28 | 1.026            | 13.48        |

### 2.2 Synthesis of P(AM-PVP) copolymer

First, PVP was pre-irradiated using a <sup>60</sup>Co gamma irradiation system (Isclavedavachel, Vietnam). The gamma source emitted photons with energies of 1.17 and 1.33 MeV (total energy of 2.50 MeV), providing a uniform irradiation field. PVP powder was irradiated in the solid state at room temperature (25 ± 2 °C) to an absorbed dose of 20 kGy at a dose rate of 0.7 kGy h<sup>-1</sup>. After irradiation, the pre-irradiated PVP was used in the subsequent graft polymerization reaction. Subsequently, 20 g of AM was dissolved in 100 g of distilled water, followed by the addition of 5 mL of 2% N-methyl pyrrolidone (NMP) solution to enhance system stability. The reaction solution was purged with nitrogen to remove dissolved oxygen and continuously stirred at 200 rpm. Next, 20 g of pre-irradiated PVP was gradually added to the reaction system. The mixture was then heated to 70 °C and maintained for 7 h under a nitrogen atmosphere. The product P(AM-PVP) was purified by Soxhlet extraction with acetone to remove unreacted monomers and other acetone-soluble impurities, followed by thorough washing with distilled water to remove residual water-soluble species, including polyacrylamide (PAM), before drying at 50 °C to constant weight.

The irradiation dose was preliminarily optimized based on product solubility. The effects of reaction time (6–8 h) and AM concentration (10–30 wt%) on reaction yield were further optimized using a second-order orthogonal design generated by Statgraphics XVIII. The optimal conditions are presented in Table 2.

*Table 2: Experimental conditions for the optimization of the polymerization reaction*

| Experiment No.         | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 |
|------------------------|----|----|----|----|----|----|----|----|----|----|----|----|
| Reaction time (h)      | 6  | 6  | 6  | 7  | 7  | 7  | 8  | 8  | 8  | 7  | 7  | 7  |
| AM concentration (wt%) | 10 | 20 | 30 | 10 | 20 | 30 | 10 | 20 | 30 | 20 | 20 | 20 |

The reaction yield was calculated according to Eq. (1):

$$\text{Reaction yield (\%)} = \frac{m_{P(AM-PVP)}}{m_{AM} + m_{PVP}} \cdot 100 \quad (1)$$

where  $m_{\text{polymer}}$  is the dry mass of the purified copolymer after Soxhlet extraction and drying to constant weight, while  $m_{AM}$  and  $m_{PVP}$  are the initial masses of acrylamide and PVP, respectively.

### 2.3 Physicochemical characterization and application potential of the material in EOR

The chemical structure, morphology, and thermal stability of the P(AM–PVP) copolymer were characterized by FT-IR (Equinox 55, Bruker, Germany), SEM (Hitachi S-4800, Japan), and TGA (Q500, TA Instruments, USA), respectively. Rheological properties were measured using a Brookfield viscometer. Polymer solutions (0.3 wt%) prepared in simulated seawater were thermally aged at 128 °C for 30 days, and their viscosity was periodically measured to evaluate long-term stability under simulated reservoir conditions.

## 3. Results and discussion

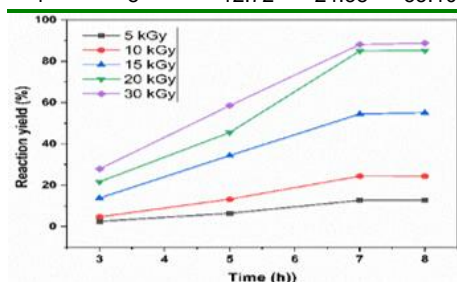
### 3.1 Effects of gamma irradiation dose and irradiation time on the yield of P(AM–PVP) copolymerization

Table 3 and Figure 1 show that the graft polymerization yield increased with irradiation dose and reached a plateau after 7 h of irradiation. The maximum yield was obtained at 30 kGy, which can be attributed to the higher generation of free radicals, promoting polymer chain propagation. However, at this dose, the solubility was only

about 40%, indicating significant crosslinking. According to Chapiro, crosslinked polymers are characterized by swelling rather than dissolving in solvents. Considering the application requirement for good water solubility, especially in seawater, the optimal irradiation dose was determined to be 20 kGy (Chapiro, 1995).

**Table 3: Reaction yield at different irradiation doses and irradiation times of PVP**

| No | Irradiation dose(kGy)<br>Time (h) | Reaction yield (%) |       |       |       |       |
|----|-----------------------------------|--------------------|-------|-------|-------|-------|
|    |                                   | 5                  | 10    | 15    | 20    | 30    |
| 1  | 3                                 | 2.50               | 4.70  | 13.80 | 21.67 | 27.87 |
| 2  | 5                                 | 6.45               | 13.25 | 34.40 | 45.52 | 58.50 |
| 3  | 7                                 | 12.70              | 24.42 | 54.50 | 85.00 | 88.12 |
| 4  | 8                                 | 12.72              | 24.38 | 55.10 | 85.15 | 88.78 |



**Figure 1: Effect of irradiation time and irradiation dose on the reaction yield**

### 3.2 Optimization results of the effects of reaction time and AM concentration on the reaction yield.

Based on the results in Section 3.1, an irradiation dose of 20 kGy for PVP provided a high yield and was considered the most suitable. Therefore, this dose was selected as the input parameter for optimizing the graft polymerization process. In addition, the relationship between grafting yield and different AM solution concentrations was also investigated. The results are presented in Table 4:

**Table 4: Grafting polymerization yield under different reaction conditions**

| Experiment No.       | 1    | 2    | 3    | 4    | 5  | 6    | 7    | 8    | 9    | 10   | 11   | 12 |
|----------------------|------|------|------|------|----|------|------|------|------|------|------|----|
| Reaction time (h)    | 6    | 6    | 6    | 7    | 7  | 7    | 8    | 8    | 8    | 7    | 7    | 7  |
| AM concentration (%) | 10   | 20   | 30   | 10   | 20 | 30   | 10   | 20   | 30   | 20   | 20   | 20 |
| Reaction yield (%)   | 34.7 | 45.5 | 45.8 | 73.6 | 85 | 72.8 | 73.7 | 85.1 | 72.7 | 85.1 | 84.9 | 85 |

The optimization results obtained using Statgraphics are presented in Table 5 with a high correlation coefficient ( $r = 0.9926$ ) and coefficient of determination ( $R^2 = 0.9865$ ), indicating excellent agreement between the model and experimental data (Bandara et al, 2019). The response surface analysis (Figure 2) shows that the optimal yield of 85.77% was achieved at an AM concentration of 19.92% and a reaction time of 7.46 h.

**Table 5: Optimization results and regression model for grafting polymerization**

| Parameter               | Low                                                                          | High | Optimal |
|-------------------------|------------------------------------------------------------------------------|------|---------|
| AM concentration (wt%)  | 10.0                                                                         | 30.0 | 19.92   |
| Time (h)                | 5                                                                            | 8    | 7.46    |
| Reaction yield (%)      |                                                                              |      | 85.77   |
| Regression equation     | $y = -326.801 + 5.67621a + 95.4365b - 0.102137a^2 - 0.215357ab - 6.10799b^2$ |      |         |
| Variance                | $R^2 = 0.9865$                                                               |      |         |
| Correlation coefficient | $r = 0.9926$                                                                 |      |         |

Where a, b, and y represent the AM monomer concentration, reaction time, and the optimized graft polymerization yield, respectively. Subsequently, the copolymer synthesis was carried out under these optimal conditions, and the viscosity of the polymer solutions at different concentrations was measured. The results are presented in Table 6:

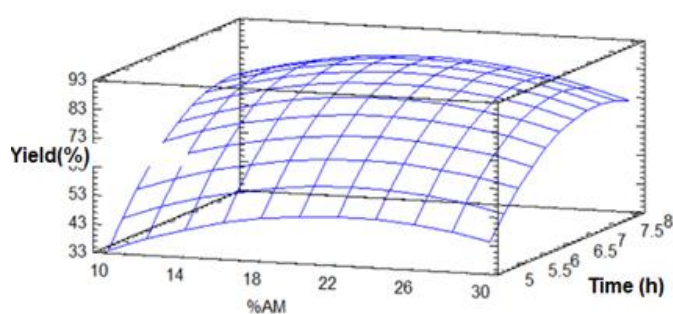


Figure 2: Response surface generated using statgraphics software

Table 6: Viscosity of P(AM–PVP) at different concentrations.

| No.                 | 1    | 2    | 3    | 4    | 5    | 6     | 7     | 8     | 9     | 10     |
|---------------------|------|------|------|------|------|-------|-------|-------|-------|--------|
| Concentration (ppm) | 500  | 1000 | 2000 | 3000 | 4000 | 5000  | 6000  | 7000  | 8000  | 10000  |
| Viscosity (cP)      |      |      |      |      |      |       |       |       |       |        |
| PVP                 | 1.13 | 1.74 | 2.16 | 2.56 | 2.87 | 3.19  | 3.94  | 5.61  | 7.45  | 12.44  |
| P(AM–PVP)           | 1.24 | 1.77 | 4.45 | 5.86 | 9.40 | 18.98 | 25.96 | 46.69 | 68.87 | 132.17 |

For the grafted polymer P(AM–PVP), the viscosity of the solution increases rapidly with increasing concentration. At a concentration of 500 ppm (0.05 wt%), the viscosity is 1.24 cP, while at 10,000 ppm (1 wt%), it reaches 132.17 cP. In contrast, the viscosity of the ungrafted PVP solution increases only slightly with concentration. At 10,000 ppm, the viscosity of the grafted P(AM–PVP) is approximately ten times higher than that of pure PVP at the same concentration.

These results confirm the successful grafting of AM monomer onto the pre-irradiated PVP backbone, resulting in the formation of P(AM–PVP), a novel polymer with significantly enhanced viscosity compared to the original PVP. The increase in viscosity is attributed to the higher molecular weight and the incorporation of acrylamide side chains into the polymer structure.

### 3.3 Physicochemical characteristics of P(AM–PVP)

The FT-IR spectrum (Figure 3 a, b, c) confirms the presence of both AM and PVP in the structure of the P(AM–PVP) copolymer. Specifically, the absorption bands in the range of  $\sim 3200$ – $3400\text{ cm}^{-1}$  are attributed to the  $\text{--NH}_2$  groups of AM, the strong peak at  $\sim 1650$ – $1700\text{ cm}^{-1}$  corresponds to the  $\text{C=O}$  stretching vibrations (amide group of AM and lactam group of PVP), and the band at  $\sim 1200$ – $1300\text{ cm}^{-1}$  is assigned to the  $\text{C--N}$  bonds characteristic of PVP (Dhumale *et al.*, 2012). Compared to the initial monomers, these peaks exhibit changes in intensity and slight shifts in wavenumber, indicating that the grafting reaction has occurred. The FTIR results indicate the presence of characteristic functional groups of both AM and PVP. Together with the thermal stability and rheological results, these findings support the formation of the P(AM–PVP) copolymer. The simultaneous presence of polar functional groups ( $\text{--NH}_2$ ,  $\text{C=O}$ ) facilitates hydrogen bonding and enhances intermolecular interactions, thereby improving the solution viscosity. Consequently, the material shows significant potential for enhancing interfacial activity and improving efficiency in EOR applications (Xu *et al.*, 2024).

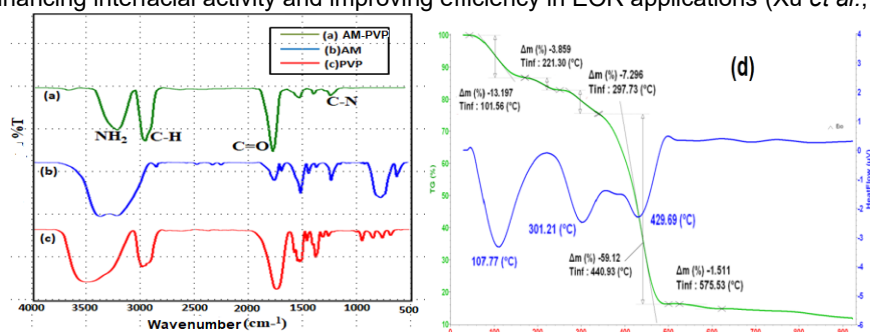


Figure 3: FT-IR spectra of P(AM–PVP) copolymer (a), AM (b), and PVP (c), and TGA curve of the P(AM–PVP) copolymer (d).

The TGA of P(AM–PVP) (Figure 3 d) reveals three main stages of weight loss. The first stage, with a mass loss of approximately 13.2% at around 108 °C, is attributed to the evaporation of absorbed water and residual volatile compounds. The second stage shows a weight loss of about 11.2% up to 302 °C, which is associated with the decomposition of residual monomers and partial degradation of PAM segments. In the final stage, a significant weight loss of 59.1% at 450 °C is observed, corresponding to the complete decomposition of the copolymer structure. Overall, the TGA results indicate that the P(AM–PVP) copolymer exhibits good thermal stability up to approximately 150 °C, with the initial mass loss mainly due to residual volatiles. Noticeable degradation of the polymer backbone begins only near 200 °C. These findings suggest that the material is suitable for EOR applications, particularly in offshore reservoirs with operating temperatures around 130 °C.

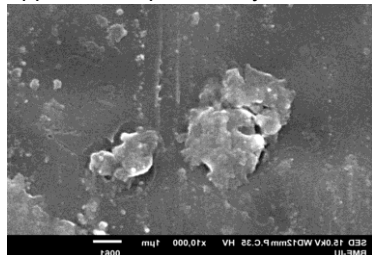


Figure 4: SEM image of P(AM–PVP).

The SEM image (Figure 4) shows that P(AM–PVP) exhibits an aggregated bulk structure with a rough and heterogeneous surface ( $\approx 1\text{--}2\ \mu\text{m}$ ). This morphology reflects the formation of a polymer network after copolymerization, in which polymer chains are interconnected and interact strongly through polar functional groups ( $-\text{NH}_2$  and  $\text{C}=\text{O}$ ). This structure differs from the relatively smooth and more dispersed morphology of the individual monomers reported in previous studies, indicating a significant structural transformation after the grafting reaction. In addition, the rough and aggregated morphology may contribute to water retention and interfacial interactions may be beneficial for EOR applications, although these properties were not directly evaluated in the present study.

### 3.4 Evaluation of the thermal stability of P(AM–PVP) and its potential application in EOR

In EOR processes, the viscosity of polymer solutions plays a crucial role in improving mobility control and sweep efficiency. The P(AM–PVP) solution at 0.3 wt% was selected based on the characteristics of the Bach Ho reservoir, with an initial viscosity of 5.86 cP, comparable to that of crude oil (4–6 cP), indicating good rheological compatibility. TGA results show that the dry copolymer is thermally stable up to approximately 150 °C. To evaluate the stability of the polymer solution under simulated reservoir conditions, thermal-aging experiments were conducted at 128 °C in simulated seawater. During the first 7 days, the viscosity slightly increased due to a post-irradiation effect, in which residual free radicals continued to participate in chain extension or limited crosslinking, resulting in an increase in the effective molecular weight of the polymer. From day 8 to day 20, the viscosity decreased slightly but remained relatively stable, indicating that the polymer structure was maintained under high-temperature and high-salinity conditions. After 21–31 days, the viscosity decreased by approximately 15–17% due to chain scission and hydrolysis. However, the remaining viscosity still falls within a suitable range for EOR applications. These results demonstrate that P(AM–PVP) exhibits good thermal and chemical stability, suggesting its potential for application under high-temperature reservoir conditions. The visual appearance of the samples is presented in Table 7:

Table 7: Appearance and viscosity of 0.3 wt% P(AM–PVP) during thermal aging

|                | Thermal aging time (days)                                                           |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     |
|----------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|                | 0                                                                                   | 3                                                                                   | 7                                                                                   | 14                                                                                  | 21                                                                                  | 31                                                                                  |
| Appearance     |  |  |  |  |  |  |
| Viscosity (cP) | 5.86                                                                                | 5.91                                                                                | 5.92                                                                                | 5.65                                                                                | 4.97                                                                                | 4.85                                                                                |

As shown in Table 7, the P(AM–PVP) solution maintained a stable dispersion state, with no significant phase separation observed over 31 days of thermal aging, indicating good stability under reservoir-like conditions. The

viscosity slightly decreased over time, mainly due to thermal degradation processes such as polymer chain scission and hydrolysis of amide groups. However, the remaining viscosity still falls within a suitable range for EOR applications, demonstrating good thermal and chemical stability of the system.

#### 4. Conclusion

In this study, a thermally stable P(AM–PVP) copolymer was successfully synthesized via gamma irradiation-induced graft polymerization. The optimal conditions were 20 kGy, 7.46 h, and 19.92 wt% AM, achieving a reaction yield of 85.77%. FT-IR, SEM, and TGA analyses confirmed the successful formation of the copolymer with a heterogeneous structure, broad molecular weight distribution, and good thermal stability up to ~150 °C. The grafted polymer exhibited significantly higher viscosity than pure PVP, indicating improved rheological properties. Under simulated reservoir conditions (128 °C, high salinity), the 0.3 wt% P(AM–PVP) solution remained stable, with only a slight viscosity reduction (~15–17%) after 31 days and no noticeable phase separation. These results demonstrate that the synthesized copolymer possesses good thermal and chemical stability, suitable viscosity, and excellent dispersion behavior, highlighting its strong potential for enhanced oil recovery applications in high-temperature offshore reservoirs such as the Bach Ho oil field. Future work should include core flooding and field-scale evaluation to further validate its applicability.

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