Shearing Effect on Aggregation Behaviour of Hydrophobically Associating Polyacrylamide

GUANG-FAN GUO[1,*], ZHONG-BIN YE[2,3], WEN-SEN ZHAO[4], HONG CHEN[2] and ZHENG SHU[1]

[1]School of Petroleum Engineering, Southwest Petroleum University, Chengdu 610500, P.R. China
[2]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, P.R. China
[3]School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, P.R. China
[4]CNOOC Research Institute, Beijing 100027, P.R. China

*Corresponding author: Tel: +86 28 83032749; E-mail: 383821889@qq.com

Hydrophobically associated polyacrylamide solutions were sheared by the waring blender at different speeds. Hydrophobically associated polyacrylamide solutions after being sheared were investigated by the viscometry using Ubbelohde viscometer, static light scattering, dynamic light scattering and atomic force microscopy. The apparent viscosity, intrinsic viscosity and apparent weight average molecular weight ($M_{w,a}$), root mean square radius of gyration $<R_g>$, hydrodynamic radius $<R_h>$ and ratio of $<R_g>/<R_h>$ were decreased with the increase in speeds of the waring blender. Its microstructure transformed from spatial network structure to independent of molecular aggregates. Shearing not only made the molecular chains of polymers fracture, but also made the polymer chains transform from stretch to curl.

Keywords: Hydrophobically associated polyacrylamide, Waring shearing, Apparent viscosity, Intrinsic viscosity, Aggregation behaviour.

INTRODUCTION

The hydrophobically associating water soluble polymer (HAWSP) is a water-soluble polymer that is introduced a few hydrophobic groups on some hydrophilic polymer back-bones[1-3] (< 2 %, mole fraction). It has broad application prospects, such as oil exploration, paint, mineral separation, cosmetic and pharmaceutical preparations *etc.*[4,5]. The essence of hydrophobically associated polyacrylamide (HAPAM) is partially hydrolyzed polyacrylamide polymer chains to introduce a small amount of hydrophobic groups. Polymer molecules in aqueous solution, the certain intensity and reversible physical association are obtained and the three dimensional mesh structures are formed through these particular association between molecules in hydrophobic groups under the condition of static electricity, hydrogen bonds or van der Waals force. Therefore, the polymer has a high viscosity at lower molecular weight and lower concentrations[6-10]. This is the reversible structure so that it has a better ability to resist shearing. Hydrophobically associated polyacrylamide is widely used in enhanced oil recovery[4]. The polymer be cut in the application process, solution properties are affected. Macroscopic properties of sheared hydrophobic associated polymer such as viscosity, visco-elastic are studied both at home and abroad, but aggregation behaviour and microstructure of sheared polymer solution are less reported in literature. The apparent viscosity, intrinsic viscosity, aggregation behaviour and microstructure of sheared hydrophobically associated polyacrylamide solution are investigated by the viscometer, Ubbelohde viscometer, static light scattering, dynamic light scattering and atomic force microscopy (AFM). There are some guiding significances on the development and production of polymer.

EXPERIMENTAL

The given raw feed ratio according to Table-1. The hydrophobically associated polyacrylamide (HAPAM) sample was synthesized and purified according to a literature[11]. Its molecular structural formula was shown in Fig 1.
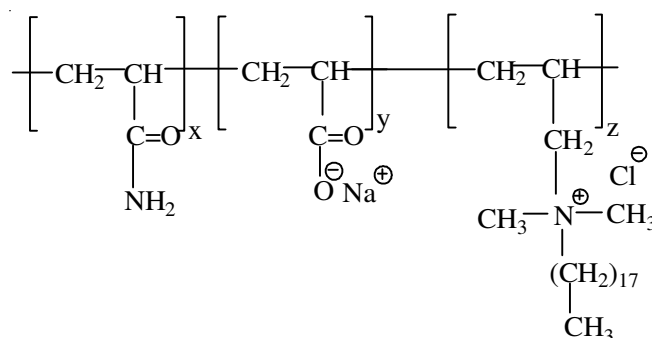

Fig. 1. Molecular structure of hydrophobically associating polymer

Refers to the method specified GB12005.1-89, the measured intrinsic viscosity [η] of hydrophobically associating polyacrylamide sample was shown in Table-1.

TABLE-1 CHARATERISTIC PARAMETERS OF HYDROPHOBICALLY ASSOCIATING POLYACRYLAMIDE				
Sample	AM (w/w %)	NaAA (w/w %)	$C_{18}DMAAC$ (w/w %)	[η] (mL g^{-1})
HAPAM	74.5	25.0	0.5	988.4
AM: acrylamide, NaAA: sodium acrylate, $C_{18}DMAAC$: hydrophobic monomer; [η] is intrinsic viscosity				

Ammonium persulfate [$(NH_4)_2S_2O_8$], sodium bisulfite (Na_2HSO_3), acrylamide (AM) and sodium acrylate (NaAA) were provided by Chengdu kelong reagent company, analysis of pure. 18-Alkyl-dimethyl diallyl ammonium chloride ($C_{18}DMAAC$), synthesized in the laboratory.

Seven-speeds waring blender was purchased from Tak Kee instrument corporation. Non-diluted Ubbelohde viscometer, the capillary diameter be 0.50 mm, was purchased Chengdu Chang Zheng Huabo corporation. Brookfield DV-III viscometer was purchased from the United States Brookfield corporation. Dynamic/static wide angle laser light scattering apparatus (BI-200SM) was purchased from the United States Brooke haven instrument corporation. Nanoscope IIIa atomic force microscope was purchased from the United States Digital Instrument corporation.

Waring shearing experiment: The polymer solution of 1500 mg L^{-1} was prepared in the distilled water. The polymer solution (350 mL) was injected into the waring blender and sheared by the waring blender at different speeds.

Determination of apparent viscosity: The polymer solution viscosities after shearing by the waring blender were measured using Brookfield DV-III viscometer with a shearing rate of 7.34 s^{-1} at 25 °C.

Determination of intrinsic viscosity: In order to reflect the change of molecular weights throug the shearing effect of the waring blender on HAPAM, the change of intrinsic viscosity was measured by the Ubbelohde viscometer. The Ubbelohde viscometer was cleaned by water many times until there was no residual polymer on the inner surface of glass and then was stovinged. All the polymer solutions were diluted to about 250-450 mg L^{-1} by the brine. At (30 ± 0.5) °C, the brine and polymer solution were injected into the Ubbelohde viscometer, respectively and the flowing time through the ball were recorded for parallel three times until flowing time difference was less than 0.2 s. The average value of three times was chosen as the final data.

Laser light scattering experiment: The diluted polymer solution was inhaled single used syringes. The solution was dusted and filtered by the Millipore corporation production of the disposable filter with a 0.8 μm aperture. The filtrate was collected in the sample pool. In the laser light scattering experiment, the laser wavelength of 532 nm, the determination temperature of 25 °C[12,13]. The weight average molecular weight M_w, root mean square radius of gyration $<R_g>$ of polymer solution and other parameters were measured by the static light scattering and particle sizes distribution and its hydrodynamic radius $<R_h>$ were measured by the dynamic light scattering.

Determination of microstructure: Atomic force microscopy measurements were performed on a Nanoscope IIIa microscope in air at the ambient temperature with standard silicon tips (RTESP Type) in the tapping mode. Operating frequency was 86 kHz and force constants were 1-5 N m^{-1}. Hydrophobically associating polyacrylamide solution is sheared by the waring blender and then stirred at low velocity for 5 min to obtain a homogeneous polymer concentration. For the AFM measurements, 0.1 mL of the polymer solution was dropped onto freshly cleaved mica and the solution was blown off simultaneously with a stream of high purity nitrogen.

RESULTS AND DISCUSSION

The polymer solution of 1500 mg L^{-1} is prepared in the distilled water. The polymer solution was sheared by the waring blender at different speeds. The viscosity of sheared polymer solution by the waring blender is measured by Brookfield DV-III viscometer with a shearing rate of 7.34 s^{-1} at a 25 °C. Its result is shown in Fig. 2.
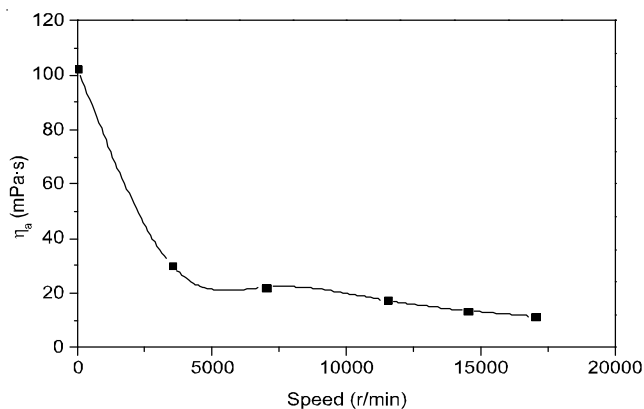

Fig. 2. Apparent viscosity of HAPAM solution after the waring blender shearing

Fig. 2 shows that the viscosity of polymer solution is sharp declined with the waring blender shearing speeds increase. The viscosity of polymer solution is higher with no shearing in the distilled water due to the molecular chains of hydrophobic association polymer results in aggregate forming the spatial network structure. Due to the polymer molecules in the stretched state, the shearing is likely to cause the molecular chains broken. The shearing is stronger, the molecular chains are more broken. On other hand, when polymer solution is sheared, the polymer molecular chains forming intramolecular hydrophobic, forming the salt key, reducing the stretching degree of polymer molecular chains, lead to the viscosity of polymer solution sharp decline.

Effect on intrinsic viscosity of polymer solution: The viscosity of polymer solution and the change of polymer molecular weight have a certain relationship through the waring blender shearing. Therefore, it is essential to study the change of molecular weight of sheared polymer solution. In order to reflect the molecular weight change by the shearing effect of the waring blender on HAPAM, the intrinsic viscosity change was measured by the Ubbelohde viscometer. Because HAPAM is a special polymer with three-dimensional structure, the constants of K and α can not be found from literatures. The

intrinsic viscosity is only chosen to reflect the molecular weight change[14]. At different shearing speeds, the change of polymer solution intrinsic viscosity are shown in Fig. 3.
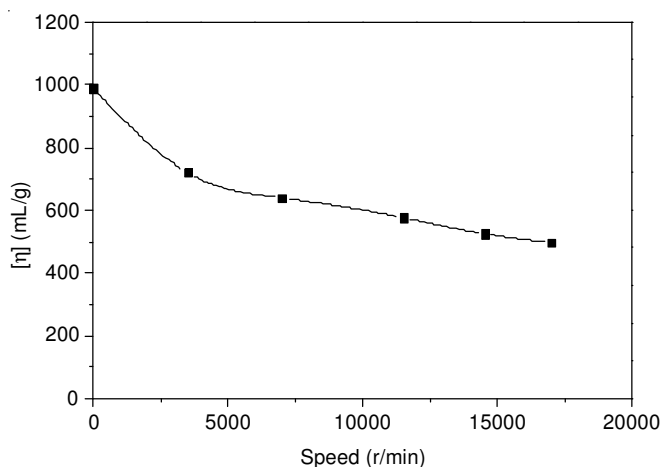

Fig. 3. Intrinsic viscosity of HAPAM solution after waring blender shearing

Fig. 3 shows that the intrinsic viscosities of polymer solution decreased with the speeds of waring blender increase. It can be seen from the results of intrinsic viscosity. The polymer chains have been strong damaged for the shearing effect of waring blender. The intrinsic viscosity of no shearing HAPAM solution is 988.4 mL g^{-1}. When the waring blender speed is 3500 rpm, the intrinsic viscosity is 720.1 mL g^{-1} with the high intrinsic viscosity retention rates through calculating be more than 70 %. When the waring blender speed is 17000 rpm, the intrinsic viscosity is 497.9 mL g^{-1} and intrinsic viscosity retention rates is more than 50 %. According to the above apparent viscosity data, it is observed that HAPAM not mainly depends on the molecular weight sizes on the increasing viscosity, but depend the molecular interaction between the hydrophobic groups on the increasing viscosity.

Laser light scattering experiments: According to the light scattering theory[15-18]. The weight average molecular weight (M_w), root mean square radius of gyration $<R_g>$ of hydrophobically associating polymer are tested by the static light scattering. The light scattering of dilute polymer solution can be expressed as:

$$\frac{Kc}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}<R_g^2>q^2\right) + 2A_2c \tag{1}$$

where: $K = 4\pi^2 n_0^2 (dn/dc)^2/(N\lambda_0^4)$, K is associated with the constant of solvent nature and incident light frequency; n_0 is the refractive index of solution. Because of solution being diluted, it is instead of the refractive index of solvent, commonly; c is the solution concentration, mg L^{-1}; $R_w(q)$ is after the removal solvent effect of scattering intensity for different angles; λ_0 is the incident light wavelength; λ is the wavelength of incident light in solution $\lambda = \lambda_0/n_0$; dn/dc is the refractive index increment and the ratio of solution refractive index and concentration, mL g^{-1}; N is the Avogadro constant; $<R_g>$ is root mean square radius of gyration and the chain quality centre to each chains segment average of squared distance. when the scattering angle is $\theta \to 0$ and concentration is $c \to 0$, some parameters are obtained such as $<R_g>$ and M_w by extrapolation[19-22].

According to the formula (1), when is $\theta \to 0$, $c \to 0$. The reciprocal of ordinate intersection is the M_w in the Zimm graph, so take advantage of the Zimm graph, M_w can be calculated. Because of aggregates of associating polymer being easily formed through the association in aqueous, the measured molecular weights are not the true average molecular weights of polymer by static light scattering in the experiment, but is a reflection of associating polymer forming molecular aggregates in aqueous solution or is the apparent weight average molecular weight of polymer. The apparent weight average molecular weights ($M_{w,a}$) of polymer are tested with different shearing speeds at a 25 °C. Its result is shown in Fig. 4.
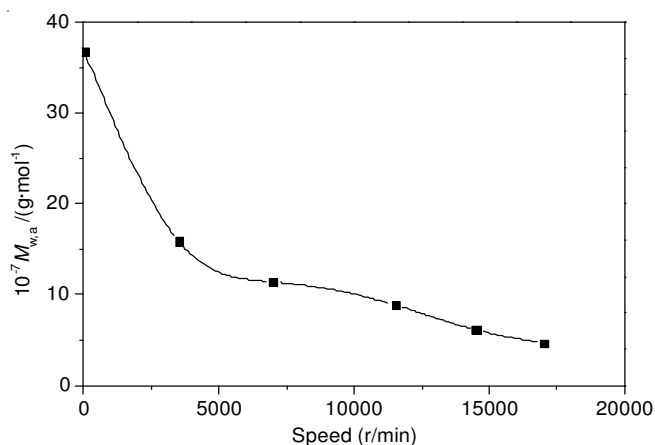

Fig. 4. Apparent weight average molecular weights ($M_{w,a}$) of HAPAM solution after the waring blender shearing

Fig. 4 shows that the apparent weight average molecular weights of HAPAM are diminished with the waring blender speeds increase. Probably because the shearing effect not only makes the polymer chains break, but also increases the intramolecular hydrophobic of polymer, forming inner salt and causes the apparent weight average molecular weights of HAPAM to sharp decline. The matches results of viscosity data is shown in Fig. 2.

Root mean square radius of gyration $<R_g>$ are characteristic parameters of polymer, which directly reflect the conformation of polymer chains. It is the chain quality centre to each chains segment average of square distance. In order to reduce the effect of polymer concentration, the preparation concentration of polymer is 2 mg L^{-1} in the experiment. For the dilute polymer solution, the root mean square radius of gyration $<R_g>$ of polymer moleculars can be concluded through extrapolation of the same concentration with different angles in solution, then in the same way some root mean square radius of gyration $<R_g>$ of polymer molecules are get under different shearing speeds. Its result is shown in Fig. 5.

Fig. 5 shows that the root mean square radius of gyration $<R_g>$ of HAPAM solution are diminished with the waring blender speeds increase. Previous results had been confirmed that shearing effect not only made the polymer chains break, but also increased the intramolecular hydrophobic of polymer, formed inner salt, caused the root mean square radius of gyration $<R_g>$ of HAPAM to sharp decline too.

In order to study the waring blenders shearing effect on the hydrodynamic sizes of polymer in solution, the preparation
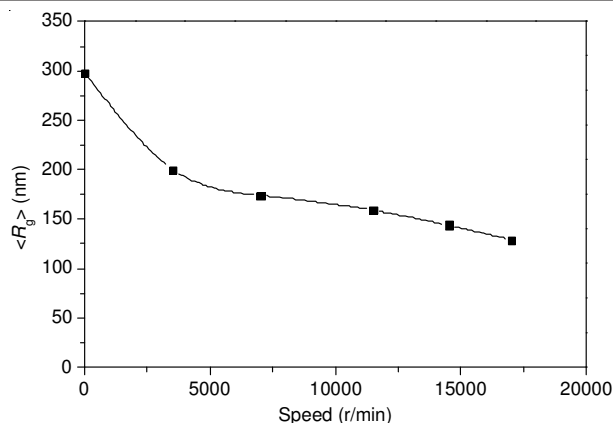
Fig. 5. Root mean square radius of gyration $\langle R_g \rangle$ of HAPAM solution after the waring blender shearing
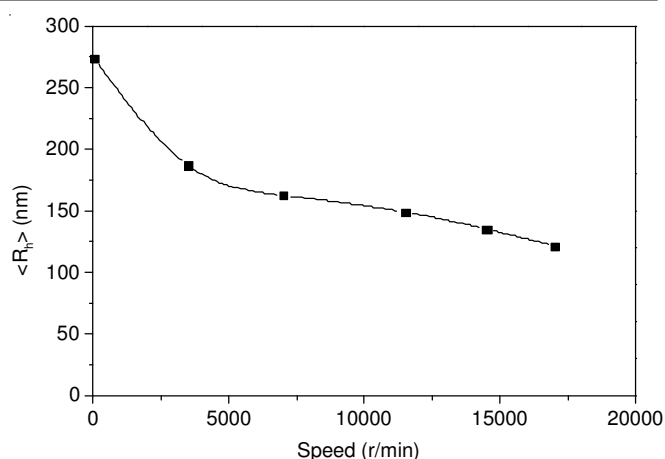
concentration of sheared polymer solution is 2 mg L^{-1} in the experiment. The particle sizes distribution and its hydrodynamic radius $\langle R_h \rangle$ of polymer under different shearing speeds are tested by the dynamic light scattering at a 25 °C and the scattering angle be 90°. Their results are shown in Figs. 6 and 7.

Fig. 6 shows that the particle sizes of HAPAM are unimodal distribution under no shearing conditions. When HAPAM solution is sheared, the particle sizes of HAPAM solution are multimodal distributions. The wide unimodal distributions move to left with the shear speeds increase. Fig. 7 shows that the hydrodynamic radius $\langle R_h \rangle$ of HAPAM solution are diminished with the waring blender speeds increase. The result has been confirmed that the shearing effect makes polymer chains some fractures and increases the intramolecular hydrophobic of polymer, forming inner salt, therefore causes the particle sizes distribution to move the left and causes hydrodynamic radius $\langle R_h \rangle$ of HAPAM to decline.

Root mean square radius of gyration $\langle R_g \rangle$ of polymer and polymer chains actual stretching of space have a certain relationship. The hydrodynamic radius $\langle R_h \rangle$ and the macromolecule have equivalent sphere radius of the same translational diffusion coefficient[23]. The root mean square radius of gyration $\langle R_g \rangle$ and hydrodynamic radius $\langle R_h \rangle$ are tested by the light scattering, then the ratios of $\langle R_g \rangle/\langle R_h \rangle$ are calculated. This parameter reflects the chains density and dispersion of system. Its result is shown in Fig. 8.
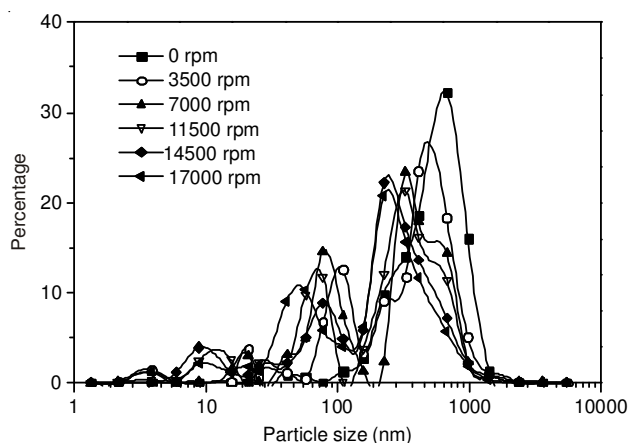

Fig. 6. Particle size distributions of HAPAM solution after the waring blender shearing
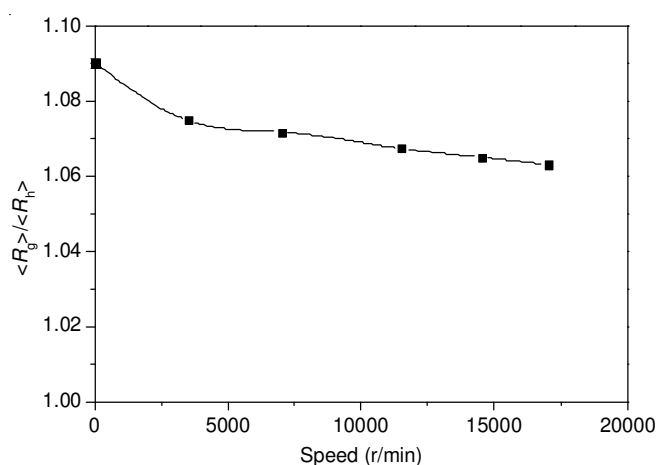

Fig. 7. Hydrodynamic radius $\langle R_h \rangle$ of HAPAM solution after the waring blender shearing

Fig. 8. $\langle R_g \rangle/\langle R_h \rangle$ of HAPAM solution after the waring blender shearing

Fig. 8 shows that ratios of $\langle R_g \rangle/\langle R_h \rangle$ appear to declining trend with the waring blender speeds increase. The waring blender shearing effect not only affects the polymer intermolecular association, but also affects the polymer intramolecular association. the waring blender shearing effect on the improved polymer intramolecular association and making aggregate sizes get smaller and become relative contraction, the ratios of $\langle R_g \rangle/\langle R_h \rangle$ appear to declining trend. Continue to increase the blender speeds, $\langle R_g \rangle$ and $\langle R_h \rangle$ are made reduce and supramolecular aggregates are broken up smaller at the same time because of polymer molecular chains being broken and intermolecular association further broken up. On the other hand. The polymer intramolecular association makes unpicked polymer coils be more contraction and makes the ratios of $\langle R_g \rangle/\langle R_h \rangle$ appear to a certain fall.

Atomic force microscope (AFM) experiment: The previous research results had been confirmed that at a certain concentration HAPAM could form a grid structure in solution. The shearing effect influences its grid structure. The polymer solution is sheared by the waring blender at different speeds. The microstructures of sheared polymer solution are observed. Its results are shown in Fig. 9.

Fig. 9 shows that the structures of HAPAM solution transform from the tight spatial network structure to loose mesh structure and form independent of aggregates finally. When
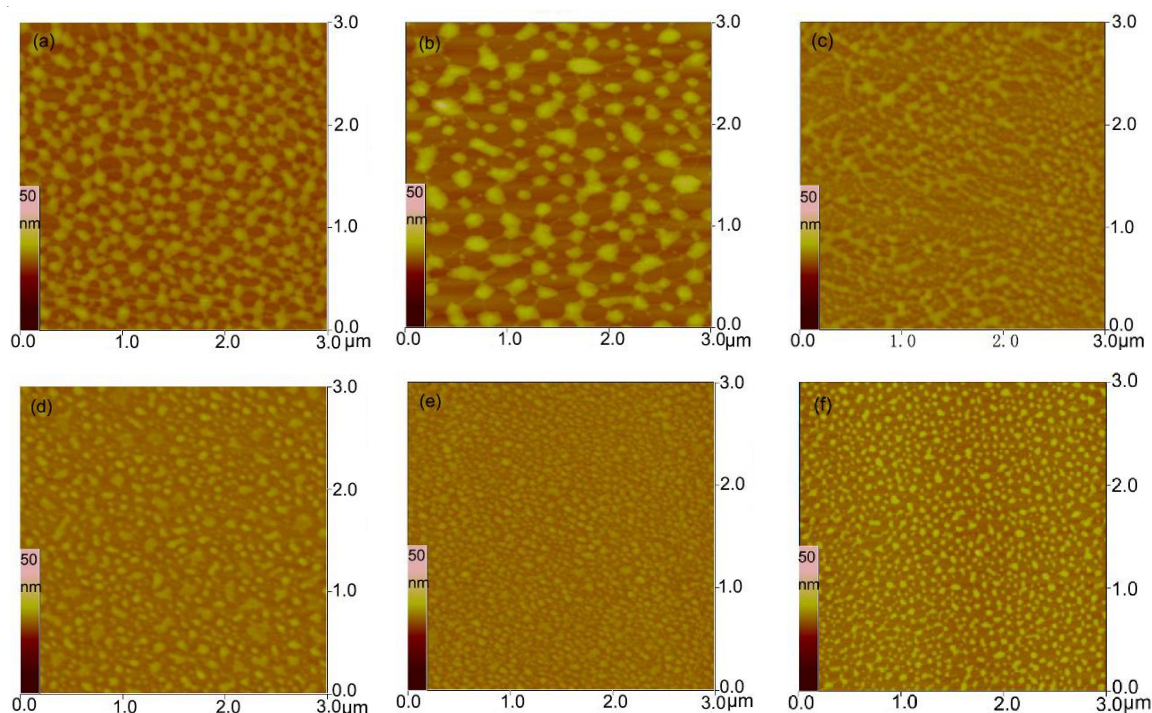
Fig. 10. Microscopic structure size of HAPAM solution after the waring blender shearing (a) 0 rpm, (b) 3500 rpm, (c) 7000 rpm, (d) 11500 rpm, (e) 14500 rpm, (f) 17000 rpm

the waring blender speeds increase to 3500 rpm. The polymer molecular aggregates form larger and looser mesh structures and loose mesh structures partly are broken. Continue to increase blender speeds, the polymer molecular aggregates become smaller and spatial mesh structures gradually disappear. When the waring blender speeds increase to 17000 rpm, the polymer molecular aggregates become very small and the gap between aggregates are larger, moreover, have formed fully independent molecular aggregates.

Conclusions

(1) The shearing effect of waring blender destroys aggregation behaviour of HAPAM solution and breaks the HAPAM intermolecular association, promoting the trend of intramolecular association. The more waring blender speeds are, the more HAPAM aggregation behaviour are broken.

(2) The shearing effect of waring blender not only makes the molecular chains of polymer fracture, but also makes the polymer chains transform from stretch to curl.

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