

Synthesis and Characterization of Polyethylene Glycol Acrylate Crosslinking Copolymer as Solid–Solid Phase Change Materials

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ABSTRACT: A kind of crosslinking copolymer as solid–solid phase change material (PCM) is synthesized by copolymerization. The scope of PCM applications is often severely limited by their heat stability and phase transition state. The solid–solid phase change materials we obtained retain basic state during phase change transitions. The crosslinking polymer is heat stable under 300° and the latent heat of crystalline and latent heat of melting is on the average of 120 J/g and 140J/g, respectively. The property of thermal stability and heat stored is related to crosslinking density of the gel. The property of thermal stability and high latent heat may expand the scope of PCMs applications. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39755.

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INTRODUCTION

Certain phase change materials(PCMs) exhibit excellent heat storage property which can be used to for energy saving applications.^{1–4} Solid–solid phase change materials are stable during phase change transition without obvious physical morphology changes. As phase change materials should have practical applications, the minor volume change of solid–solid phase change materials avails in actual manufacture.^{5,6} Therefore, solid–solid PCMs attract researchers' attention and numerous researches concentrate on this material.^{7,8}

Swanson and Rozvadovsky⁹ prepared a modified hydroxyl-terminated polybutadiene which had irreversible crosslinks by Diels-Alder chemistry. Polyethylene glycol with high latent heat enthalpy is widely used to obtain solid–solid phase change materials.^{10,11} Tang and Yang¹² got a kind of poly(polyethylene glycol methyl ether methacrylates) which had a comblike structure with PEG long side-chain. Another comblike copolymer was investigated by Alkan and Encari.¹³ This PCM had phase change property and better thermal and chemical stabilities. Alkan and Gunther¹⁴ made one solid–solid phase change material of polyurethane by copolymerizing diisocyanate and polyethylene glycol. Xi and Duan¹⁵ made PEG into thermoplastic polyurethane solid–solid PCM and immobilized PEG in chains by copolymerization. A modified PEG was used to synthesize a novel solid–solid PCM which had phase change properties and luminescent properties.¹⁶ Chen and Liu¹⁷ prepared solid–solid PCMs by making polyethylene glycol and poly(glycidyl methac-

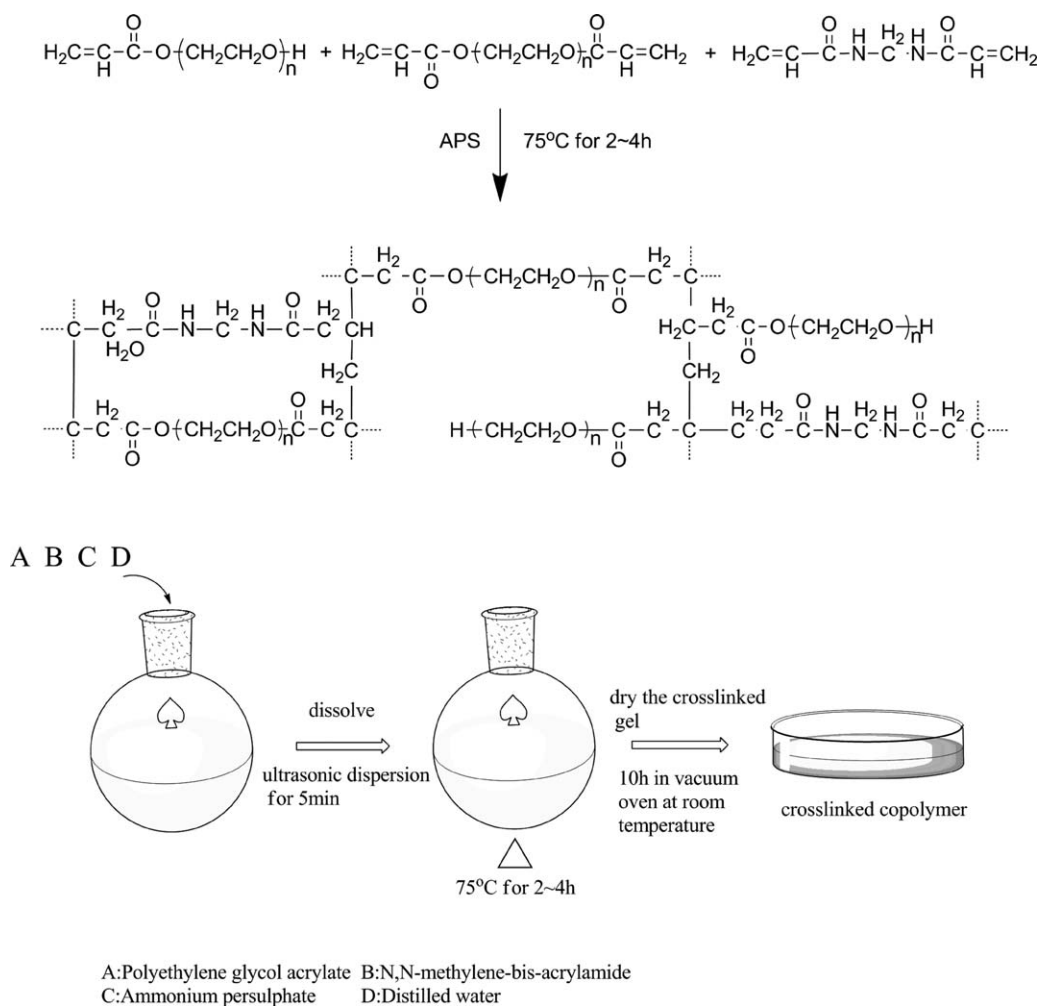
rylate) crosslinks. The most useful methods of immobilizing polyethylene glycol chains are grafting and copolymerization. The fiber with PCM which is thermo regulated is a new kind of functional fiber.¹⁸ Its textile can provide people a comfortable microclimate environment.¹⁹ It also can be used as building materials. The wall surface with PCMs can make indoor environment more comfortable.²⁰

Here we report the synthesis of phase change materials forming covalently crosslinking copolymer. Polyethylene glycol acrylate has parallel heat storage property like polyethylene glycol and it will turn into liquid during phase transition at the same time. We prepared a novel copolymer by immobilizing polyethylene glycol acrylate molecular chain in network and this structure could efficiently avoid leakage and the melting of polyethylene glycol acrylate. This phase change material which has high latent heat enthalpy and great heat stability has a great potential in manufacture by melt spun or melt extrusion. We look forward to its application in thermo regulated textile.

EXPERIMENTAL

Materials

Polyethylene glycol acrylate(PEGA) was prepared by Dalian Polytechnic University, the molecular weight of which is about 4050 and the crystalline enthalpy is 154.52 J/g. Ammonium persulphate (APS) and *N,N*-methylene-bis-acrylamide (MBA) were obtained from Tianjin Chemical Reagent. Kermel (Tianjin, China).



Scheme 1. The schematic synthesis route of PEGA crosslinking copolymer and the experimental steps diagram.

Preparation of PEGA Crosslinking Copolymer

We used Orthogonal test to prepare different PEGA crosslinking copolymer specimens. The mass fractions of MBA/PEGA are 0.5%, 0.8%, 1%, 25%, 30%, 35%. The schematic synthesis route of PEGA crosslinking copolymer and the experimental steps diagram are shown in Scheme 1.

We put crosslinking copolymers into distilled water after weighing (m_1). We weighed the swelling copolymer every 6 h until the weight was constant (m_2). The swelling ratio was $Q = (m_2 - m_1)/m_1$.

Characterization

We use polarizing microscopy (POM, USFEN, XPB) and scanning electron microscope (SEM, JEOL JSM-6460LV) to investigate the morphology of PCMs. Crystalline morphology of PCMs was shown in proper magnification. The cross section of PCMs was observed by SEM.

The microstructures of PEGA and PEGA crosslinking copolymer were investigated and compared with PEG by using Fourier transform infrared spectrometer (FTIR, PerkinElmer, Spectrum One-B).

Differential scanning calorimeter (DSC, Mettler-Toledo, Switzerland) was used to measure the phase change temperatures and latent heat storage capacity of PCMs. Rates of heating and cooling were $10^\circ/\text{min}$ from 25° to 70° in a nitrogen atmosphere. Thermogravimetric analyzer (TGA, TA Instruments, Q50) was used to characterize heat stability of specimens. Totally 5 mg of each sample was in a crucible. Nitrogen flow rate was $50 \text{ mL}/\text{min}$. Temperature was raised from room temperature to 700° by $20^\circ/\text{min}$.

RESULTS AND DISCUSSION

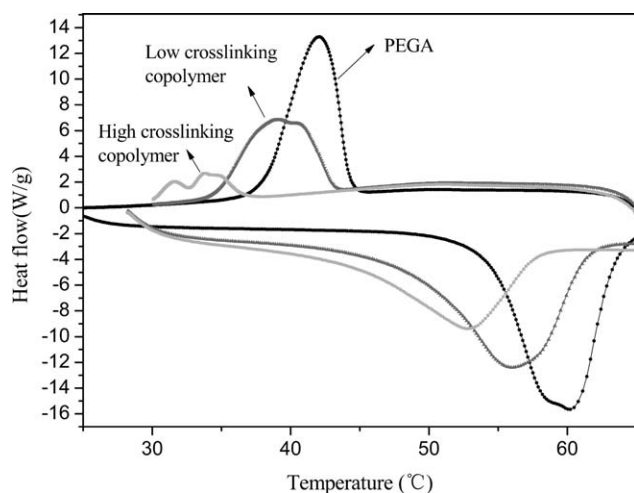
Phase Change Properties of PEGA Crosslinking Copolymer

Differential scanning calorimetry (DSC) is a necessary measurement to investigate the phase change properties of the synthesized crosslinking copolymer. Table I shows the thermal transition enthalpies and temperatures of crosslinking copolymer with different concentration of crosslinker. We use Orthogonal test to prepare 18 PEGA crosslinking copolymer specimens. Specimens No.5 (0.8% crosslinker) and No.10 (25% crosslinker) performed good phase change property. We use these two samples to compare with pure PEGA. From Table I, it can be seen that the melting enthalpy of the crosslinking

Table I. Thermal Transition Enthalpies and Temperatures of Different Specimens

	Melting temperature (°C)			Latent heat of melting (J/g)	Crystalline temperature (°C)			Latent heat of crystalline (J/g)
	Onset	Peak	Endset		Onset	Peak	Endset	
1	52.4	56.95	61.41	141.38	40.4	38.27	34.39	122.32
2	51.52	56.42	60.36	143.62	38.58	37.01	33.41	121.39
3	51.84	56.65	61.31	140.03	37.98	36.58	32.97	120.2
4	52.8	57.15	61.61	140.33	39.62	38.12	34.27	120.51
5	52.13	56.84	61.83	168.96	38.54	36.91	32.92	145.97
6	51.5	55.87	60.64	145.54	37.82	36.13	32.89	125.24
7	52.46	56.56	60.82	139	39.16	37.7	34.07	121.26
8	52.38	56.5	60.67	144.69	38.87	37.26	33.85	122.97
9	51.15	56.17	60.88	140.27	37.72	36.18	32.49	119.99
10	48.54	54.38	57.73	89.06	36.23	34.05	30.67	65.22
11	49.3	55.06	58.54	86.73	36.05	33.79	30.5	58.43
12	49.51	55.37	58.93	85.86	36.61	33.85	30.85	57.01
13	47.1	54.34	57.73	84.17	35.39	32.8	29.43	54.29
14	47.66	54.46	58.03	85.94	34.99	32.46	29.84	52.11
15	46.76	53.94	57.41	80.52	35.22	32.17	29.58	51.44
16	44.84	53.19	56.7	77.36	34.74	32.07	28.53	45.4
17	42.98	52.99	56.46	74.13	34.06	30.59	27.46	42.01
18	45.34	53.49	56.9	78.53	34.43	31.96	28.23	46.57

copolymer is 144.69 J/g and 89.06 J/g, respectively. The crystalline enthalpy of the copolymer is 122.97 J/g and 65.22 J/g, respectively. The enthalpies and temperatures are lower than those of PEGA and both reduce with the increasing crosslinking density of the network. The exothermic and endothermic abilities have been weakened after crosslinking. The phase change decreased with the increasing crosslinking density. The reason for the decline of those abilities can be interpreted by the limitation of PEGA chains' movement by network and the reduction of crystal regularity. But pure PEGA and different crosslinking copolymer all have supercooling, which made differences between crystallization and the melting. From Figure 1

**Figure 1.** DSC curves of pure PEGA and crosslinking copolymer.

we found that the more crosslinkers introduced into the copolymer the more enthalpy lost. Crosslinking density is a negative effect for phase change performance. It also can be affirmed in the POM images in the following discussion. However, the high crosslinking density obviously decreased the phase change temperatures. The crosslinking structure limited the molecular mobility. The movement units of high crosslinking copolymer are segment and other smaller units but not the single molecular chain, the temperature of these small units' movement is low. Figure 2 shows DSC curves of different crosslinking copolymer after cycles. The phase transition enthalpy and temperature of specimen No. 5 have slightly variations for three cycles. It can be seen that the less crosslinking copolymer performs better thermo regulated stability than the one with more crosslinking. Low crosslinking copolymer possessed strong molecular movement capacity, which is good for the functional material's application.

Analysis of the Structure for PEGA and Its Crosslinking Copolymer

FTIR spectra test was performed to reveal the structure of PEGA crosslinking copolymers. FTIR spectra of crosslinking copolymers were shown in Figure 3. Curve a is the crosslinking copolymer with 0.8% crosslinker, the crosslinker's mass fraction of curve b is 25%. (We choose these specimens because they have good crystalline enthalpy.) The peaks at 1656 cm^{-1} belongs to the stretching vibration of amide group. The amide group absorption peak of specimen b became stronger with the more amide formation and it related with the introduced of crosslinker. The stretching vibration of $\text{C}=\text{O}$ (1100 cm^{-1}) in curve b became weaker, it is due to

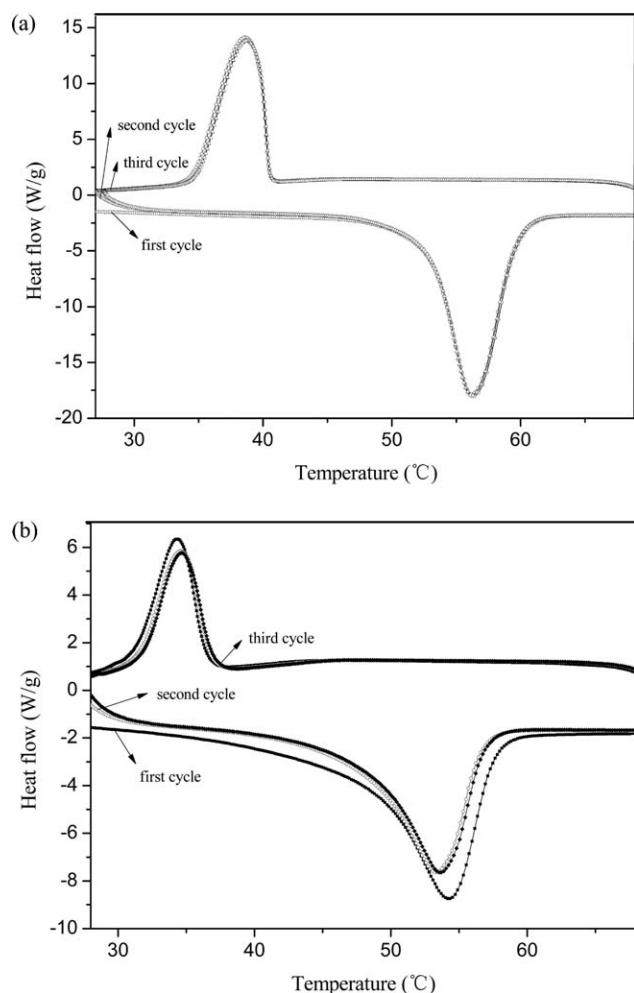


Figure 2. DSC curves of different crosslinking copolymer after cycles (a-low crosslinking copolymer, b-high crosslinking copolymer).

the increasing effects of N—H group on C—O position. The changes N—H group's increase brought proved the different crosslinking density of two samples.

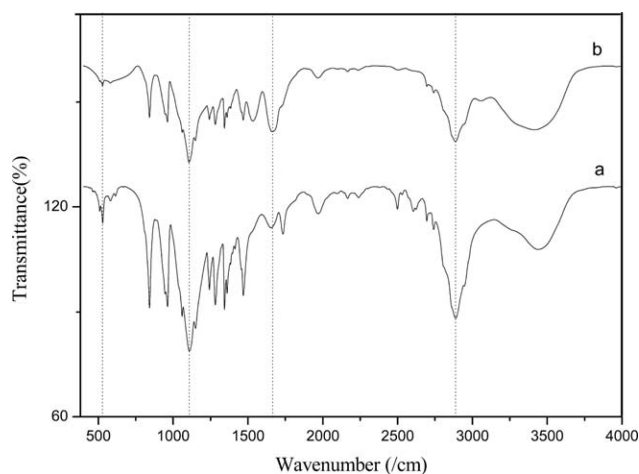


Figure 3. FTIR curves of different crosslinking copolymer after cycles (a-low crosslinking copolymer, b-high crosslinking copolymer).

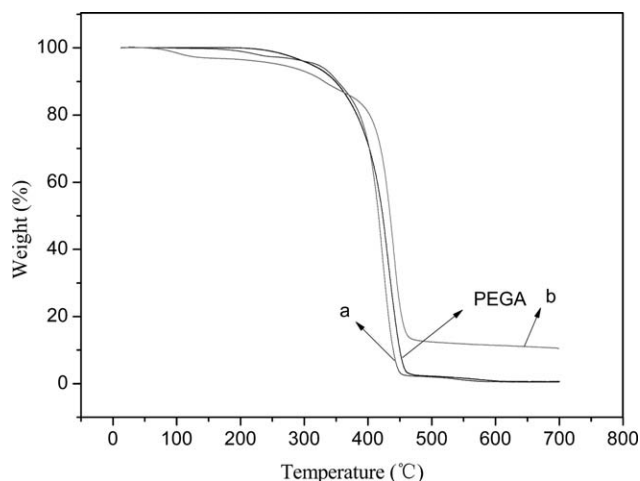


Figure 4. TGA curves of crosslinking copolymer (a-low crosslinking copolymer, b-high crosslinking copolymer).

Thermal Performances of PEGA Crosslinking Copolymer

Figure 4 shows TGA curves of PEGA and copolymer with different mass fractions of crosslinker. We can observe that thermal decomposition of PCMs appears slightly under 300°. The maximum decomposition peak points of PEGA, low and high concentration of crosslinker are 431.5°, 422.5°, and 440°, respectively. Heat resistance increases with increasing of crosslinker's mass fraction. The copolymer with more covalent bonds which provide resistance of heat. The more covalent bonds the copolymer has the tougher and more heat stable the copolymer is. Table II shows characteristic temperatures of different samples. The results indicate that these samples have wider processing temperature ranges. It is important and necessary property for applications of PCM. That is because most PCM products, such as fiber and membrane, are subject to high temperature. Thermal stability is pretty important for fabrication and industrialization.

Crystalline and Surface Morphology of PEGA Crosslinking Copolymer

Figure 5 shows the optical microscopy images of crosslinking copolymer. The samples were both observed at room temperature. Figure 5(a) is the copolymer with 0.8% MBA/PEGA and Figure 5(b) is the sample with 25% MBA/PEGA. The samples were crystalline, while the copolymer with fewer crosslinker had

Table II. Characteristic Temperatures of TGA Curves of PEGA and the Crosslinking Copolymers

Sample	T10% (°C)	T50% (°C)	Tmax (°C)
PEGA	348.5	423	431.5
PEGA low crosslinking copolymer	352.5	417	422.5
PEGA high crosslinking copolymer	331.5	435	440

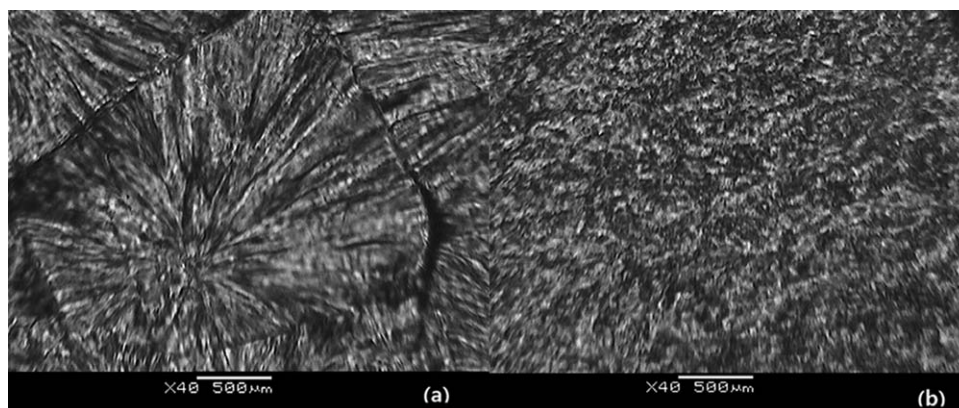


Figure 5. TGA curves of PEGA and crosslinking copolymer (a-low crosslinked copolymer, b-high crosslinked copolymer).

significant structure of spherulitic characteristics. The crystal structures obviously corresponds to the crosslinking network. The network limits the movement of macromolecule chains and the growth of spherulites. The crystalline properties decrease with the increasing of crosslinker' concentration. This result concurs with the DSC results. High crosslinking provides better thermal stability but lower crystalline property and less thermo-regulated property.

The SEM results of the copolymer are given in Figure 6. It can be seen that the network structure of the copolymer with fewer crosslinker is looser but clear. Structure of the copolymer with more MBA is compact. Surface morphology concurs with the internal structure of macromolecule. The loose network performs better plasticity and deformation capacity. These properties are beneficial to toughen composite material.

CONCLUSIONS

PEGA crosslinking copolymer was synthesized as solid–solid phase change materials for thermal energy storage. FT-IR results confirmed that the crosslinking structure was successfully prepared by copolymerization. DSC analyses showed the crosslinking copolymer had typical behavior of solid-solid phase transitions. Especially, the thermal storage capacity of copolymer with low concentration of crosslinker approached to pure PEGA. The copolymer showed good heat stability and resistant under 300° during TGA characterization, that will satisfy practical processing temperature requirement. The crosslinking copolymer with good thermal storage capacity and heat resistant property has a great potential for energy storage applications. And we will continue study the deep structure and expanding the application field of the low crosslinking PEGA copolymer.

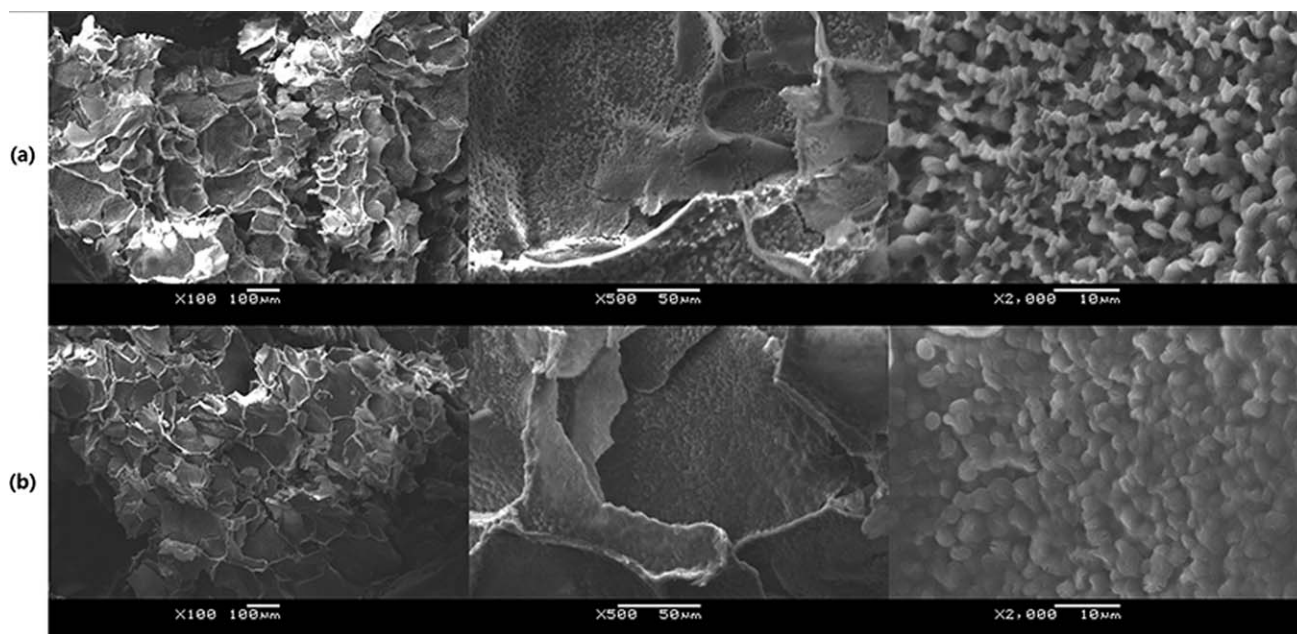


Figure 6. Figure POM images of crosslinking copolymer (a-low crosslinking copolymer, b-high crosslinking copolymer).

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