

Preparation and Characterization of PEG/PVP blend, with Sepiolite Clay as Compatibilizer

¹Mohsan Nawaz*, ¹Ali Bahader, ²Sad Ullah Mir, ¹Zia Ur Rehman, ¹Masroor Ahmed Bangash,
¹Hameedullah and ¹Sidra Shaoor

¹Department of Chemistry, Hazara University Mansehra, Pakistan.

²Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad Pakistan.
mohsannawaz@hotmail.com*

(Received on 18th April 2017, accepted in revised form 15th February 2017)

Summary: In this work, blend of poly(ethylene glycol) and poly(vinyl pyrrolidone) were prepared. The prepared blend was then reinforced with the inorganic sepiolite clay (SC). All samples were prepared through solvent casting technique. The end-product (nanocomposites) was characterized for thermal stability, morphology, structure as well as the developed interactions among the ingredients. The x-ray diffraction data verified well intercalation and exfoliation of the clay in the polymer matrix. The compatibility and synergistic effects of sepiolite on the properties of PEG/PVP blend were deduced from the FTIR signals. The corresponding peaks shift from lower to higher frequency. The elemental composition of the nanocomposite was determined by energy dispersive X-ray (EDX). The obtained data reflects that addition of SC have synergetic effect on the properties of the polymer blends.

Key Words: Blending, Sepiolite, Compatibilization, FT-IR, PVP-PEG

Introduction

Polymer blend is a material of choice in industry, where economics is the driving force for cost effective production of the materials. Polyethylene glycol, commonly abbreviated as PEG: HO-(CH₂CH₂O)_n-H, is an amorphous polymer. It is available in different molecular weights ranging from 200 to tens of thousands. It is water soluble and hygroscopic at room temperature. It is colorless and the low molecular weight fraction (600) is a viscous liquid while at molecular weight, 800 it is found in a waxy, white solid form. Typically PEG is not mono-disperse polymer. PEG is water miscible in all ratios for example PEG-2000 has a solubility of about 60% in water at 20°C. Lower molecular weight liquid PEGs can be used as solvents with or without addition of water [1, 2]. Poly (vinylpyrrolidone), also called povidone or PVP composed of electronegative nitrogen and oxygen forming lactam ring. The glass transition temperature of PVP ranges from 150 to 180°C. PVP is easily soluble in water and also in many organic solvent. The reason for this is PVP posses both hydrophilic and hydrophobic functional groups. PVP cannot be processed in the melt state, because of its low thermal decomposition profile and extremely poor flow. The amorphous structure of PVP also provides a low scattering loss, which makes it as an ideal polymer for composite materials for different applications. PVP easily dissolve in water so it prefers to avoid phase separation in the system [3]. An ideal blend has interfacial tension nearly or equal to zero. Such low interfacial tension, arise from the strong association through interaction between

complementary functional groups of two polymers. Such inter-polymer association (usually labeled as H-bonding) is called inter-polymer complexation and the property of the inter-polymer complex should be completely different from the constituent polymers [4, 5]. One such example is the inter-polymer complexation between polyvinylpyrrolidone (PVP) and poly (ethylene glycol) (PEG). H-bonding occurs between the terminal hydroxyl groups of short chain PEG molecules (Mw: 200–600) and the carbonyl groups of long chain PVP molecules, resulting in a high free volume structure of PVP chains cross-linked by flexible PEG chains [6, 7]. The PEG/PVP blend may be used in Pharmaceutical and as corrosion inhibiting agent on other industry. Filler addition into polymers is an important methodology, as it improves tensile strength, heat distortion temperature, electrical and thermal properties of the polymer [7-9]. In contrast to conventional composites, the large surface area of the nano-filler may lead to enhance interactions between the organic flexible matrix and nano-fillers [10]. Similarly, the addition of nano-filler into bio-based matrices could yield a material with improved properties and may help in controlling environmental pollution. Due to the light weight, high liquid absorption capacity, non-flammability, chemical inertness and odor control it can be used as Industrial absorbents as well as sealants. Clay is also one of the most employing nano-fillers. Due to its inorganic nature, it has been used as a plastic additive to improve mechanical thermal, and chemical barrier properties as other

*To whom all correspondence should be addressed.

clays such as bentonite, organically modified nanoclays, halloysite nanotubes [11]. Clay is available in the form of layered silicate, organically modified montmorillonite (OMM) and needle like sepiolite (SC). Sepiolite has elongated morphology with lengths of 2–10 μ m and diameters in the range of 2–100nm. Sepiolite composed of hydrated magnesium silicate with a formula equivalent to $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4\cdot(\text{H}_2\text{O})_4\cdot 8\text{H}_2\text{O}$. The vast surface area (374-m²/g) makes it an ideal candidate for various industrial applications. In sepiolite, two layers of tetrahedral silica which sandwiched an octahedral magnesium oxide/hydroxide layer, thus make a tunnel like morphology. These tunnels act like pigeon holes or lines for the water attached to the sepiolite functionality. Like other silicates the inherent silanol (SiOH) groups appear at the external surface edges of the sepiolite structure. Many authors claimed that availability of silanol groups provides an anchoring point for the establishment of hydrogen bonding and Van der Waals interactions [11, 12].

In this paper, we have prepared the blend of PEG and PVP. The blend was then transformed into nanocomposites with the addition of SC, in order to enhance the properties of PEG/PVP blend. It is believed that the interactions developed between PEG and PVP will be reinforced with the addition of SC, which contains silanol groups on its surface. Besides, the SC may perform compatibilizer role in the blend.

Experimental

Materials

Poly (ethylene glycol) (PEG) methyl ether having molecular weight of 5000g/mol was purchased from Sigma Aldrich, Australia. PEG was in the form of white to light yellow pellets. The melting temperature of PEG was 60-64°C. Poly (vinylpyrrolidone) (PVP) was purchased from Sigma Aldrich, Australia. The white pellets of PVP have melting temperature (T_m) of 150-180°C with density of 1.2 g/cm³. The sepiolite having density of 2-2.2 g/cm³ was obtained from International Laboratory USA. Distilled water (DW) was used to prepare solutions.

Methods

Briefly, different proportions of PEG, PVP and sepiolite (Table-1) were mixed in water to prepare its solution. The mixture was stirred using mechanical stirrer at the rate of 100 rpm on a hot plate for 30 minutes. The temperature was kept

constant at 70 °C. The solution was then poured on to clean petri dishes and left overnight in the oven at 45°C to evaporate solvent. After evaporating the solvent, films of the nanocomposites were obtained and used directly for characterization.

Table-1: Composition of the PEG/PVP/Sepiolite nanocomposites.

| S.No | Sample Code | PEG (wt %) | PVP (wt %) | Sepiolite (wt %) |
|------|-------------|------------|------------|------------------|
| 1 | ZR3 | 50 | 50 | 0 |
| 2 | ZR7 | 50 | 48 | 2 |
| 3 | ZR9 | 50 | 44 | 6 |
| 4 | ZR10 | 50 | 40 | 10 |

The prepared polymer nanocomposite films were characterized by the following techniques as follow;

Thermo Gravimetric Analysis (Tga)

Thermal degradation study on the nanocomposites was performed on Q50, TGA by TA Instruments USA. The heating rate was adjusted to 10°C/min under N₂ atmosphere in the temperature regime of 25°C-500°C.

Fourier Transform Infrared (Ftir) Spectroscopy

To get the image of the internal structure of the nanocomposites the film was subjected to FTIR analysis. The FTIR spectrometer used in the range of 4000-350 cm⁻¹ was Nexus 6700 Nicolet, UK.

X-Ray Diffraction

X-ray diffraction data was obtained by subjecting the films to analysis in XPert Pro (Panalytical). The instrument was operating at a voltage of 40 KV and 30mA current.

Morphological Observations

Scanning electron microscopy (SEM) verified the dispersion of sepiolite clay in the polymer matrix. The instrument used was Philips XL30 FESEM. The sample was immersed in liquid nitrogen and fractured. The cross section of the fractured sample was observed using FESEM.

Energy Dispersive X-Ray

The elemental composition was studied by energy disperse X-ray unit, attached to the FESEM machine. The samples prepared for FESEM analysis were used in this case.

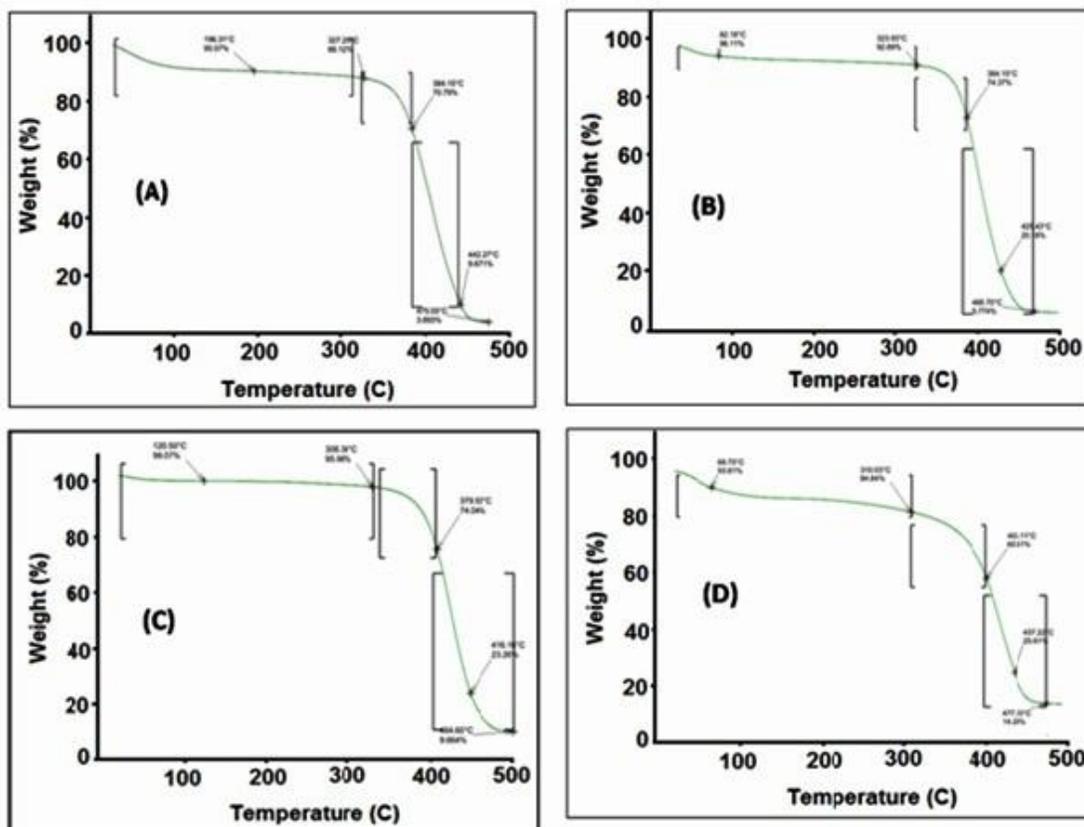


Fig. 1: TGA thermograms of nanocomposite (A) ZR3 (B) ZR7(C) ZR9 (D) ZR 10.

Results and Discussion

Thermo Gravimetric Analysis (TGA)

Thermal gravimetric analysis was used to study the thermal stability of the polymer clay nanocomposites as shown in Fig. 1.

Comparison of the data displayed in Fig. 1, shows that ingredients mixed in different proportions have different thermal stabilities. The sample (A) is less thermally stable as it contains no clay, to offer reinforcement. The thermal stabilities of the nanocomposites linearly increase with the clay addition. It means that the interface between PEG and PVP is modified and compatibilized with the addition of SC.

Fourier Transform Infrared (FTIR) Spectroscopy

In the IR spectrum presence or absence of absorption bands of specific functional groups gives information, which is helpful in the structural elucidation of the materials (Sheng et al., 2013).

In Fig. 2, peaks at various frequencies can be observed. The peak appears at 2881.2 cm^{-1} is assigned to the asymmetric stretching of CH_2 , which is contributed in the system from the presence of PEG and PVP [13, 14]. The peak at 1652.4 cm^{-1} , arise from the occurrence of carbonyl moiety ($\text{C}=\text{O}$) of amide and is exclusively assigned to the PVP [3, 13]. Peaks at 1060 cm^{-1} indicate the stretching of Si-O moiety and peak at 841.6 cm^{-1} shows the stretching of Mg-O moiety both are present in sepiolite clay [14-16]. The prevailing trend is that the values of frequencies shift from lower to higher with the addition of SC. This shifting of frequency means that the established interactions become more reinforced, leading to enhance compatibility.

X-Ray Diffraction

In order to fully illustrate the structural configuration, which is generated in the nanocomposite, it is necessary to subject it to the XRD analysis. The increase of d-spacing designated to the development of nano-composite structure with intercalation and exfoliation of SC in the galleries of blended polymer.

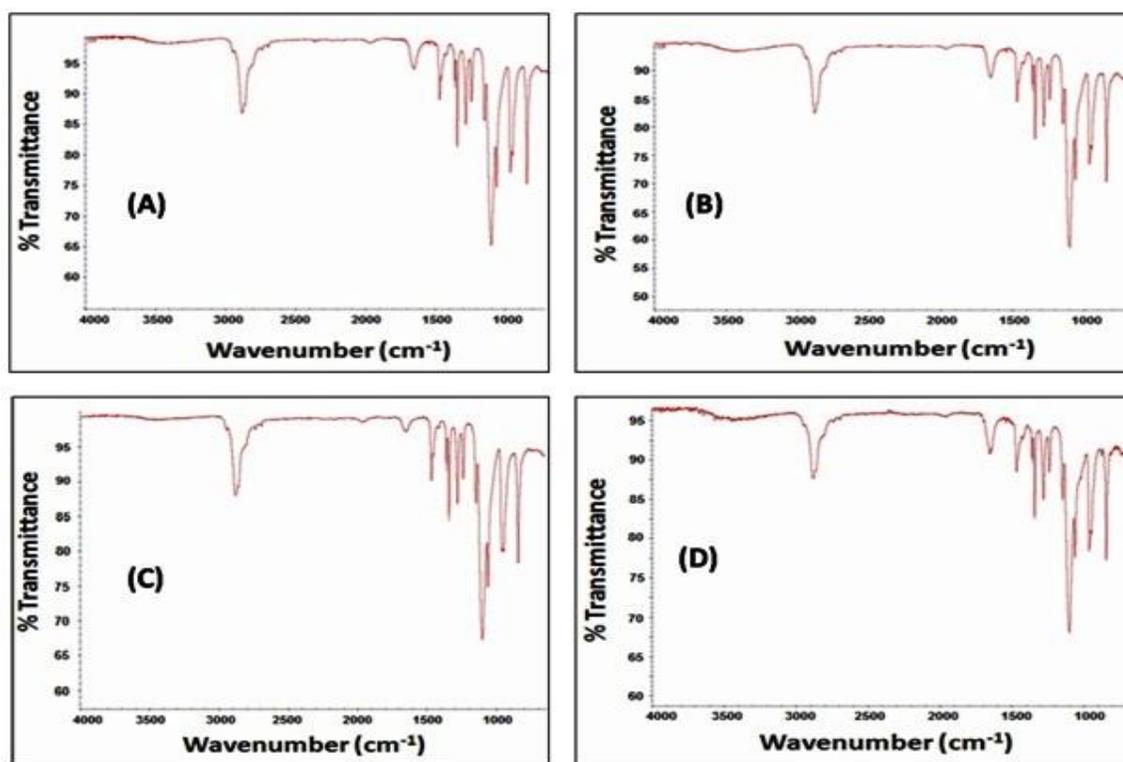


Fig. 2: FTIR spectra of nano-composite (A) ZR3 (B) ZR7 (C) ZR9 (D) ZR 10.

The data calculated as shown in Fig. 3 shows that addition of clay in different proportion has pronounced impact on the developed crystal structure. The low value of 2θ , and high value of d -spacing show that sepiolite clay is better intercalated and exfoliated [17]. The reflection at 11.82° in 2θ corresponding to the folded monoclinic structure, which can be observed in the Fig. 3. The main peak at 20.21° is progressively increasing in intensity; show the exfoliated SC [15].

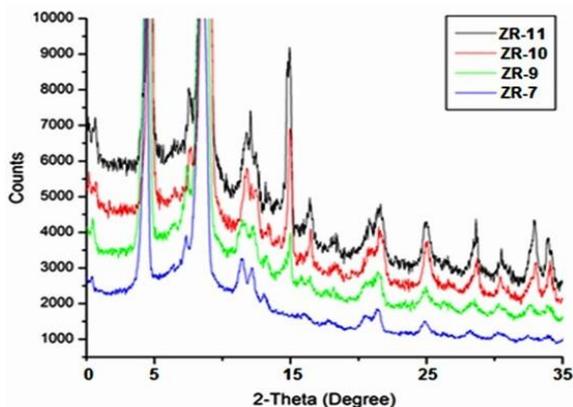


Fig. 3: Representative XRD spectra for the various nanocomposites.

Morphological Observations

The morphology and homogeneity of the resultant polymer nanocomposites were studied by scanning electron microscopy as shown in Fig. 4. Scanning electron microscopy verified the dispersion of sepiolite clay in the polymer matrix. Scanning electron microscopy, that gives us the information about the nano-scale dispersion of filler in polymer nanocomposites, was exploited to investigate the morphology of the obtained cured polymer/sepiolite nanocomposites.

The snapshots well represent the state of the samples; as can be observed that no agglomerated particles can be seen. The structure of the nanocomposites looks very uniform by SEM. The lower magnification picture shows bright spots corresponding to small bundles of sepiolite fibers [18]. When light fall on film surface, the protruded part of the sepiolite fibers tend to luminance and appears as bright spots. The morphology also presents filled pores distributed throughout the observed area. All of the SEM images present some small but uniform irregularities and look like filled pores on the surface of all pores. These are spherical in shape and distinguishable throughout the polymer matrix and are well distinguishable. Such type

of contours may be interpreted in light of classical polymer plasticization–dissolution principle. Accordingly, it is a two step process, in the first stage when PVP is mixed with PEG; the PVP becomes plasticized, where in the second phase the plasticized PVP tend to dissolve in the excess of PEG. Consequently, the pores generated due to the insertion of the fibrous sepiolite become capped due to the dissolution of the PVP in the PEG and appears as filled pores [6, 19].

Energy Dispersive X-Ray

The microscope was equipped with an EDX spectrometer which was used to analyze the elemental composition of some fractured samples at an accelerating voltage of 20 kV. The elemental composition was studied by energy disperse X-ray. EDX spectrum as shown in Fig. 5, confirms the elemental composition of Mg, Mg-O, Si, Si-O which are present in the sepiolite clay [20].

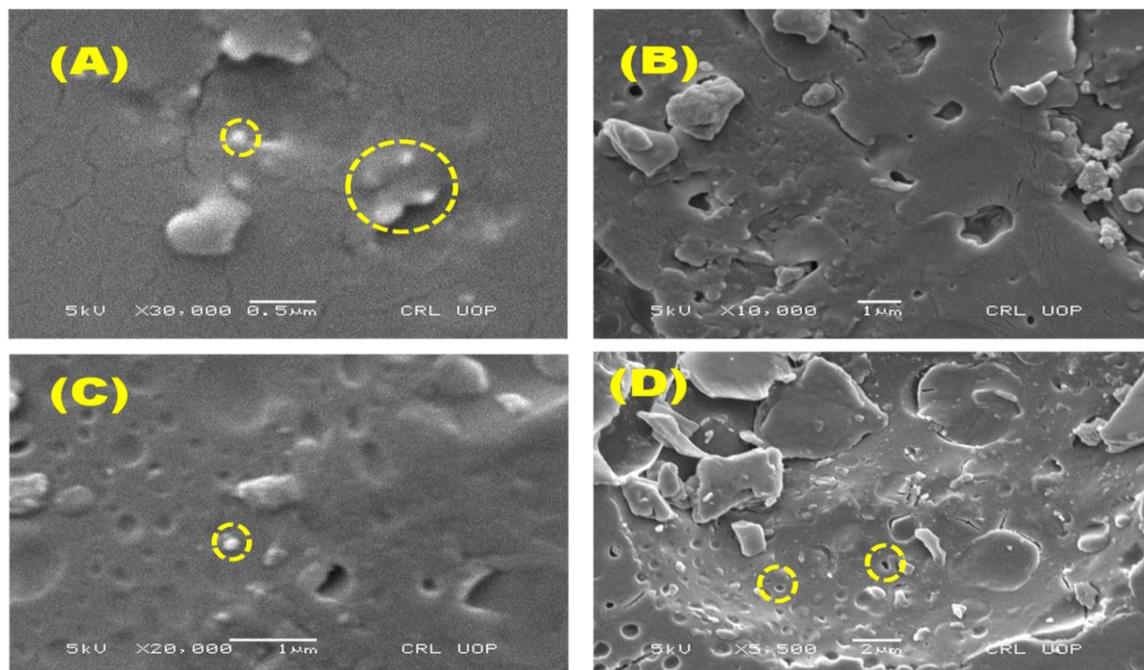


Fig. 4: SEM images of the sample ZR7 at various magnifications.

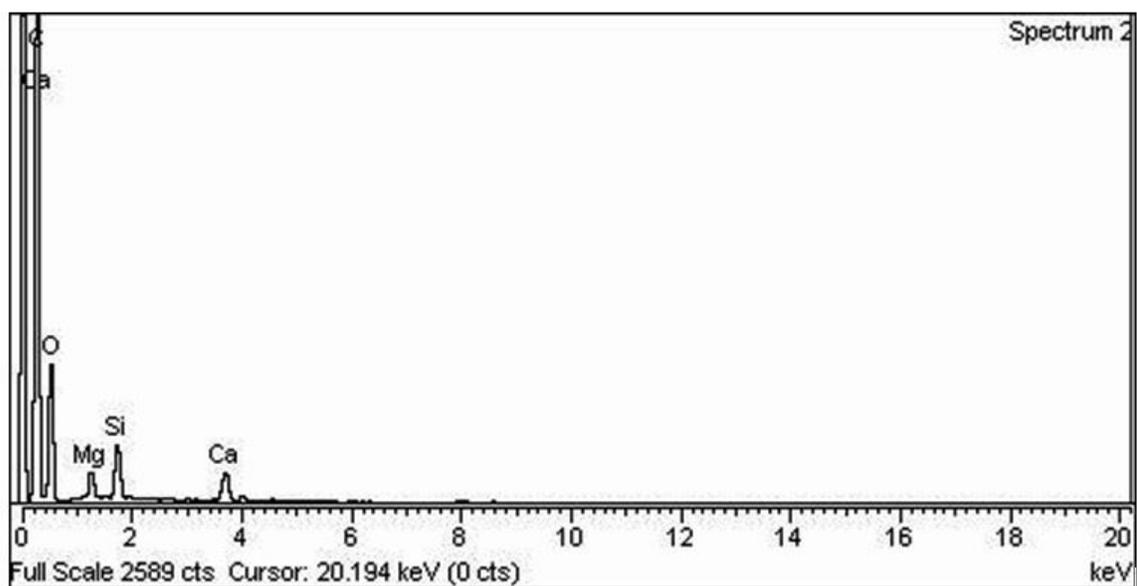


Fig. 5: The energy disperse X-ray spectrum of the sample ZR7.

Conclusions

FDA approved polymers (PVP and PEG) were selected for this study which are bio degradable, environment friendly and bio-compatible. Being inorganic in nature, needle-shaped sepiolite clays composed of silanol groups show remarkable compatibilizing effect on the biodegradable PEG/PVP blend. The surface silanol groups offer good reactivity and attachment points for the polymer matrix, predominantly contains nitrogen and oxygen functionality. The presence of such functionality on the nanofiller surface leads to enhance compatibility and compactness in the developed nanocomposites. This enhancement in properties such as TGA also confirms the aforesaid claim. The shifting of infrared frequencies also validates the TGA results. The crystalline morphological evaluation by XRD also reveals that the sepiolite clay perform its intended role of nanofiller. The SEM micrograph also confirms the plasticizing role of the PEG for PVP. The uniform distribution of the pores throughout the film surface also confirms that greater thermal stability was achieved at the expense even distribution and exfoliation of the sepiolite needles.

References

1. F. E. Bailey, J. Koleske, Poly(Ethylene Oxide), Academic Press, New York, (1976).
2. H. Fang, F. Jiang, Q. Wu, Y. Ding and Z. Wang, Supertough polylactide materials prepared through in situ reactive blending with PEG-based diacrylate monomer, *ACS Appl. Mater. Interf.*, **6**, 13552 (2014).
3. K. Sivaiah, K. N. Kumar, V. Naresh, S. Buddhudu, Structural and Optical Properties of Li⁺: PVP & Ag⁺: PVP Polymer Films, *Mat. Sci. & Applications.*, **2**, 1688 (2011).
4. R. Langer, Polymer-controlled drug delivery systems., *Acc. Chem. Res.* **26**, 537 (1993).
5. V. V. Khutoryanskiy, Hydrogen-bonded interpolymer complexes as materials for pharmaceutical applications., *Intern. J. of Pharma.*, **334**, 15 (2007).
6. M. M. Feldstein, T. L. Lebedeva, G. A. Shandryuk, S. V. Kotomin, S. A. Kuptsov, V. E. Igonin, T. E. Grokhovskaya, Kulichikhin, V.G. Complex formation in poly (vinyl pyrrolidone)-poly (ethylene glycol) blends. *Polymer Science: Series A*, **41**, 854 (1999).
7. Y. Zheng, Y. Zheng, Study on sepiolite-reinforced polymeric nanocomposites. *J. Appl. Polym. Sci.* **99**, 2163 (2006).
8. L. A. Utracki, A. M. Jamieson, Polymer Physics: From Suspensions to Nanocomposites and Beyond. John Wiley & Sons: Hoboken, New Jersey, (2010).
9. M. Darder, M. López-Blanco, P. Aranda, A. J. Aznar, J. Bravo, E. Ruiz-Hitzky, Microfibrinous Chitosan–Sepiolite Nanocomposites. *Chem. Mater.* **18**, 1602 (2006).
10. V. Miri, S. Elkoun, F. Peurton, C. Vanmansart, J. M. Lefebvre, P. Krawczak and R. Seguela, Crystallization Kinetics and Crystal Structure of Nylon6-Clay Nanocomposites: Combined Effects of Thermomechanical History, Clay Content, and Cooling Conditions. *Macromol.*, **41**, 9234 (2008).
11. M. D. Samper-Madrigal, O. Fenollar, F. Dominici, R. Balart and J. M. Kenny, The effect of sepiolite on the compatibilization of polyethylene–thermoplastic starch blends for environmentally friendly films. *J. Materials Science*, **50**, 863 (2015).
12. A. H. Omran Alkhayatt, A. H. Al-Azzawi and Z. ALakayshi, Rheological and Optical Characterization of poly(vinylpyrrolidone)-poly(ethylene glycol) polymer blend, *J. App. Phy.*, **8**, 11 (2016).
13. P. Barmapalexis, I. Koutsidis, E. Karavas, D. Louka, S. A. Papadimitriou and D. N. Bikiaris, Development of PVP/PEG mixtures as appropriate carriers for the preparation of drug solid dispersions by melt mixing technique and optimization of dissolution using artificial neural networks. *Euro. J. Pharma. and Biopharm.* **85**, 1219 (2013).
14. T. Kumar, Fourier transform infrared spectrometric determination of polyethylene glycol in high-density polyethylene, *Analyst*, **115**, 1597 (1990).
15. J. L. Valentín, M. A. López-Manchado, A. Rodríguez, P. Posadas and L. Ibarra, Novel anhydrous unfolded structure by heating of acid pre-treated sepiolite, *Applied Clay Sci.* **36**, 245 (2007).
16. N. García, M. Hoyos, J. Guzmán and P. Tiemblo, Comparing the effect of nanofillers as thermal stabilizers in low density polyethylene. *Polym. Degrad. and Stab.*, **94**, 39 (2009).
17. A. J. Aznar, J. Sanz, E. Ruiz-Hitzky, Mechanism of the grafting of organosilanes on mineral surfaces. IV. Phenyl derivatives of sepiolite and poly (organosiloxanes), *Colloid and Polym. Sci.*, **270**, 165 (1992).
18. X. Li, J. Luo, Q. Gao and J. A. Li, Sepiolite-based united cross-linked network in a soybean meal-based wood adhesive and its performance, *RSC Adv.*, **6**, 45158 (2016).
19. M. M. Feldstein, Peculiarities of glass transition temperature relation to the composition of poly(N-vinyl pyrrolidone) blends with short chain poly(ethylene glycol), *Polymer*, **42**, 7719 (2001).
20. C. P. Dhanalakshmi, L. Vijayalakshmi, V. Narayanan, Synthesis and preliminary characterization of polyethylene glycol (PEG)/hydroxyapatite (HAp) nanocomposite for biomedical applications, *Intern. J. of Phys. Sci.*, **7**, 2093 (2012).