

Dissolution behaviour of polyethersulfone in diglycidyl ether of bisphenol-A epoxy resins

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Abstract. Polyethersulfone (PES) is considered as an important and useful toughener for epoxy resins (EPs). Generally, PES was first dissolved in EP oligomer to form a homogeneous solution, which considerably affected the properties of cured EPs. Turbidity measurement was carried out to characterize the dissolution behaviour. Different PES/EP systems exhibited the same dissolution behaviour, albeit different swelling rate (R_s) and dissolution rate (R_D). Compared to molecular weight, the particle size and hydroxyl content of PES exerted considerable effects on dissolution. The smaller epoxy equivalent these diglycidyl ether of bisphenol-A (DGEBA) oligomers possessed, the better dissolubility they had; the more small molecules they contained, the more apparent the swelling observed. Moisture prevented the diffusion of the DGEBA oligomer molecules into PES. With increasing temperature, R_s and R_D first rapidly increased and then slowly increased, and the optimal dissolution temperature was 120°C. At the final steady, the turbidity increased linearly with increasing PES concentration; in addition, these values can be used as reference for homogeneous solution. Only one glass transition temperature (T_g) was observed for PES/EP systems, indicative of the good compatibility between PES and EP.

1. Introduction

Cured EPs have been widely used in coatings, adhesive materials, insulating materials, matrix resins for composites and many other fields [1-6]. Unfortunately, because of the high crosslink density, the cured resins tend to have a low resistance to brittle fracture [7]. The lack of toughness limits their further applications which demand better fracture resistance [8-9]. Therefore, toughening EPs has been an important issue for a long time.

PES is one of the most suitable commercially thermoplastic resins to toughen EPs, based on its good toughness, proper modulus, chemical resistance and thermal properties, and so on [10-12]. PES can improve the toughness without significantly decreasing the modulus and T_g of cured EPs [6]. The academic researches on PES toughening of EPs have long been focused on the morphological structures, mechanical and thermal properties, and toughening mechanism [7, 9, 6, 13-15].

Most of thermoplastic toughened systems are prepared starting from a homogeneous solution of thermoplastic polymers in epoxy oligomers. During the epoxy-hardener curing reaction, the miscibility between thermoplastic and epoxy resin decreased, and the phase separation occurred. These phase separations lead to toughness of cured epoxy resins improved [16]. Some researchers have mentioned the preparation of thermoplastic and EP systems, including solvent method and melt method [17]. In Alessi S's research [18], PES was first dissolved in dichloromethane and then added to EP anhydride



system, the solvent was removed at 120°C for 1.5h. When solvents are used in EPs, they must be completely evaporated prior to cure, or otherwise bubbles could be formed during curing process, and causing weak joints [1]. Therefore, it's necessary to minimize the use of solvents. In Mimure K's study [13], PES, EP and curing agent compound was stirred at 135°C, until PES dissolved homogeneously in the mixture. In Yu Y's research [14], PES was added to the stirring epoxy monomer at 150°C under nitrogen gas to form homogeneous mixture, then the curing agent was added to the mixture. Obviously, it is important to reach total dissolution of PES in order to obtain a homogeneous solution.

To date, few researches concerning the dissolving behavior and critical influences of PES in EP oligomer have been reported, to the author's knowledge. L. Bonnaud [19] used cloud-point curves to research the influence of different factors on the miscibility of the DGEBA/ thermoplastic systems, and a phenomenological model was proposed to predict the epoxy precursor and thermoplastic blend miscibility. Unfortunately, cloud-point curves had a low automation degree and a large impact on human factors.

In this study, we adopted turbidimetry [20-21] as a novel and simple technique to study the dissolution behavior of PES/EP oligomer systems for the first time. The dissolution behavior of different systems was explained, and the influence of solubility temperature, moisture, the properties of PES and DGEBA were studied. These results had important implications for determining the dissolving process conditions, distinguishing the final state of solution, and improving the raw material. At the same time, this study can provide a scientific basis for doing further research on toughening mechanisms.

2. Materials and methods

2.1. Materials

Two types of commercial PES and three trades of DGEBA were used. Their properties were shown in Table.1 and Table.2, and formulas were shown in Figure 1.

Table 1. Properties of the PES particles.

	PES1	PES2
Commercial code	Ultrason E2020P	Virantage VW 10200RFP
Company	BASF	Solvay Specialty Polymers
Country	Germany	Germany
Average molecular weight (g/mol)	55000	46500
-OH end groups (%)	>50 (typically>75)	32
Glass transition temperature (°C)	225	220
Particle size (μm)	20	63

Table 2. Properties of the DGEBA according to the suppliers.

	EP1	EP2	EP3
Commercial code	DER331	CYD-128	CYD-144
Supplier	Dow Chemical Co.	YueYang Petrochemical Ltd	YueYang Petrochemical Ltd
Country	USA	China	China
Epoxy equivalent (g/eq)	182-192	184-200	210-240

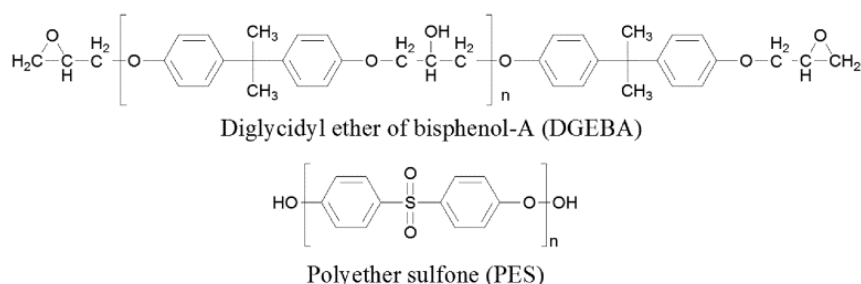


Figure 1. Molecular structure of DGEBA and PES.

2.2. Preparation of raw material

In order to avoid the influence of absorbed moisture, the raw materials should be dried before using. PES1 powder was dried 4h at 140°C in a vacuum drier. PES2 powder should be dried in vacuum oven at 130°C for 4h. Three DGEBA oligomers were dried at 70°C for 10h in vacuum drier.

2.3. Turbidimetric measurements

Turbidity was measured by WGZ-3B (Xinrui, China) turbidimeter with a scattered light detector perpendicular to the light beam. With the help of turbidimeter, the intensity of light scattered from these insoluble particles in transparent solution can be tested, what's more, the content of these insoluble particles can be characterized quantitatively. The units of turbidity are called Nephelometric Turbidity Units (NTU). The range of the nephelometer is between 1 and 1000NTU. Formazine calibration solutions are used for correction.

2.4. Dissolution of PES in EP oligomers

A precise quantity of PES and EP oligomers were added to a beaker, after rapid stirring, the PES/EP systems were defoamed in vacuum oven at 70°C. Then, the mixture was transferred to a clear glass vial slowly until reach the calibration line. After that, the glass vial was defoamed in vacuum oven at 70°C again. Following the above steps, these samples with different systems and different concentrations were prepared. The turbidity of these samples was measured every 3 minutes until a stable NTU value was reached under designed condition. Unfortunately, the turbidity of systems with high PES contents at the initial dissolution could not be reached because the solution is completely opaque.

2.5. Characterization

2.5.1. X-ray diffraction. The crystal structure of PES powder was characterized by X-ray diffraction (XRD). XRD patterns of PES were obtained with X-ray diffractometer (D/max-2550 PC, Rigaku Corporation, Japan) using 18 kW Cu-K α ($\lambda=1.5406$ Å) radiation. The scanning range was set from 5° to 80°.

2.5.2. Thermal platform microscope. High speed mixer (DFY-1000C, BILON, China) was used to mix PES powder and EP with different weight ratios. The dissolving process of PES/EP blends was observed using thermal platform microscope at 120°C. The photos were shot every 30 seconds.

2.5.3. GC-MS. The three trades of EPs were analyzed by gas chromatography mass spectrometry (GC-MS, QP2010Ultra, Shimadzu, Japan) system at 500°C for 30min.

2.5.4. Differential scanning calorimetry (DSC). Differential scanning calorimetry scans were performed on a Mettler 822 DSC (Mettler, Switzerland) in a heating-cooling-heating cycle at a heating rate of 10°C/min under a nitrogen flux of 50mL/min. The weight of each simple was approximately 5-

8mg. To check the reproducibility and uniformity, the procedure of every solution was repeated two more times.

3. Results and discussion

3.1. Dissolving process of PES in EP oligomers

Turbidimetry was chosen to characterize the dissolution behavior of different PES/EP systems for the first time, as shown in Figure 2-5. Like the other polymer dissolution behavior, the dissolution of PES powder in EP oligomers did not instantaneous, but involved two transport processes, namely solvent diffusion (swell) and chain disentanglement (dissolve). It can be further described that PES powder in EP oligomers at first swelled (turbidity values increased), then started to dissolve (turbidity values decreased), at the end of the dissolution process, the clear and transparent solution was obtained (turbidity values became stable). The dissolution behavior can be explained as follows: the molecular structure of PES and EPs had some same functional groups (Figure 1); PES is the amorphous character (shown as Figure 2b, only one prominent peak at $2\theta=18.1^\circ$ [22-23]), the molecular interactions were weak, and the EP oligomers can diffuse into PES easily [24]. Due to plasticization of PES by EP oligomers, the volumetric expansion of PES powder occurred. After time has passed, EP molecular entered into the intermolecular chains of PES, which led chain disentanglement, in other words, PES powder dissolved. The amorphous structure was widely considered to be one of the main causes of the good compatibility between PES and EP. On the other hand, PES can dissolve in NMP, DMAc, DMF, while, EP oligomers can dissolve in acetone. Based on the theory of “similarity and intermiscibility”, the PES and EP is both polar molecule, and the polarity of PES is stronger.

The other information can be obtained from this turbidity versus time curves: the slope of upward section (from the start point to the peak point) can be used to characterize R_S ; the slope of downward section (from peak point to equilibrium point) can be used to characterize R_D ; different systems have same dissolution behavior but different R_S and R_D .

3.2. The influence of solution composition

The influences of different PES on dissolution behavior were shown in Figure 2. At the beginning of dissolution process, the turbidity values of PES2/EP1 were smaller than that of PES1/EP1, that maybe because particle size of PES1 (20 μm) was smaller than PES2 (63 μm). On the other hand, R_S and R_D of PES1/EP1 were bigger than PES2/EP1, which can be attributed to the difference of particle size and hydroxyl content (Table 1.). But, the dissolution behavior did not follow the rule that the dissolution rate decreased with increased polymer molecular weight. We can indicate that, compared to molecular weight, particle size and hydroxyl content of PES had more important influence on dissolution process. In order to observe the dissolving process visually, the macroscopic and microscope photographs were supplied in Figure 2a at the corresponding position.

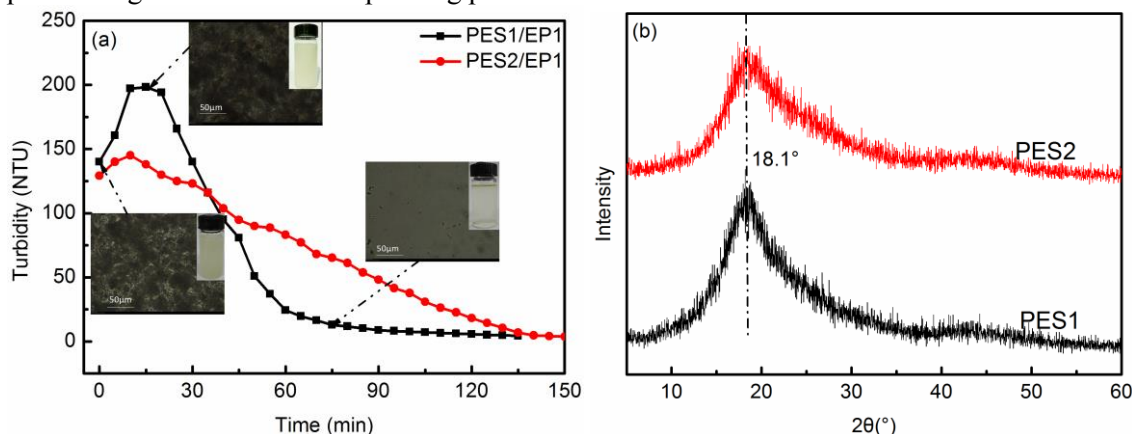


Figure 2. Turbidity versus time for PES/EP systems (PES 0.1 wt%) at 120 °C (a) The influence of PES on dissolution behaviour; (b) XRD patterns of PES powder).

The influences of different EPs on dissolution were shown in Figure 3. The turbidity peak value of PES1/EP2 and PES1/EP3 was larger than that of PES1/EP1. This phenomenon maybe because there were more small molecules in EP2 and EP3, as shown in the upper-right corner of Figure 3b, these small molecules can enter into PES easier, which caused the powder swelled. R_D and dissolution time of PES1/EP1 and PES1/EP2 were almost the same, and larger than that of PES1/EP3, which can be explained that the molecular weight (for DGEBA, the molecular weight is twice of epoxy equivalent) of EP1 and EP2 was close to each other and smaller than EP3 (Figure 3c). In conclusion, the small molecules in EP mainly affected the swelling process, while, the epoxy equivalent mainly affected R_D and dissolution time.

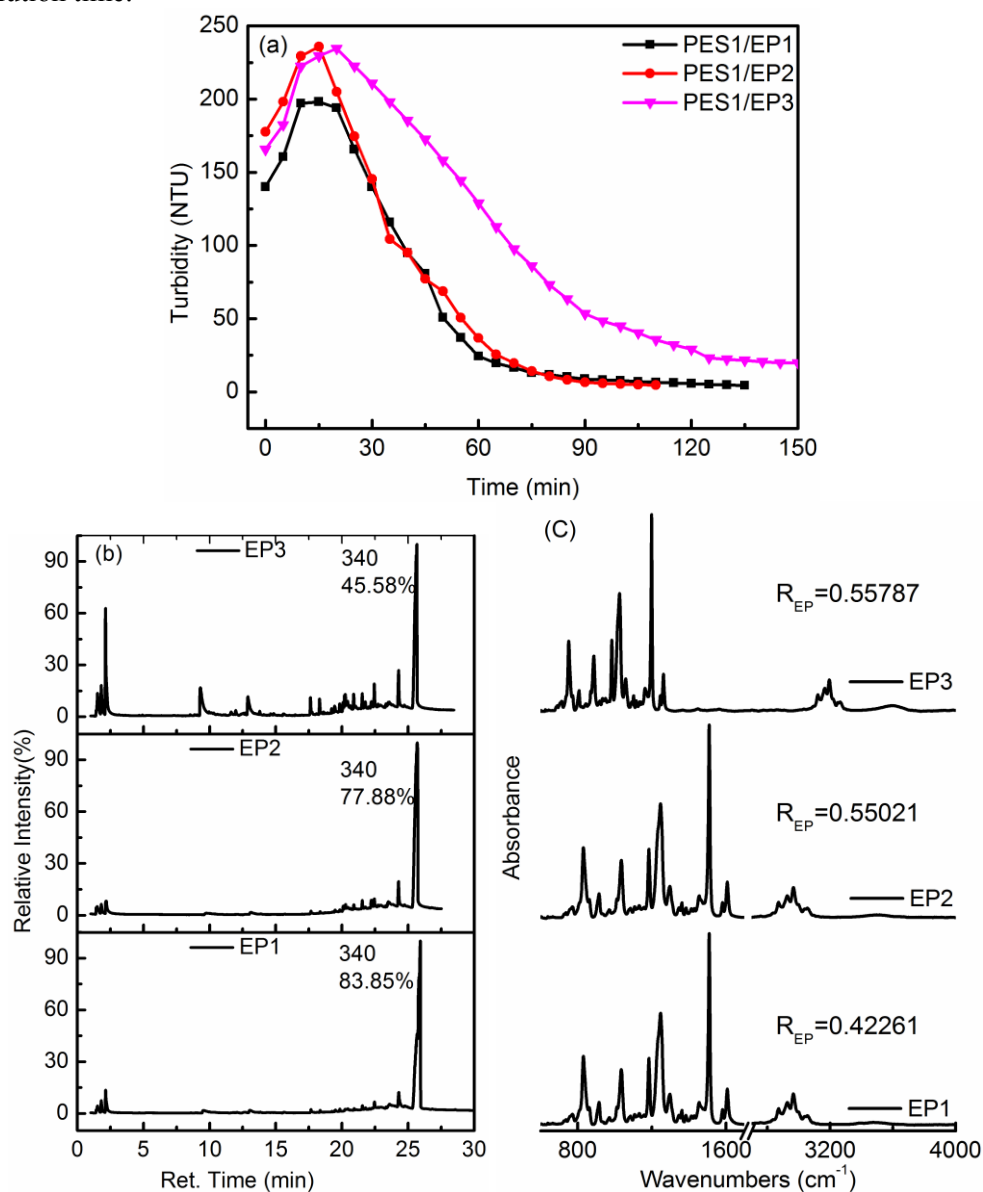


Figure 3. Turbidity versus time for PES/EP systems (PES 0.1 wt%) at 120 °C (a)The influence of EPs on dissolution behaviour; (b) thermal volatiles detected as the TICs at 500 °C; (c) FTIR transmission spectra of three types of EPs and the relative content of epoxy group (R_{EP}).

3.3. The influence of moisture

In order to study the influence of moisture absorption of PES on dissolution, PES1/EP1 and undried PES1/EP1 systems were chosen, as shown in Figure 4.

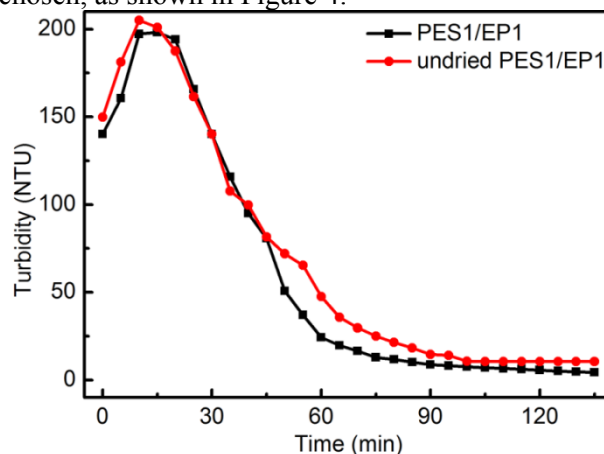


Figure 4. Turbidity versus time for PES and undried PES/EP systems (PES 0.1 wt%) at 120 °C.

The turbidity values of PES1 were bigger than that of undried PES. Based on ISO62 (equilibrium 23°C/50% r.h.), the moisture absorption of PES1 was 1.00%. This moisture occupied the free volume of PES, and prevented EP oligomer molecules diffusing into PES. Therefore, PES should be dried before use.

3.4. The influence of dissolution temperature

Temperature has an important effect on dissolution process. In order to observe the dissolution process of PES in DGEBA oligomer at different temperature clearly, PES1/EP1 with wt0.1% PES was prepared. With the increasing of temperature, R_s and R_D both increased, and the time of swelling and dissolution reduced. In detail, from 100°C to 120°C, the above values changed significantly, and from 100°C to 120°C, and the above values changed slightly, as shown in Figure 5. These results showed that the swelling and dissolution process of PES speeded with temperature increased, this may be due to an increase in temperature corresponded to faster motion of the molecules, and produce a certain volume expansion, while, when temperature up to 120°C, there were almost no variation of molecule motion and volume. Therefore, the dissolution temperature was chosen 120°C.

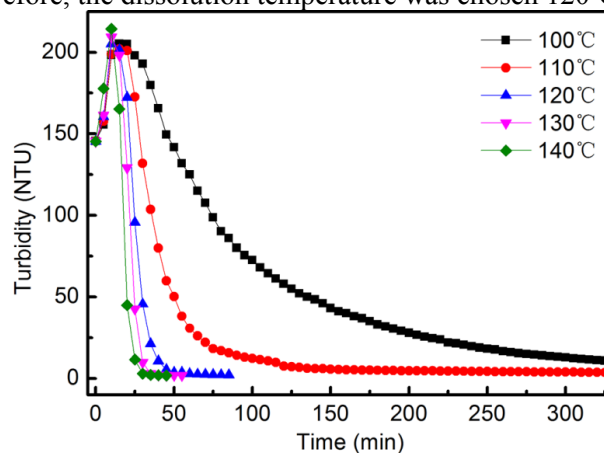


Figure 5. Turbidity versus time for five PES1/EP1 system at different temperature (PES 0.1wt%).

3.5. The influence of solution concentration

The relationship between turbidity and concentration (shown in Figure 6), can be used to characterize the dissolving capacity of PES in EP oligomers. The turbidity values of final steady state (turbidity values became stable) increased with the concentration increasing. There was no an abrupt change of turbidity in every system except PES1/EP3, therefore, the maximum solubility of PES was not reached. Sample with higher PES content could not be reached because the solution became too viscous to stir and measure. For PES1/EP3 system, when PES content was larger than 4%, the turbidity increased rapidly. This indicated that the solvents may be need for EP3 to dissolve PES. These values of turbidity of different systems can be used to determine the final dissolution state.

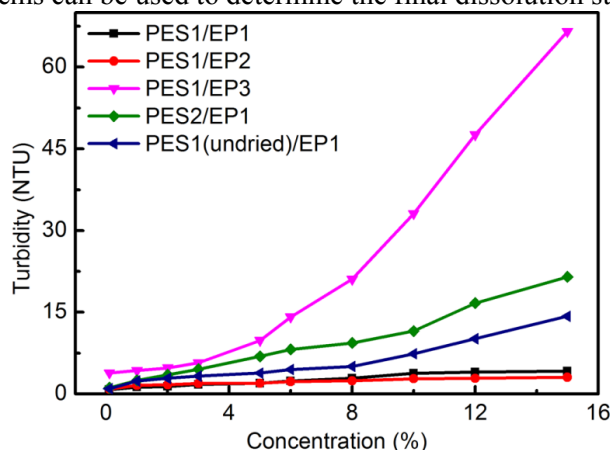


Figure 6. Turbidity versus PES concentration for five PES/ EP systems at the final steady state.

3.6. Thermodynamic compatibility

In fact, DSC has been proposed to be a simple, rapid and effective method to evaluate the compatibility between PES and DGEBA epoxy oligomer[25]. As shown in Figure 7, only one T_g was found in different systems, what's more, T_g of mixture located between T_g of PES and T_g of EPs. These results showed that the system composed by PES and EP was thermodynamic compatibility.

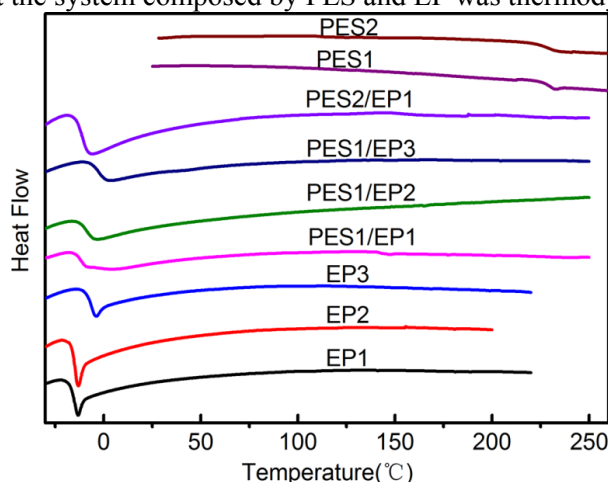


Figure 7. DSC curves of different DGEBA and system (PES 15 wt%).

4. Conclusions

It was demonstrated that turbidity can be used to characterize the dissolution behavior of PES in DGEBA epoxy oligomer. Different systems had same dissolution behavior but different R_s and R_D ; what's more, R_s and R_D can be used to compare the dissolubility of different systems. For PES, the influence of particle size and hydroxyl content was more important than that of molecular weight. Moisture could occupy the free volume of PES and effect dissolving process. In order to improve the

dissolubility of PES, it's necessary to decrease the particle size, increase the hydroxyl content, and dry PES before dissolution. EPs with higher molecular weight had smaller R_s and R_D . Melt method is suitable for EPs with lower epoxy equivalent. The turbidity values at the final steady state increased linearly, with the increasing of PES concentration. DSC curves of different system had only one T_g , the result showed that the mixture of PES and DGEBA epoxy oligomer was thermodynamic compatibility.

Acknowledgements

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References

- [1] Petrie E 2005 *Epoxy adhesive formulations* (New York: McGraw-Hill Education)
- [2] Karger-Kocsis J 2010 *Macromol. Chem. Phys.* **211** 1836-42
- [3] Fan M, Liu J, Li X, Cheng J and Zhang J 2013 *Thermochim. Acta.* **554** 39-47
- [4] Burger, N., Laachachi A, Mortazavi B, Ferriol M, Lutz M, Toniazio V and Ruch D 2015 *Int. J. Heat Mass Transfer* **89** 505-13
- [5] Lee J, Bhattacharyya D, Zhang M and Yuan Y 2015 *Composites Part B* **78** 515-9
- [6] Lee S E, Jeong E, Lee M Y, Lee M K and Lee Y S 2016 *J. Ind. Eng. Chem.* **33** 73-9
- [7] Yu Y, Zhang Z, Gan W, Wang M, Li S 2003 *Ind. Eng. Chem. Res.* **42**(14) 3250-6
- [8] Hodgkin J, Simon G and Varley R 1998 *Polym. Adv. Technol* **9**(1) 3-10
- [9] Yang G, Zheng B, Yang J P, Xu G S and Fu SY 2008 *J. Polym. Sci., Part A: Polym. Chem* **46**(2) 612-24
- [10] Paul D R and Yampol'skii Y P 1993 *Polymeric gas separation membranes* (Florida: CRC press)
- [11] Zhou X M and Jiang Z H 2005 *J. Polym. Sci., Part B: Polym. Phys* **43**(13) 1624-30
- [12] Linares A and R Benavente 2009 *Polym. J.* **41**(5) 407
- [13] Mimura K, Ito H and Fujioka H 2000 *Polymer* **41**(12) 4451-9
- [14] Yu Y, Wang M, Gan W, Tao Q and Li S 2004 *J. Phys. Chem. B* **108**(20) 6208-15
- [15] Del Saz-Orozco B, Ray D, Kervennic A, McGrail P and Stanley W F 2016 *Mater. Des.* **93** 297-303
- [16] Hameed N 2007 *Composites Part A* **38**(12) 2422-32
- [17] Xu Y J and Liu S B 2010 *Thermosetting Resin* **6** 016
- [18] Alessi S, Conduruta D, Pitarresi G, Dispenza C and Spadaro G 2011 *Polym. Degrad. Stab.* **96**(4) 642-8
- [19] Bonnaud L, Bonnet A, Pascault J, Sautereau H and Riccardi C 2002 *J. Appl. Polym. Sci.* **83**(6) 1385-96
- [20] Li X D, Lan A, Tang J W, Zhang Y, Gibril M E and Yu M H 2015 *Trans. Tech. Publ.* **1073** 282-5
- [21] Mazza M, Catana D A, Vaca-Garcia C and Cecutti C 2009 *Cellulose* **16**(2) 207-15
- [22] Khayet M and García-Payo M C 2009 *Desalination* **245**(1) 494-500
- [23] Li J F 2009 *Appl. Surf. Sci.* **255**(9) 4725-32
- [24] Sharma S, Dhiman N, Pathak D and Kumar R 2016 *Ionics* **22** 1865-72
- [25] Kumar R, Sharma S, Pathak D, Dhiman N and Arora N 2017 *Solid State Ionics* **305** 57-62