Comparative Study on Experimental and Kerner Model Predictions of Viscoelastic Properties of Polyamide 6/ Polyvinyl Alcohol Blends

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Abstract: The Polyamide 6 (PA6) / Polyvinyl alcohol (PVOH) blends of different compositions (80/20, 60/40 and 50/50) were prepared by melt mixing in a Haake Rheomixer. The selected blend systems (80/20 and 60/40) were modified with dicumyl peroxide (DCP) and tertiary butyl cumyl peroxide (TBCP). The dynamic mechanical properties of blends were systematically investigated with special reference to the effect of blend ratio and effect of presence of peroxide over a temperature range -20°C to 110°C. The effect of change in the composition of the polymer blends on tan δ was studied to understand the damping characteristics. The mean field theory developed by Kerner has been used to estimate the dynamic properties and the estimated values are compared with the experimental values. The loss tangent curve of the blend exhibited single transition peak corresponding to the glass transition temperature (T_g) of Polyamide 6. Kerner model was found to satisfactorily predict the viscoelastic properties of the blends with polyamide content in the range 50 to 80 wt% assuming PA6 as matrix and for all compositions except 80/20 assuming PVOH as matrix. The Kerner model predictions for the selected blend systems with peroxides are not satisfactory and the co-continuous morphology of the peroxide treated blends were revealed by SEM observations.

Keywords: Polymer blends, Dynamic mechanical analysis, Kerner model, Morphology, peroxide modified blends.

INTRODUCTION

Polyamide 6 (PA6) is a semi-crystalline thermoplastic polymeric material that has been widely used as engineering thermoplastic, well known for its processability, high tensile properties, abrasion and chemical resistance. PA6 is ductile at room temperature, but at high strain rates and low temperatures it becomes brittle [1]. Several blends of PA6 are reported in literature for specific applications. It is well known that PA6 has poor compatibility with other polymers because of its strong hydrogen bonding characteristics [2]. The miscibility of different polyamide based blends such as aliphatic/aromatic Polyamides, Nylon 6/ Nylon 66, Poly (ethylene-*co*-vinyl alcohol)/Nylon 6, 12 blends has been established by several authors from last five decades [3-6].

Polyvinyl alcohol (PVOH) is a transparent, flexible, biodegradable polymer known for its good gas barrier properties and low cost. PVOH cannot be used as a thermoplastic polymer due to its high water absorption capacity and week thermal stability. However, PVOH can be used as a modifier to other polymers through melt blending process. Miscible blends of PA6 and PVOH has been extensively studied by several groups during the last fifteen years. Most of the previous works on PA6/PVOH blends is focused on biodegradability [7], miscibility [8], and isothermal crystallization [9]. It has been reported that Ethylene vinyl alcohol (EVOH) in presence of peroxide is likely to form cross-links [10]. Hu *et al.* have used in situ cross-linking using dicumyl peroxide to control the dispersion phase morphology and to improve the interfacial adhesion between the components in Nylon 11/EVOH blend [11].

The dynamic mechanical test can provide insight into various aspects of material structure besides being a convenient measure of polymer transition temperatures. The computational modeling based on the mean field theories developed by Kerner can be applied to predict the dynamic viscoelastic properties of polymer blends [12, 13]. Recently Ishak *et al.* studied the mechanical properties of protein based polymer blends and predicted the values using Kerner and Hashin equation [14]. Greenwood *et al.* used Kerner's equation to predict elastic and flexural moduli of polyethylene based conductive blends [15]. In the present investigation, blends of PA6/PVOH in the composition range 0 to 50 wt% PVOH were prepared by melt mixing with and without peroxides (dicumyl peroxide - DCP and tertiary butyl cumyl peroxide - TBCP). The viscoelastic behavior of the resulting blends was characterized by DMA. The computational model based on the mean- field theories developed by Kerner is applied to predict the viscoelastic properties of polymer blends. The main purpose of the present study is to analyze the dynamic mechanical properties of PA6/PVOH blends with and without peroxides and

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examine the validity of Kerner model to predict these properties.

EXPERIMENTAL

Materials

Polyamide 6 was supplied by Gujarat State Fertilizers and Chemicals Ltd, Vadodara, Gujarat India. Polyvinyl alcohol was supplied by S D Fine Chemicals Ltd, Mumbai, India. Di cumyl peroxide (DCP) and tertiary butyl cumyl peroxides (TBCP) were procured from Qualigens, India and Sigma-Aldrich respectively. TBCP is a liquid while DCP is in pellet form at ambient conditions.

Preparation of Blends and Test Specimens

PA6 and PVOH were pre-dried in a hot air oven for about 24h at 100°C and subsequently melt mixed at 220°C in a Haake Rheomix internal mixer fitted with roller rotors operating at 40 rpm. PA6 was introduced first to the internal mixer and PVOH was added after 5 minutes to ensure uniform mixing. To study the effect of addition of peroxides in PA6/PVOH blends, the selected blend composition namely 80/20 and 60/40 were prepared by employing 2 Phr of DCP or TBCP. In case of blends with DCP, 2 phr of DCP was added to the mixer at the eighth minute, whereas in case of blends with TBCP, the peroxide was added along with PVOH. The blend in melt state from the mixer was cooled and shredded into granules. The composition and designation of blend systems are shown in Table **1**.

CHARACTERIZATION

The DMA studies were conducted using TA Instruments Model Q 800 DMA at a constant frequency of 1Hz and strain amplitude of 15μm in tension mode deformation. The blend test specimens in the form of rectangular films (30mm×3mm×0.1mm) were prepared by compression molding at 230°C. The test temperature was increased from -20°C to 110°C with a heating rate of 5°C/min under liquid nitrogen flow. The SEM of tensile fractured samples was obtained using Jeol JSM-6390 scanning electron microscope.

RESULTS AND DISCUSSIONS

Dynamic Mechanical Analysis

DMA is based on oscillatory disturbances, such as sinusoidal strains, to create resonance with molecular motions. The DMA is widely used to study the glass transition temperature (T_g), viscoelastic properties of polymers and miscibility of polymer blends. The viscoelastic parameters are defined by equation (1) and (2).

$$E^* = E' + iE'' \quad (1)$$

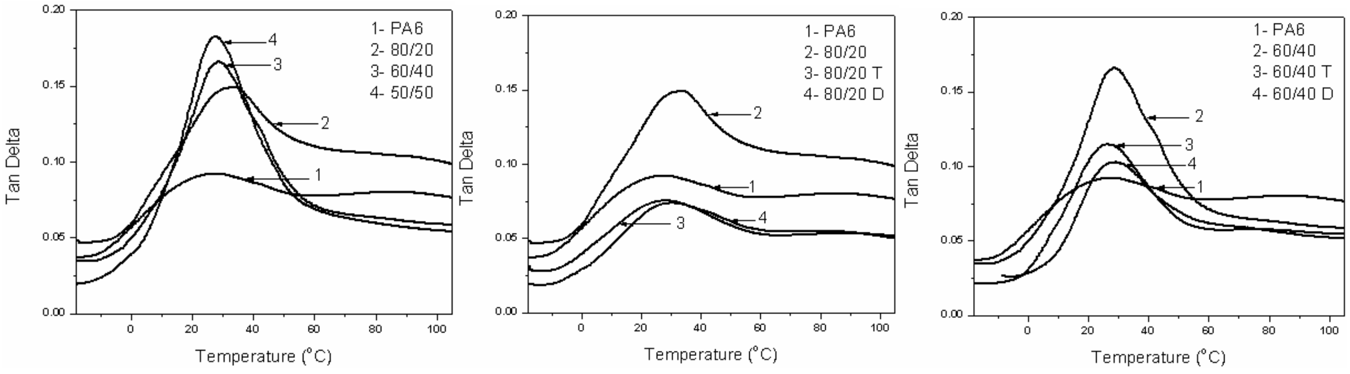
$$\tan\delta = E' / E'' \quad (2)$$

where E^*, E' and E'' are complex, storage and loss moduli respectively. Tan δ, the loss tangent or loss factor reflects the magnitude of mechanical loss and is associated with the motion ability of polymer chain segments [16, 17].

Typical DMA curves of PA6/PVOH blends, with and without peroxides are shown in Figure **1a**, **b** and **c**. The T_g values corresponding to peak values (tan δ) of PA6 and the blends are listed in Table **2**. The loss tangent curve of the blend exhibited single transition peak corresponding to the glass transition temperature (T_g) of Polyamide 6. The shift in the T_g values upon the addition of the PVOH especially at higher concentration of PVOH may be due to enhanced chain mobility of

Table 1: Blend Composition and Designation

PA6 (wt%)	PVOH (wt%)	DCP (phr)	TBCP (phr)	Designation
100	0	-	-	100/0
80	20			80/20
80	20	2	-	80/20 D
80	20	-	2	80/20 T
60	40	-	-	60/40
60	40	2	-	60/40 D
60	40	-	2	60/40 T
50	50	-	-	50/50



a b c

Figure 1: Tan δ curve of (**a**) PA6/PVOH blends (**b**) and (**c**) PA6/PVOH blends with Peroxide.

Table 2: T_g of PA6/PVOH Blends from DMA Studies

PA6/PVOH blends		PA6/PVOH/Peroxide blends	
Blend	**T_g °C (Tan δ max)**	**Blend**	**T_g °C (Tan δ max)**
100/0	26.83	80/20 D	28.17
80/20	29.98	80/20 T	29.24
60/40	28.70	60/40 D	25.32
50/50	27.16	60/40 T	26.56

polyamide 6 due to the plasticizing action of the flexible PVOH phase. It is believed that higher the tan δ max the greater the mechanical losses. These losses are related to high energy input required for the motion of the molecular chains of the polymer as the transition is being approached [18].

Prediction of Viscoelastic Behavior by Kerner's Dispersed Phase Model

Kerner [14] developed the mean field theory and introduced two models (i) the dispersed phase model and (ii) co-continuous phase model to predict the viscoelastic properties of polymer blends. The dispersed phase model assumes one of the components in the blend to be the matrix and others to be dispersed inclusion. Co-continuous phase model assumes neither of the components to be the matrix but approximates a co-continuous structure. Kerner's dispersed phase model for predicting the shear modulus of a polymer blend is as follows.

$$\frac{G^*}{G_m^*}=\frac{\sum_{i=1}^{n}\frac{G_i^*\phi_i}{[(7-5\upsilon_m)G_m^*+(8-10\upsilon_m)G_i^*}+\frac{\phi_m}{15(1-\upsilon_m)}}{\sum_{i=1}^{n}\frac{G_m^*\phi_i}{[(7-5\upsilon_m)G_m^*+(8-10\upsilon_m)G_i^*}+\frac{\phi_m}{15(1-\upsilon_m)}} \tag{3}$$

where *i* is 1, 2, 3…….*n* (number of dispersed-phase components), G^* is the shear modulus of the blend, G_m^* is the shear modulus of the matrix, G_i^* is the shear modulus of the dispersed-phase component, υ_m is the Poisson ratio of the matrix, ϕ_i is the volume fraction of the dispersed-phase component, and ϕ_m is the volume fraction of the matrix. The Kerner equation for a binary blend of viscoelastic materials can be adapted for the complex Young's modulus through the correspondence principle and the relation, $E^*=2(1+\upsilon^*)G^*$ where $\upsilon^*=\upsilon'\upsilon''$ is the viscoelastic Poisson ratio [17]. Here υ^* is assumed as υ' (a real quantity), that is the elastic Poisson ratio. The transformed equation is represented as follows:

$$\frac{E^*}{E_m^*}=\gamma\frac{(1-\phi_i)E_m^*+\beta(\alpha+\phi_i)E_i^*}{(1+\alpha\phi_i)E_m^*+\alpha\beta(1-\phi_i)E_i^*} \tag{4}$$

Where

$$\alpha=2(4-5\upsilon_m)/(7-5\upsilon_m)$$
$$\beta=(1+\upsilon_m)/(1+\upsilon_i)$$
$$\gamma=(1+\upsilon)/(1-\upsilon_m)$$

υ = Poisson ratio of the blend,

υ_m = Poisson ratio of the matrix,

υ_i = Poisson ratio of the dispersed inclusion.

The Poisson ratio (υ) of polymers generally varies from 0.32 to 0.5 (glassy plastic to rubbery zone). Its

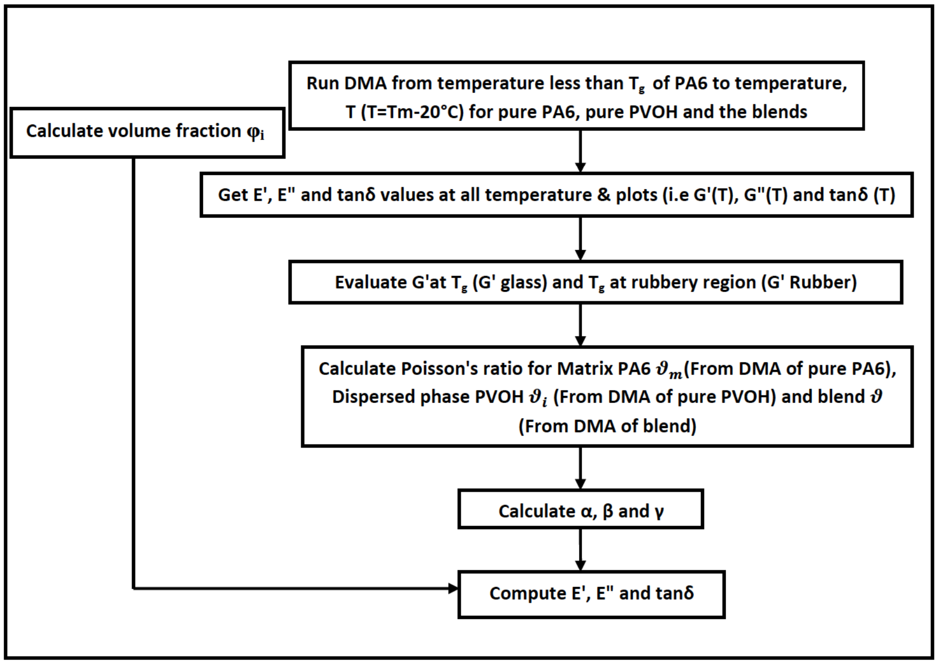


Figure 2: Flow chart showing computational protocol to estimate E', E" and tan *δ* values from DMA.

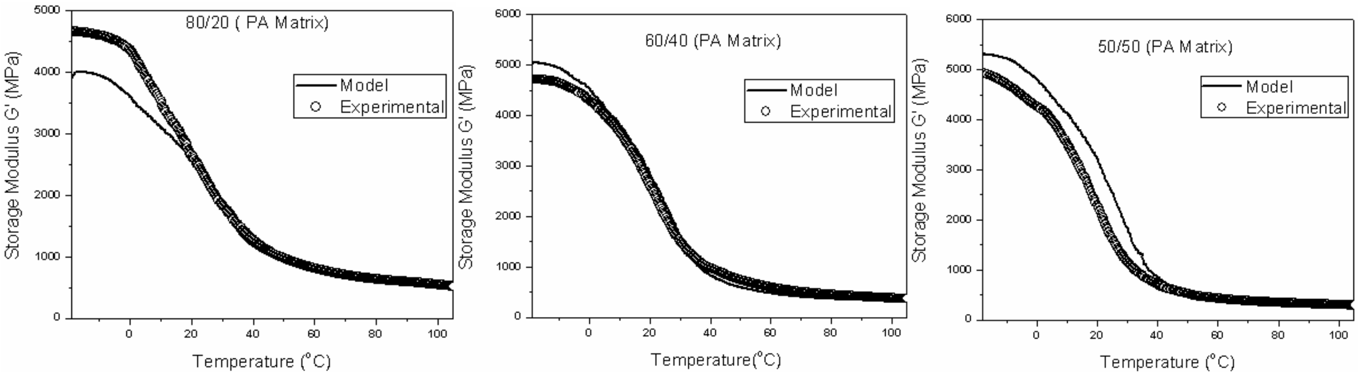
variation with temperature can be calculated by means of Mazich equation [19]

$$\upsilon(T)=\frac{0.17[\log G'_{glass}-\log G'(T)]}{\log G'_{glass}-\log G'_{rubber}}+0.39 \qquad (5)$$

For the PA 6 component, Poisson ratio may be taken as 0.39 up to its T_g, and calculated using Equation (5) when temperature is higher than T_g.

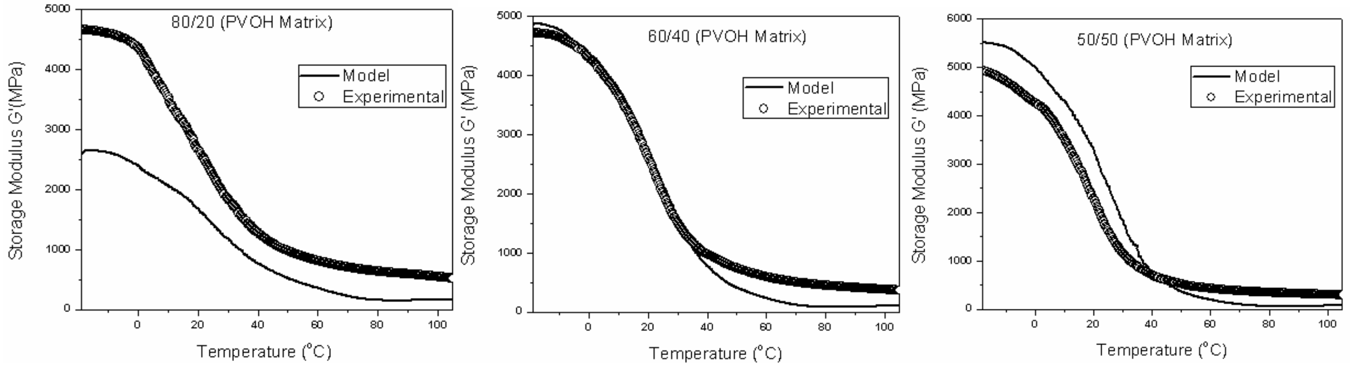
The values of E', E'' and tan δ of PA6/PVOH blends can be computed using the model as shown in the flow chart (Figure **2**). The predicted E' values of PA6/PVOH blends in the temperature range -20°C to 110°C are presented in Figures **3** and **4**. The comparison between the predicted and experimental values of the storage modulus E' as a function of temperature for PA6/PVOH blends using Kerner's dispersed phase model, considering PA6 as matrix is shown in Figure **3**. The predicted E' values for the PA6/PVOH blends are concordant with the experimental data in the entire temperature range. However, when PVOH is considered as matrix (shown in Figure **4**) we can see significant difference in E' among the experimental and predicted values of E' and in particular the deviation is considerable in 80/20 blend.

Figure **5** shows the comparison between experimental and predicted data of storage modulus PA6/PVOH 80/20 blends with TBCP assuming PA6 (Figure **5a**) and PVOH (Figure **5b**) as matrix. It can be



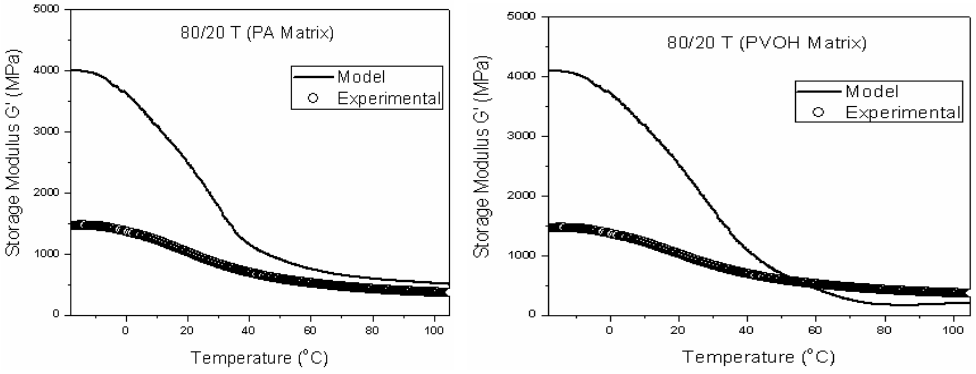
a **b** **c**

Figure 3: Comparison between the experimental and predicted data of storage modulus for PA6/PVOH.
a) 80/20, **b**) 60/40 and **c**) 50/50 blends using Kerner's dispersed phase model considering PA6 as matrix.



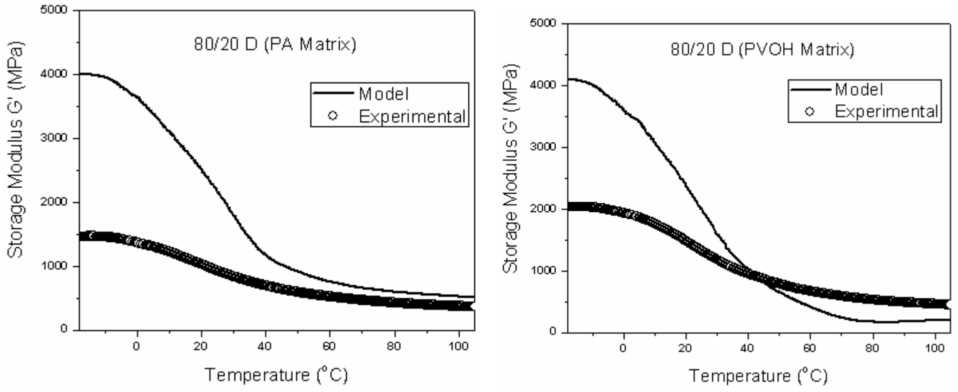
a **b** **c**

Figure 4: Comparison between the experimental and predicted data of storage modulus for PA6/PVOH. **a**) 80/20, **b**) 60/40 and **c**) 50/50 blends using Kerner's dispersed phase model considering PVOH as matrix.



a **b**

Figure 5: Comparison between the experimental and predicted data of storage modulus of PA6/PVOH 80/20 blends with TBCP using Kerner's dispersed phase model **a**) PA6 assumed as matrix and **b**) PVOH assumed as matrix.

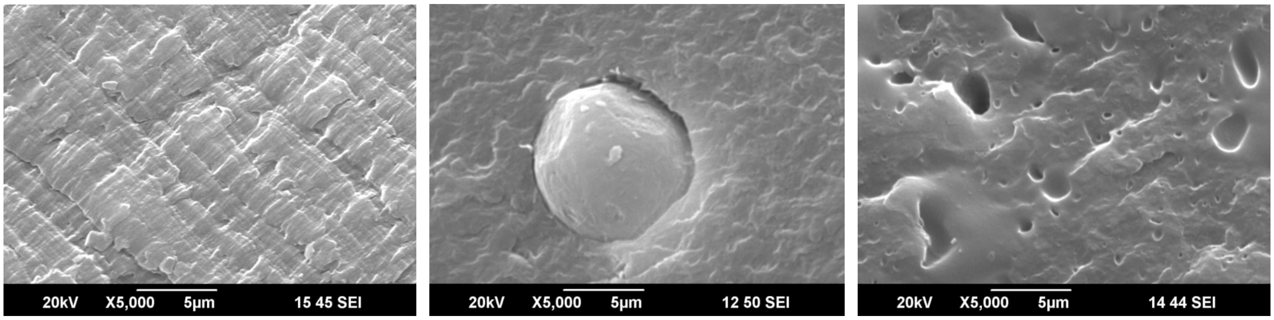


a **b**

Figure 6: Comparison between the experimental and predicted data of storage modulus of PA6/PVOH 80/20 blends with DCP using Kerner's dispersed phase model **a**) PA6 assumed as matrix and **b**) PVOH assumed as matrix.

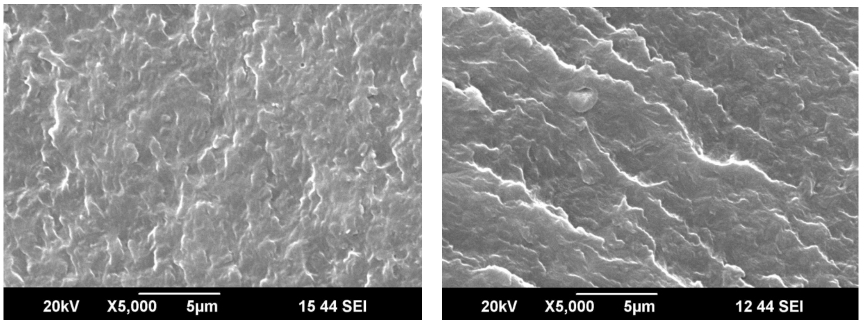
seen that the differences between predicted and experimental E' values are considerable and predicted values of E' are higher than the experimental values irrespective of whether PA6 or PVOH is assumed as matrix. Similar observations are made when DCP used as co-cross linking agent as shown in Figure **6a** and **b**.

The blends with peroxides showed obvious differences between experimental and predicted data. The Kerner model equations used in this study are valid for only a system in which one phase is dispersed in another continuous (matrix) phase, thus the failure in predicting the viscoelastic properties in blends with peroxides



a **b** **c**

Figure 7: SEM images of PA6/PVOH blends (**a**) 100/0, (**b**) 80/20 and (**c**) 60/40.



a **b**

Figure 8: SEM images of PA6/PVOH blends with peroxides **a**) 80/20 D **b**) 80/20 T.

may be attributed to a new type of blend morphology, which is different from dispersed phase.

Morphology

The morphological studies of PA6/PVOH blends of different composition were conducted by SEM analysis of tensile fractured surfaces. In the SEM image of PA6 (Figure **7a**) the rough texture of the micrographs reveal the crystalline character of PA6. The SEM micrographs of PA6/PVOH showed partial compatibility. In case of 80/20 (Figure **7b**) the PVOH clustered together and formed big agglomerates with spherical shape, showing the distinct boundaries that separate the PVOH agglomerate and PA6 matrix. The agglomerate formation is the evidence for the increased interfacial tension of PA6 and PVOH components [20]. The small holes were present in the matrix in case 60/40 blends (Figure **7c**) because of phase separation during tensile fracture. This phenomenon indicates that the interfacial adhesion between PA6 and PVOH is not sufficient [21].

However, the 80/20 blends with the addition of 2phr peroxides (Figure **8a** and **b**) showed smoother morphology without any holes and agglomeration. The resulting smoother morphology is due to successful stress transfer across phases, indicates the compatibility or strong interaction between PA6 and PVOH phases which leads to the uniform dispersion of PVOH in PA6. Thus it may be concluded that the peroxides can act as co cross-linking agent, which connects the boundaries of two polymers and form compatible blend as we expected [22].

The SEM observation of the blends without peroxides confirms the result obtained from Kerner's dispersed phase model. The results indicate that the Kerner's dispersed phase model with PA6 as matrix material can satisfactorily predict the viscoelasticity of polymer blends. Probably co-continuous phase model is satisfactory for those blends with peroxides.

CONCLUSIONS

Predictions of Kerner model, which assumes PA6 as matrix and PVOH as inclusions are found to be satisfactory in the case of 80/20, 60/40, 50/50 PA6/PVOH blends but not for PVOH rich blends. The addition of DCP and TBCP during melt mixing resulted in change of blend morphology, probably due to chemical reaction between peroxide radicals and blend components. The Kerner model failed to predict the viscoelastic properties of peroxide modified PA6/PVOH blends. The SEM revealed co-continuous phase morphology for peroxide treated PA6/ PVOH blends. Bandyopadhyay *et al.* [23] have proposed packed grain model according to which, co-continuous structure is likely to exist in certain blends where neither of the components to be the matrix. Hence a co-continuous structure of the two can be tried to predict experimental data on peroxide treated PA6/PVOH blends for which a co-continuous morphology was revealed by SEM observations.

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