PVDF/PMMA/Basalt Fiber Composites: Morphology, Melting and Crystallization, Structure, Mechanical Properties, and Heat Resistance

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ABSTRACT: This paper is to study the effect of basalt fiber on morphology, melting and crystallization, structure, mechanical properties, melting and crystallization of PVDF/PMMA composites using scanning electron microscopy (SEM), X-ray, differential scanning calorimeter (DSC), dynamical mechanical analysis (DMA), etc. Basalt fiber may disperse well in PVDF/PMMA matrix and form compact fiber network, and this makes tensile and flexural strength of fiber reinforced PVDF/PMMA composites get to the maximum value of 62 and 102 MPa, respectively. However, the mechanical properties begin to decrease when basalt fiber content exceeds 20 wt %. The α and β phase of PVDF can coexist in composites, and basalt fiber and PMMA can induce β phase of PVDF. The melting temperature of PVDF in composites is kept unchanged, but the degree of crystallinity of composites increases as basalt fiber content increase, and then declines when fiber content exceeds 20%. The DSC results confirm that the nucleation ability of PVDF is enhanced by basalt fiber. Also, the heat resistance of PVDF/PMMA composite is improved from 133 to 146.1°C due to basalt fiber. The DMA shows that basalt fiber increases the storage modulus of PVDF/PMMA composite, and the loss peak of PMMA increases from 116.1 to 130°C. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40494.

INTRODUCTION

As a member of fluororesin, poly (vinylidene fluoride) (PVDF) has many merits, such as high degree of crystallinity, excellent mechanical properties, weather resistance, long-term application between -40 to 150°C and lower processing temperature than PTFE, and those traits make PVDF widely use in scientific and industrial fields: Sensors, actuator, piezoelectric materials, solar cells, medicine, robotics, food beverage, coatings, and so on.[1–3]

However, the very low surface energy and high cost limit PVDFs application, therefore, many researchers have tried their best to elevate PVDF surface energy by the incorporation of polar groups into PVDF molecules or blending with polar polymers using grafting, copolymerization, solution blending, and melting blending.[2] Among these methods, the melting blending method is believed to be the most convenient and cost-effective method to achieve the required properties, and this method not only decreases PVDF production costs, but also gives PVDF composites special function and expands potential application fields.

For PVDF blend, the most widely used polar polymer is PMMA since PMMA can be compatible with PVDF at random mass ratio.[4–9] At the same time, the brittleness of PMMA is also solved by blending with PVDF.[6] Additionally, PMMA may also decrease the degree of crystallinity of PVDF. If PMMA content exceeds 50%, a completely amorphous PVDF/PMMA composite is obtained.[8] Huang et al.[7] studied PVDF/PMMA composites and found water contact angle was decreased from 103° to 88° as PMMA content increased from 20 to 80%. Mohamadi et al.[9] observed that 20, 30, and 40% of PMMA could induce the formation of β phase of PVDF, but as temperature increased, the β phase would completely transform into α phase. Freire et al.[10] observed that the crystallization temperature of PVDF was decreased due to the addition of PMMA; also, the nonisothermal crystallization process was slowed down. Pawde et al.[6] demonstrated that the tensile strength of PVDF/PMMA blend increased largely as PVDF content increased and got to the maximum value of 38.665 MPa within 50% PVDF, but the Young's modulus of the PMMA/PVDF blend only showed a

little increase. Lee et al.[11] found 20% PMMA could influence the crystallization of α and β phase of PVDF. Literature reported that the blend containing 70 wt % of PVDF and 30 wt % of PMMA was thought to be the best because it had desirable physical and optical properties: Gloss, hardness, and solvent resistance,[4] but the mechanical property was needed to be improved further if such blend was used as structural materials.[10]

In the past 10 years, basalt fiber, made of basalt rock, has been applied widely in reinforced material fields and became one of the most important and effectively enhancing fibers along with polyamide fiber, aramid fiber, carbon fiber, and glass fiber. Among these fibers, basalt fiber, owing to high modulus, fire resistance, and excellent acid/alkali resistance, has been successfully used in polymer composites. The noticeable merits of basalt fiber are the excellent heat resistance and mechanical property. Experiments demonstrated that basalt fiber could withstand as high as 600°C without weight loss and reduction in mechanical property.[11–16] Botev et al.[17] observed that the tensile strength of polypropylene (PP)/basalt fiber composite was elevated from 29.5 to 35.5 MPa and the izod impact strength was improved from 6 to 32.8 J m^{-1}. Wei et al.[18] mentioned that interfacial property of basalt fiber-reinforced epoxy composite was still better than that of glass fiber-reinforced epoxy composite after sea water treatment. Chairman et al.[19] observed that the tensile strength of basalt fiber reinforced epoxy composites reached 340 MPa or so, 23% higher than that of glass fabric-reinforced epoxy composites, and the compression strength of basalt fiber composite was 43.8% higher than that of glass fiber composites. Liu et al.[20] presented the tensile strength and flexural strength of basalt fiber reinforced polylactide (PLA) composite got to 110.2 and 147.8 MPa, respectively. Also, the degree of crystallinity was also observed to decline due to the basalt fiber, but the melting temperature of PLA did not show changes by and large. Zhang et al.[21] reported that basalt fiber could improve tribological properties of polyimide.

So in this paper, in the light of PVDF/PMMA (70 : 30) blend, we introduce basalt fiber into PVDF/PMMA blend to improve mechanical property of composite, concurrently, the effect of basalt fiber on morphology, zero shear viscosity, melting/crystallization behaviors, structure, and heat resistance of PVDF/PMMA composite is also investigated using SEM, rheometer, DSC, Vicat softening temperature meters, DMA, etc.

EXPERIMENTAL

Materials and Preparation
PVDF (21216) was bought from Solvay Corporation of USA; PMMA (CM205) was bought from Chi Mei Industrial Factory; basalt fiber with the diameter of 7 μm and the length of 3 mm was supplied by Southeast University of China, and it was coated with γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH560) during production process in order to improve the compatibility between basalt fiber and polymers.[22]

Before use, PMMA and basalt fiber were dried in oven at 80°C for 12 h, and then PVDF, PMMA and basalt fiber were blended at 230°C using melt blending method. The mass ratio of PVDF

and PMMA was controlled to be 7 : 3 in all composites. Basalt fiber content in composites was 10, 20, and 30 wt %, respectively.

According to the standard of ISO 527-2:1993 and ISO 178/:2001, PVDF, PMMA and basalt fiber with certain mass ratio were injected into the sample with dimensions of 150 ×20 × 4 mm (tensile sample) and 80 × 10 × 4 mm (flexural sample) using an injection molding machine (HY500, Ningbo Haiying Plastics Machinery) with the injection pressure of 95 bars and holding time of 30 s. The three temperature regions from inlet to nozzle were 220, 225, and 230°C, respectively.

Characterization
The morphology observation of fracture surface of PVDF/PMMA/basalt fiber composites were carried out using a scanning electron microscope (JSM-5500LV, JEOL Japan Electronics) with an accelerating voltage of 20 kV. Firstly, composites were dipped into liquid nitrogen and fractured and then the fracture surface was coated with gold particles.

XRD experiments were performed at room temperature using a Rigaku D/max 2500VPC X-ray diffractometer in combination with an 18 kW rotating-anode generator operated at 40 kV and 200 mA and curved graphite crystal-filtered CuKa$_1$ radiation ($\lambda = 0.15406$ nm). The XRD data were collected from $2\theta = 5°$ to 30° and the scanning velocity was 4° min^{-1}.

Attenuated total reflection (ATR) infrared spectroscopy (Nicolet380, Thermo Fisher Scientific Corporation) was used to study PVDF structure. Each spectrum was obtained by performing 32 scans between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}.

The zero shear viscosity was measured on rheometer MARS III, produced by Thermo Company of Germany. The measuring temperature was controlled to be 240°C and shear rate ranged from 0.0001 to 1 s^{-1}.

The DSC Diamond of PE Corporation of America was used to investigate the melting and crystallization behaviors of PVDF/PMMA/basalt fiber composites. The weight of sample was 5–6 mg and all the DSC runs were carried out in nitrogen atmosphere to minimize the oxidative degradation.

For melting and crystallization temperature measurement, sample was heated from 25°C to 230°C at a heating rate of 10°C min^{-1}, held at 230°C for 10 min, and then cooled to room temperature at a cooling rate of 10°C using liquid nitrogen.

The degree of crystallinity X_c of composites could be calculated by the following equation:

$$X_c = \frac{1}{x} \times \frac{\Delta H}{\Delta H_m} \times 100\% \tag{1}$$

where ΔH was the actual melting enthalpy of sample; ΔH_m was the equilibrium melting enthalpy of PVDF (104.7 J g^{-1})[15]; x was the mass fraction of PVDF in composites.

According to the standard of ISO 527-2:1993 and ISO 178:2001, the tensile strength and flexural strength of PVDF/PMMA/basalt fiber composites were performed on material mechanical testing machine (Shenzhen SANS Company of China) and tensile speed
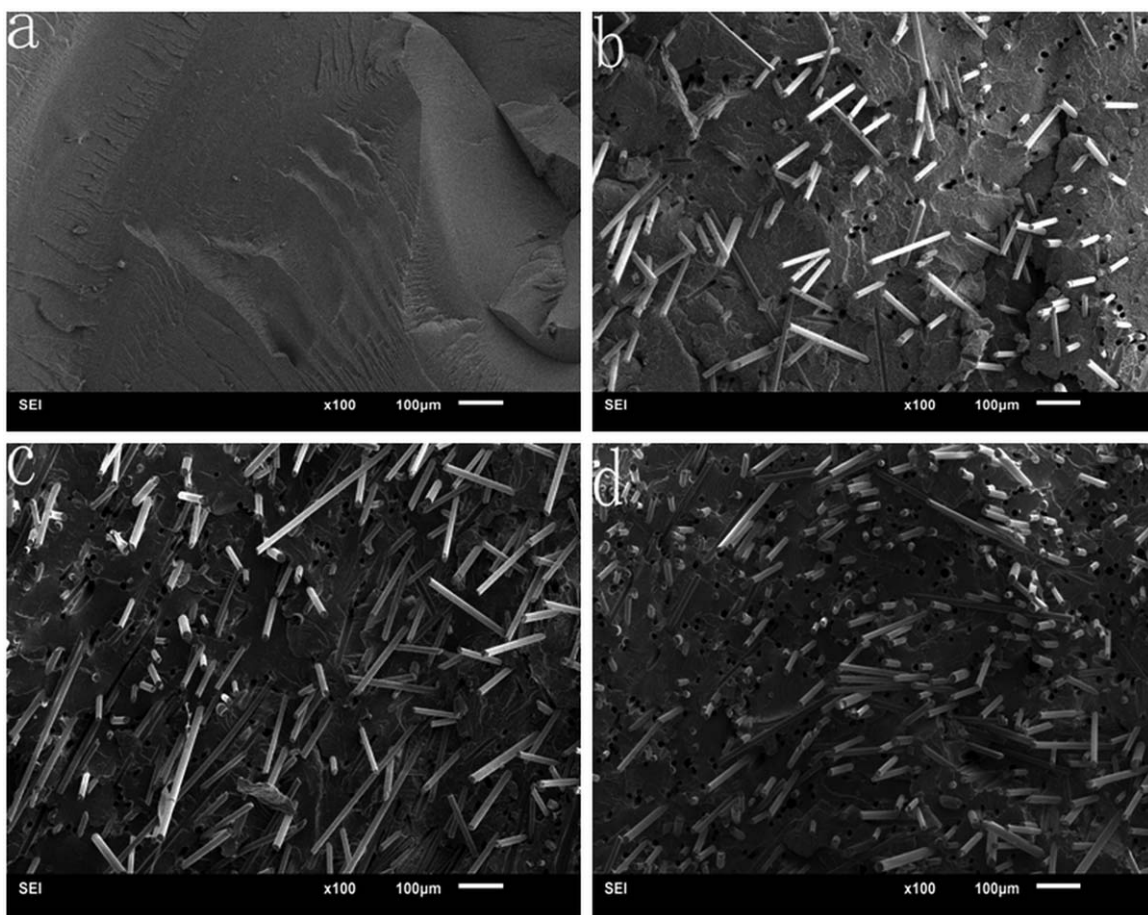
Figure 1. The SEM images of PVDF/PMMA/basalt fiber composites.

and flexural speed were 10 mm min^{-1}. The five samples for every group were measured and the average was obtained.

The heat resistance of PVDF/PMMA/Basalt fiber composites was assessed by the Vicat soften temperature (VST), which was carried out in vicat softening point meter of Shenzhen SANS Corporation of MTS, and the heating rate was 120°C h^{-1}. The three samples for every group were measured and the average was obtained.

The dynamical mechanical analysis was carried out in NETZSCH DMA242; samples were heated from 20 to 150°C at heating rate of 2°C min^{-1}. The fixed frequency was 1 Hz and the three-point bending mode was adopted.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the fracture surface morphology of PVDF/PMMA composites with different basalt fiber content. As can be seen [Figure 1(a)], the fracture surface of PVDF/PMMA composite is even and no obvious interface appears in matrix, which indicates PVDF could be miscible with PMMA. As 10 wt % basalt fiber is added into PVDF/PMMA composite [Figure 1(b)], it is observed that basalt fiber disperses well in polymer matrix by and large. In addition, some small pores are also observed in composites, this is due to basalt fiber is pulled out

from polymer matrix when composites are fractured. Importantly, near to these pores, there are considerable cracks in polymer matrix, as indicated by white arrow in Figure 2 [it is the magnified images of Figure 1(d)], and the formation of cracks may absorb lots of energy, which indicates that basalt fiber
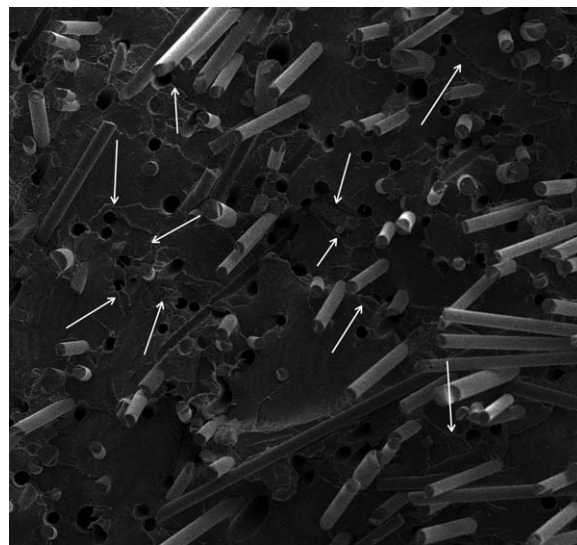

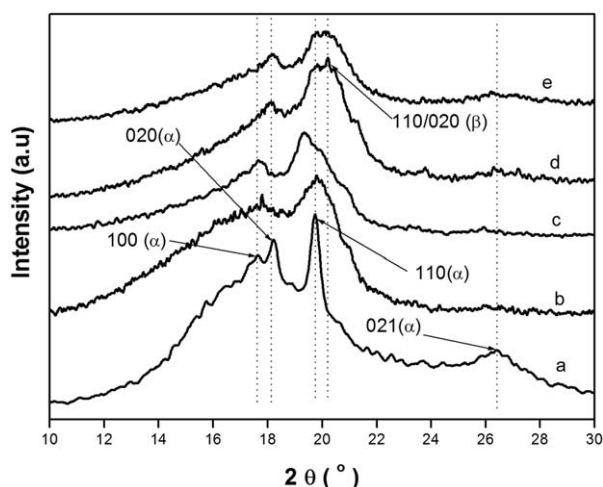**Figure 2.** The SEM images of PVDF/PMMA composites with 30% fiber.

Figure 3. XRD patterns of PVDF composite: (a) Neat PVDF, (b) PVDF/PMMA composite, (c) PVDF/PMMA composite with 10% basalt fiber, (d) PVDF/PMMA composite with 20% basalt fiber and (e) PVDF/PMMA composite with 30% basalt fiber.

reinforced PVDF/PMMA materials exhibited better mechanical property. When basalt fiber content increase further [Figure 1(c,d)], it is found that basalt fiber can contact with each other and form compact network, and such compact basalt fiber network is favorable for improvement in mechanical properties.

XRD and FTIR Analysis

Figure 3 shows the variation of crystalline structure of PVDF/PMMA composite as a function of basalt fiber content. As can be seen from Figure 3, neat PVDF presents the crystalline diffraction peaks at $2\theta = 17.4°$, 18.1°, 19.7°, and 26.3°, and those are attributed to the (100), (020), (110), and (021) planes of PVDF α phase.[23] The diffraction peak at 20.2° is ascribed to the (110/200) plane of PVDF β phase.[11] As PVDF is blended with PMMA, the diffraction peaks at $2\theta = 17.4°$, 18.1° are difficult to be detected by XRD, which indicated that regularity of PVDF α phase crystals began to decrease. Also, the diffraction peak of PVDF β phase started to appear at 20.2°, which indicates that PMMA could induce β phase of PVDF. When basalt fiber is added into PVDF/PMMA blend, the diffraction peaks position of composites did not change except for composites with 20% basalt fiber despite basalt fiber loadings. Importantly, the diffraction peak of PVDF β phase became apparent gradually with basalt fiber loadings. It suggests that basalt fiber, like PMMA, was also favorable to the formation of PVDF β phase.

To study the structure changes of PVDF further, the FTIR-ATR (attenuated total reflection) is used, and the results are shown in Figure 4. Characteristic vibration absorption bands of α and β phase of PVDF are identified and assigned in the light of literatures.[5,6,24] The vibration absorption peaks of 1257, 1149, 1074, and 799 cm^{-1} are ascribed to the α phase of PVDF, while the peaks at 1431, 1273, 877, and 840 cm^{-1} belong to the β phase of PVDF. It is clear that α and β phase of PVDF coexist over the whole ratio range. Additionally, it should be noted that some characteristic peaks of α phase was not observed in Figure 4, such as peaks at 766, 855, and 976 cm^{-1}.[6] The absence of these peaks indicates that PMMA or basalt fiber led to the
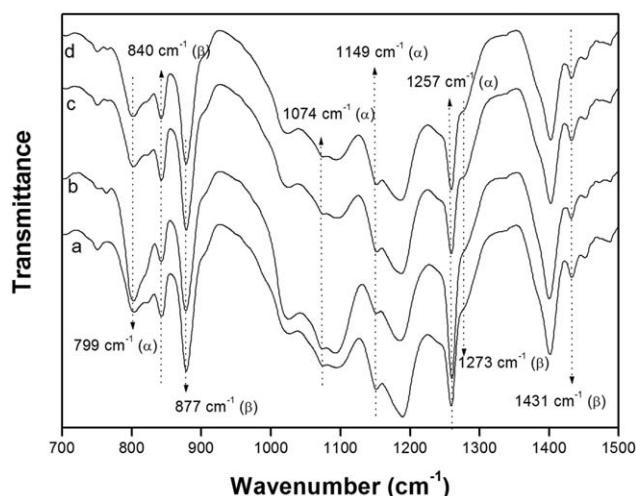

Figure 4. FTIR-ATR spectrum of PVDF composite: (a) PVDF/PMMA composite, (b) PVDF/PMMA composite with 10% basalt fiber, (c) PVDF/PMMA composite with 20% basalt fiber, and (d) PVDF/PMMA composite with 30% basalt fiber.

decline in regularity of PVDF α phase crystals, which agrees with XRD results. However, all peaks of β phase of PVDF are easy to be found, suggesting that PMMA or basalt fiber were favorable to the formation of β phase.

Rheological Property

For many polymers, the viscosity will gradually decrease as the shear rate increases, which is the typical feature of pseudo-plastic fluid. But at the very low shear rate near to zero, the viscosity will be constant basically, and this viscosity is defined as zero shear viscosity η_0. In nature, the η_0 can be used to measure the internal friction and is related to the microstructure and intermolecular interaction, and has nothing to do with shear rate or stress. These factors, such as strong molecular interaction force, entanglement and cross-linking will lead to the increase in η_0. Figure 5 exhibits the changes of apparent viscosity of PVDF/PMMA composites as a function of shear rate (0.0001 to 1 S^{-1}), the η_0 can be measured from the platform portion of every curve, and the according values of η_0 are
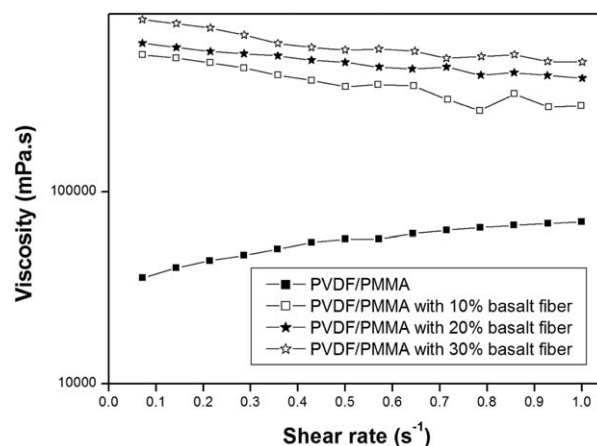

Figure 5. The changes of the apparent viscosity of PVDF/PMMA/basalt fiber composites as a function of shear rate.
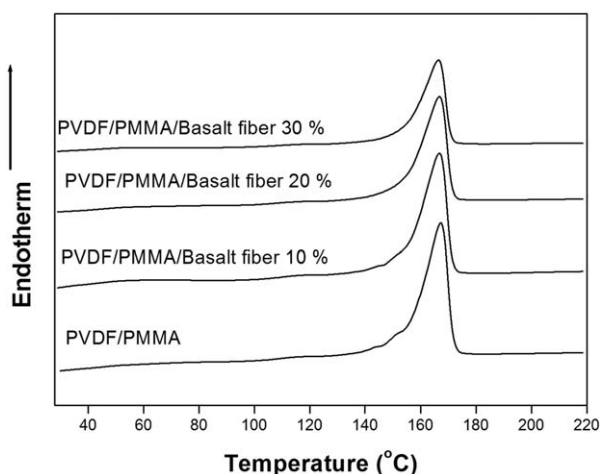
Table I. The η_0, T_m, T_c, and X_c of PVDF/PMMA/Basalt Fiber Composites

	PVDF/PMMA	PVDF/PMMA/ basalt fiber 10%	PVDF/PMMA/ basalt fiber 20%	PVDF/PMMA/ basalt fiber 30%
η_0 (mPa S)	4.4×10^4	5.7×10^5	6.1×10^5	6.5×10^5
T_m (°C)	167.4	167.1	166.9	166.8
ΔH (J/g)	40.2	37.8	36.4	29.0
X_c (%)	54.9	57.4	62.1	56.6
T_c (°C)	119.3	120.6	121.0	122.0
C_p (J/g K) (165°C)	4.346	3.443	3.203	2.513
Tensile strength (MPa)	37.2 ± 1.0	50.4 ± 1.4	62.4 ± 0.7	54.7 ± 0.5
Elongation at break (%)	24.2 ± 0.40	5.8 ± 0.16	5.4 ± 0.24	3.6 ± 0.33
Flexural strength (MPa)	40.7 ± 1.9	85.2 ± 2.0	101.7 ± 2.9	93.8 ± 1.5
VST (°C)	133 ± 0.24	136.9 ± 0.23	142.3 ± 0.16	146.1 ± 0.20

shown in Table I. The η_0 of PVDF/PMMA composites is observed to increase as basalt fiber content increases. The increasing in η_0 suggests that the internal structure of PVDF/PMMA composites changed due to the addition of basalt fiber. The reason for this, the authors think, is due to the following two factors: The first is the intermolecular interaction force between polymer and basalt fiber, and the second is the basalt fiber network. The KH560 includes many epoxy groups in its molecules, forming strong interaction with PMMA and PVDF, which bring inhabitance for movement of polymer. Concurrently, the excessive basalt fiber also produce the compact basalt fiber network, which acts as physical hindrance and effectively inhibits the movement of polymer molecular chain, as a result, the increase in η_0 is found. Also, the increasing in viscosity means that the processing properties of basalt fiber reinforced composites became poorer in comparison to PMMA/PVDF composite.

DSC Analysis

Figure 6 is the heating DSC curves of PVDF/PMMA composites with different basalt fiber contents and the heating rate is 10°C

min^{-1}. It is observed that melting temperature of PVDF in PVDF/PMMA composite is 167.4°C and decreases a little but indistinctively as basalt fiber content increases (as shown in Table I). However, the quantity of PVDF crystals is affected since the ΔH and X_c vary with basalt fiber. As shown in Table I, the degree of crystallinity X_c of PVDF firstly increases and gets to the maximum value (62.1%) at 20 wt % basalt fiber, and then decreases as basalt fiber content exceeds 20 wt %. The reason is possibly that the addition of basalt fiber can provide PVDF with more heterogeneous nucleation point and accelerate PVDF crystallization within 20 wt % basalt fiber, but the distance between basalt fibers starts to shorten and form compact network gradually as basalt fiber content exceeds 20 wt %, and such case can inhibit PVDF molecular chains movement and prevent PVDF chains from arranging and crystallizing into crystals, consequently, the X_c begins to decrease at above 20 wt % basalt fiber.

The variation of crystallization temperature T_c can be used to evaluate nucleation ability of PVDF. As shown in Figure 7 and Table I, PVDF exhibits its crystallization temperature T_c at

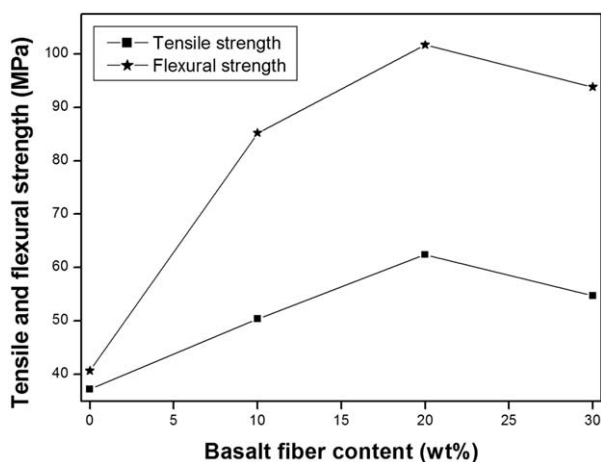**Figure 6.** The DSC heating curves of PVDF/PMMA/basalt fiber composite.
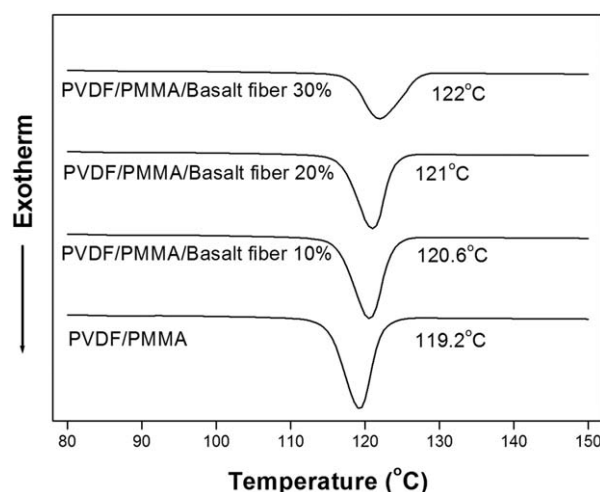
Figure 7. The DSC cooling curves of PVDF/PMMA/basalt fiber composite.

Figure 8. The mechanical properties of PVDF/PMMA/basalt fiber composites.

Figure 9. The changes of storage modulus as a function of temperature for PVDF composites. (a) PVDF/PMMA composite, (b) composite with 10% basalt fiber, (c) composite with 20% basalt fiber, and (d) composite with 30% basalt fiber.

119.3°C in PVDF/PMMA composite, lower than that of neat PVDF (139.84°C).[16] However, when adding basalt fiber into PVDF/PMMA composites, the T_c is found to increase from 119.3 to 122°C as basalt fiber content increase from 10 to 30 wt %, it indicates that nucleation ability of PVDF was enhanced. Such result seems to contradict to the above conclusion from degree of crystallinity X_c, where PVDF crystallization is inhibited at above 20 wt %. In fact, it is known that there is a competitive process between nucleation and crystal growth during crystallization process. Although the nucleation process of PVDF in composites is accelerated by basalt fiber, the crystal growth of PVDF is not promoted at higher content basalt fiber (>20 wt %). The reason is due to basalt fiber network causes PVDF chains to take more time and energy to shift to the crystal growth front and crystallize. As a result, the whole crystallization process begins to slow at above 20 wt % basalt fiber. Also, the degree of crystallinity starts to decrease.

Mechanical Properties

Figure 8 and Table I shows the effect of basalt fiber on tensile and flexural strength of composites. The tensile strength of PVDF/PMMA composite without basalt fiber is 37 MPa. When basalt fiber is introduced, the tensile strength of basalt fiber reinforced composites sharply increases to 62 MPa (20 wt % basalt fiber), and then it decreases to 55 MPa (30 wt % basalt fiber). In addition, the elongation at break of composites quickly decreases as basalt fiber content increases, which suggests that the toughness of composites began to decline. Similar to tensile strength, it is expected that flexural strength of composites increases as basalt fiber content increases, as shown in Figure 5. The flexural strength of composites increases from 41 to 102 MPa when basalt fiber content increases from 0 to 20 wt %, followed by a decrease to 94 MPa (30 wt % of basalt fiber).

It is well known that the mechanical properties of composites are determined by the fiber types, orientation and content, polymer type and the interface between polymer and fiber. At low content, basalt fiber can disperse well in composite and act as carrier of stress when composite is subjected to stress, and the stress can be transferred and dispersed from polymer matrix along with basalt
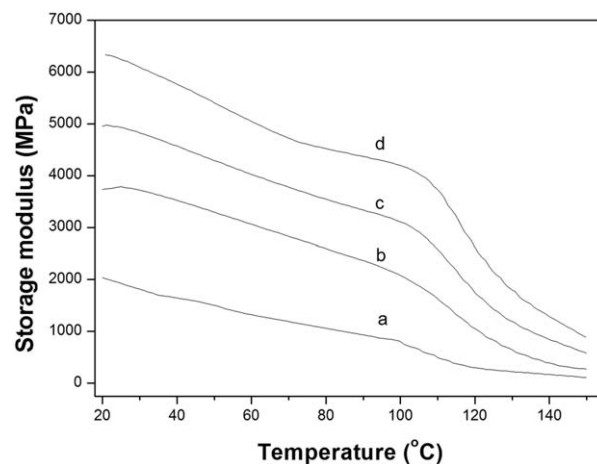
fiber. Additionally, as basalt fiber content increases, rigid basalt fiber will connect with each other and form compact network, which is helpful to the mechanical property of composite. As a result, the improvement of tensile and flexural strength of composites (below 20 wt % basalt fiber) is observed. However, when basalt fiber increases further, basalt fiber can not be wetted completely by polymer and the interface between basalt fiber and polymer starts to become poor, so the decline in mechanical property of composites is detected at above 20 wt % basalt fiber.

Heat Resistance

The heat resistance of materials can be evaluated by vicat softening temperature (VST), which is defined as the temperature of sample pressed into 1 mm depth using 1 mm^2 needle at a certain load and a certain temperature, and the higher the vicat softening temperature, the more excellent heat resistance of materials is. Table I shows the changes of vicar softening temperature of PVDF/PMMA composites with different content of basalt fiber. As basalt fiber content increases, the VST of composites increases linearly. In comparison with PVDF/PMMA composites (133°C), the VST of composites with 30 wt % basalt fibers (146.1°C) is elevated 13°C or so, which indicates rigid basalt fiber could improve heat resistance property of PVDF/PMMA composite. The reason are as follows: On the one hand, rigid basalt fiber has excellent thermal stability and shows no changes in dimension on heating, on the other hand, the strong interaction, entanglement with fiber and the fiber network can largely restrain the movement of polymer chains. In addition, the heat capacity (C_p) of every composite is measured at temperature of 165°C and the results are shown in Table I. It is found that the heat capacity of composites decreases as basalt fiber content increases; the reason for this is due to basalt fiber includes many kinds of metallic oxide. Such result means that composite with low heat capacity was more sensitive to caloric than composite with high capacity under identical conditions.

DMA Analysis

The viscoelasticity is another important property of polymer, which can be characterized by DMA. Storage modulus (E') is
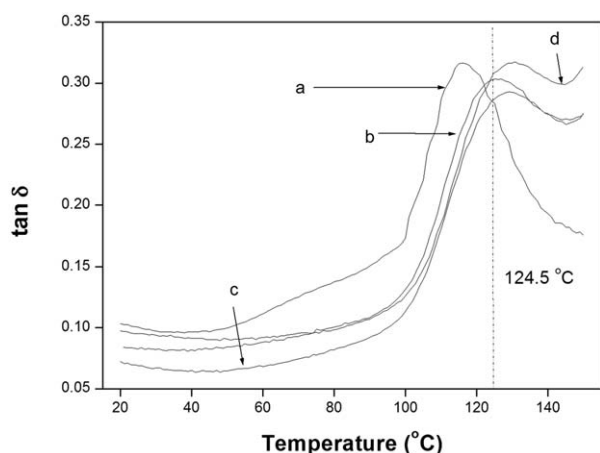
Figure 10. The changes of loss tangent as a function of temperature for PVDF composites. (a) PVDF/PMMA composite, (b) composite with 10% basalt fiber, (c) composite with 20% basalt fiber, and (d) composite with 30% basalt fiber.

related to elastic response of material and is the reflection of stiffness; the ratio of E'' (loss modulus) versus E' is defined as loss factor (tan δ), material with higher tan δ suggests that more heat was produced and more deformation could not recover when outside force was removed. In nature, tan δ is the response of inner friction force. The variation of storage modulus E' and damping tangent (tan δ) of PVDF/PMMA composites as a function of temperature are exhibited in Figures 9 and 10. As expected, the storage modulus of basalt fiber reinforced composites increased with increasing basalt fiber content, indicative of augment of rigidness, which is attributed to the rigid basalt fiber network and strong interaction between basalt fiber and polymer.

Figure 10 is the changes of tan δ of composites as a function of temperature. A relaxation process with the maximum tan δ is observed at 116.1°C, and this temperature is assigned to the glass transition temperature of PMMA. As basalt fiber loading increases from 10 to 30 wt %, the loss peak position of composite also increases from 124.5 to 130°C, and this is because of the strong interaction and basalt fiber network, which leads to the increase of rigidity and difficulty of internal rotation of segment. In addition, it can be seen from Figure 9, as temperature surpasses 124.5°C, PVDF/PMMA/basalt fiber composites have higher value of tan δ than that of PVDF/PMMA composite, and it indicates that more deformation for basalt fiber reinforced composites could not recover when outside force is removed., i.e., the elastic part decreases.

CONCLUSION

The PVDF/PMMA(70:30)/basalt fiber composites are prepared by melting blending method and morphology, viscosity, melting, crystallization, mechanical property, and heat resistance of composites are studied by XRD, SEM, rheometer, DSC, and material mechanical testing machine in detail. Basalt fiber can disperse well in matrix and form fiber network. The α phase and β phase of PVDF can coexist and PMMA or basalt fiber is favorable to the formation of β phase. The zero viscosity of composite increases as basalt fiber increases. The melting tem-

perature of PVDF in composites is 167°C and does not change by and large in spite of basalt fiber content, but basalt fiber can elevate PVDF nucleation ability and PVDF crystallization process is also accelerated at below 20 wt % basalt fibers and is inhibited at above 20 wt %, which is confirmed by variation of degree of crystallinity. Basalt fiber has important effect on mechanical property of PVDF/PMMA composite: The tensile strength increases from 37 to 62 MPa; the flexural strength also elevated from 41 to 102 MPa. However, the decline in tensile and flexural strength is found at above 20% basalt fiber. The VST of composites increases as basalt fiber content increases. The DMA results show that the storage modulus of PVDF/PMMA composite increase with basalt fiber content and the loss peak of composites increases from 116.1 to 130°C.

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