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The dynamic rheological behavior and morphology of nylon/elastomer blends

WANJIE WANG, QIANG ZHENG*
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
E-mail: zhengqiang@zju.edu.cn

In the recent decades, there has been an increasing interest in preparing novel polymeric blending materials with combined and additional characteristics of each component. Having a relatively high modulus, toughness and strength, low creep, and good temperature resistance, nylons have been widely applied in the automotive industry, machinery, electronic equipment, and military applications [1]. It is well-known that blends consisting of nylon and elastomer possess excellent toughness; however, due to its highly polar amide end-groups, nylon is incompatible with elastomer. In general, it is believed that functionalization of the elastomer is a preferred approach to enhance the interfacial properties between these polymers. Research concerning nylon/functionalized elastomer blends has mostly focused on the aspects of mechanical and thermal properties. To our knowledge, only a few reports have dealt with dynamic rheological behavior of their melts [2–4]. The rheological measurements not only give much useful information for material moulding and processing, but also is an important way to characterize the structure and properties of polymer materials [5, 6]. The aim of this article is to study the influence of the graft reaction between nylon1212 and SEBS-g-MA on dynamic rheological behavior and morphology of their blends.

Nylon1212 (melt-flow index = 22.43 g/min) used here was obtained from Shandong Dongchen Engineering Plastic Co., Ltd., China. The elastomer, a triblock copolymer styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS 4033) was supplied by the Yuyao Huiju Polymer Co., Ltd. China. The maleated triblock copolymer styrene-*b*-(ethylene-*co*-butylenes)-*b*-styrene (SEBS-g-MA) was supplied by Yuyao Yongcheng Engineering plastics Co., Ltd., China. The grafting ratio of maleic anhydride is 1.84 wt%. Both SEBS and SEBS-g-MA consist of 30 wt% polystyrene end-blocks. The nylon1212/SEBS blends and nylon1212/SEBS-g-MA blends including 1 wt% antioxidant (1010) were prepared in a corotating twin-screw extruder (PRISM TES 16TC, UK) at 210 °C. All the samples were compression-moulded into disks of 25 mm in diameter and 1.2 mm in thickness at 180 °C, 50 MPa. Melt rheological tests were conducted in an ARES Rheometer (Advanced Rheometric Expansion system, Rheometrics Inc. USA) in parallel plates oscillatory mode. The strain amplitude was maintained at 3% in order to ensure that rheological behavior was located in the linear viscoelasticity region. The morphologies of the blends were determined using a JSM-5510LV scanning electron microscope (SEM). All samples were fractured in liquid nitrogen and etched in boiling xylene for 24 hr in order to remove elastomeric phase of the blends. The etched surface after proper drying was coated with a conductive gold layer before SEM analysis.

Fig. 1 shows relationship between dynamic storage modulus G' and frequency ω for nylon 1212/SEBS blends containing different amount of SEBS at 190 °C. It can be seen that within the ω range tested, curves of G'–ω for blends are located between that of virgin nylon and SEBS, and almost follows a linear mixing rule. The virgin nylon seems to obey the linear viscoelasticity model [7], i.e., $G' \propto \omega^2$ at low ω, to log G′ $\propto$2log ω; while the blends do not, which are in agreement with the results for other blends systems [8, 9]. It is worth noting that whether the slope of plotting log G′ $\propto$ log ω at lowω is close to 2 or not is in general used

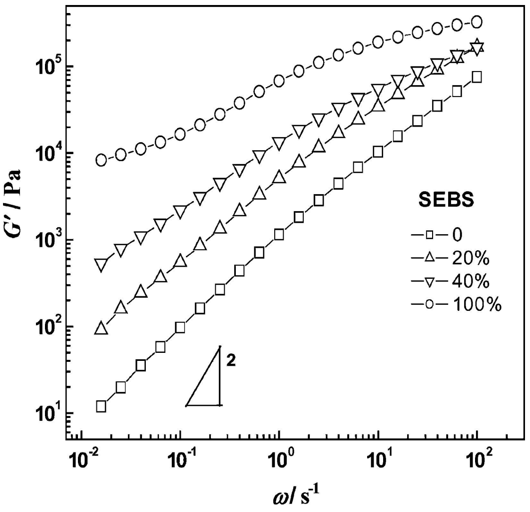

Figure 1 Relationship between the dynamic storage modulus G' and frequency ω for nylon1212/ SEBS blends containing different amount of SEBS at 190 °C.

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* Author to whom all correspondence should be addressed.

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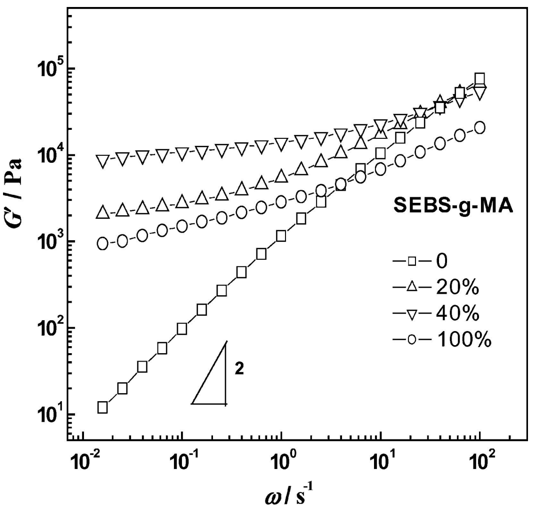

Figure 2 Relationship between dynamic storage modulus G' and frequency ω for nylon1212/ SEBS-g-MA blends containing different amount of SEBS-g-MA at 190 °C.

as a criterion for examining whether heterogeneous (or homogenous) structure in multi-component polymer systems exists or not [10]. As for the nylon1212/SEBS blends, G' increases significantly with the content of SEBS increasing. On the other hand, compared with the virgin nylon, the slopes of blends at low ω appear to be slightly increased. The reason for these is due to the fact that the dynamic rheological behavior of blends is mainly dependent on nylon1212 matrix because nylon1212 is the continuous phase in the case of low SEBS content.

Fig. 2 gives the relationship between G' and ω for nylon1212/SEBS-g-MA blends containing different amount of SEBS-g-MA at 190 °C. It is clear that their dynamic rheological behavior is quite different from those of the nylon1212/SEBS blends. The values of G' for the blends within the whole ω region are not only higher than those of virgin nylon, but also of SEBS-g-MA, indicating the new structure formation in these blends. Similar behavior has been also reported in references [11, 12]. It is well known that one of the end-groups of nylon1212 is amine, which is capable of reacting with the maleic anhydride groups in the SEBS-g-MA and forms co-polymers at the interface of the blends (Fig. 3) [13]. These interactions can stabilize the interface by reducing the coalescence and interfacial tension, resulting in enhancement of the interfacial viscosity and adhesion. This is the reason why nylon/SEBS-g-MA blends exhibits higher G' than those nylon/SEBS blends. On the other hand, it should be emphasized that with the increasing content of SEBS-g-MA, the rheological behavior of the blends at low ω region seems to gradually deviate from that of virgin nylon1212 and the so called "second plateau", which is responsible for the existence of heterogeneous structure appears. These phenomena mentioned above are attributed to be the result of increase of the relaxation time due to the enhancement of macromolecular chains in the nylon1212/SEBS-g-MA blends.

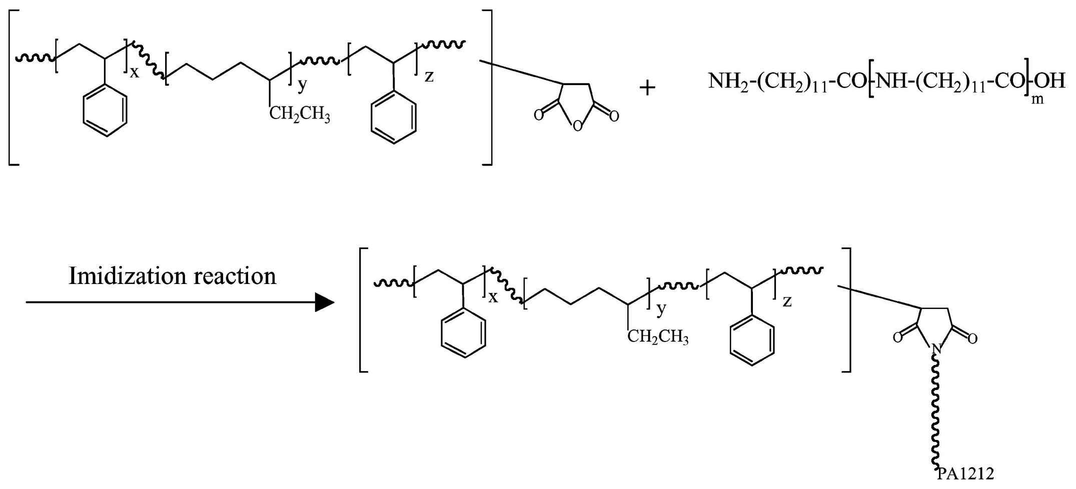

Figure 3 Graft reaction between nylon1212 and SEBS-g-MA.

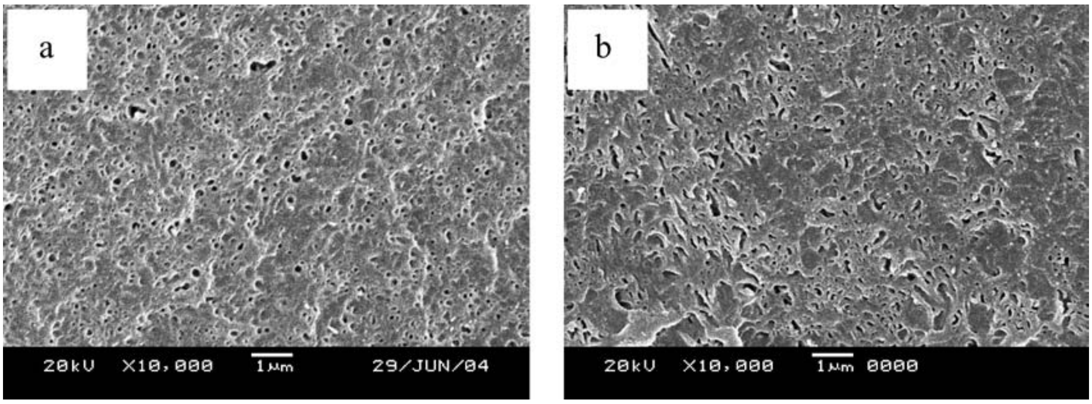

Figure 4 SEM micrographs (×10 000) of (a) nylon1212/SEBS (80/20) blends and (b) nylon1212/SEBS-g-MA (80/20) blends.

Fig. 4 presents SEM photographs of nylon1212/SEBS (80/20) blends and nylon1212/SEBS-g-MA (80/20) blends after extraction, respectively. It can be seen that the etched surface of the nylon1212/SEBS blends shows a typical droplet-matrix morphology and that the droplet size varies largely. As for nylon1212/SEBS-g-MA (80/20) blend, there exist some long strands and small droplets in the etched surface of the blends. The reason for the morphological difference between the two kinds of blends is a consequence of the graft reaction mainly occuring in the interface and parts of SEBS-g-MA diffuse to the interface and aggregate, leading to an enhancement of the compatibility of the two phases. The results of the morphological studies are in accord with the rheological measurements mentioned above.

Acknowledgments

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